Environmental Exposures in Early Childhood Education Environments

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Abstract

Little information is available about environmental quality in child care facilities. Environmental characteristics and contaminant levels in air and dust were determined in 40 California early childhood education (ECE) facilities. Average temperature and relative humidity were within ASHRAE standards; however, 7.5% of the facilities had ventilation rates below recommended levels. Over 40 volatile organic compounds (VOC) were detected in air. Two VOCs commonly found in cleaners and personal care products, d-limonene and decamethylcyclopentasiloxane, had the highest concentrations compared to other chemical groups, with medians of 33 and 51 $\mu g/m^3$, respectively. For these and most other chemicals, health-based dose or exposure benchmarks were not available, but when they were available, estimated exposures were usually below levels of concern. However, formaldehyde levels exceeded the California 8-hour Reference Exposure Level (REL) and chronic REL in 87.5% of facilities. Acetaldehyde concentrations were lower than the California RELs, but exceeded the U.S. EPA Reference Concentration (RfC) in 30% of facilities. In most facilities, levels of formaldehyde, acetaldehyde, chloroform, benzene, or ethylbenzene exceeded child-specific Safe Harbor Levels computed by the report authors based on Proposition 65 guidelines for carcinogens. Phthalates, flame retardants, pesticides, perfluorinated compounds, and lead were also frequently detected in dust and/or air. Child dose estimates from ingestion of dust for two brominated flame retardants (BDE-47 and -99) exceeded the non-cancer U.S. EPA reference health dose (RfD) in 10.3% of facilities for children <1 year old. PM_{10} concentrations collected over approximately 8 hours exceeded the level of the 24-hour California Ambient Air Quality Standard (CAAQS) in 46% of ECE facilities. The screening risk assessment did not consider mixed exposures. Overall, findings suggest that ECE environments are similar to other indoor environments such as schools and residences, and that mitigation strategies may be warranted to reduce exposures to some chemicals, especially formaldehyde. More research is needed to identify sources of toxicants and support outreach efforts to improve environmental quality.

Executive Summary

Background

Many infants and young children spend as much as ten hours per day, five days per week, in child care and preschool centers. California, where approximately 1.1 million children five years or younger attend child care or preschool, has the largest number of licensed child care centers in the United States at 49,000, 80% of which are family-based centers located in homes. By the time they enter kindergarten, over 50% of all California children have attended some type of licensed child care facility. Additionally, 146,000 staff work in California's licensed child care facilities. Collectively, Early Childhood Education (ECE) facilities are varied and include home-based child care providers, private for-profit or non-profit preschools, and programs run by government agencies (e.g., preschools in school districts or Head Start) or religious institutions.

Recent studies indicate that ECE environments may contain lead, pesticides, allergens, and other contaminants hazardous to children's health. Because children exhibit exploratory behaviors that place them in direct contact with contaminated surfaces, they are likely to be exposed to any contaminants present. Children have higher exposures because they breathe more air, eat more food, and drink more water per unit of body weight compared to adults. They are also less developed immunologically, physiologically, and neurologically and therefore may be more susceptible to the adverse effects of chemicals and toxins. This study includes development of new concentration and exposure data for young children on several volatile and semi-volatile toxic air contaminants (TACs) and other chemicals and particles in California ECE environments, an environment with little or no available monitoring data. This study is the first and largest to examine particulate matter and a broad spectrum of chemical contaminants, including emerging pollutants such as flame retardants, phthalates, and perfluorinated compounds, in ECE facilities in California and nationally. This information will help the California Air Resources Board (CARB) and other agencies better protect children's health by identifying key exposures that can be reduced through regulations or other approaches.

Methods

For this study, levels of specified contaminants were measured in air and dust sampled from 40 ECE facilities located in Monterey (n=20) and Alameda (n=20) counties. Research activities included the development of validated questionnaires and inspection forms to characterize environmental quality in ECE facilities. Chemical measurements in indoor air included Volatile Organic Compounds (VOCs), aldehydes and acetone, flame retardants, phthalates and pesticides. Because the VOC measurement techniques indicated a large number of unknown chemicals were also present, National Institute of Science and Technology (NIST) mass spectral libraries were used to identify these chemicals. Flame retardants, pesticides, perfluorinated compounds (PFCs), phthalates, and metals were also measured in dust. Coarse, fine and ultrafine particulate matter (PM) were measured in indoor air. See Table 1 for a summary of sampling and laboratory methods. Air exchange rates were also estimated. Finally, a screening-level risk assessment was conducted to interpret the health significance of the findings. Outdoor air samples were collected at a subset of ECE facility locations.

Table 1. Sample Collection and Analytical Methods Summary.

Media	Analyte	Sampling Method	Analytical Method	Analytical Laboratory
Air	VOCs	Sample tube with Tenax-TA sorbent	TD-GC/MS	LBNL
Air	Aldehydes and acetone	XPoSure aldehyde sampler	HPLC	LBNL
Air	$PM_{2.5}$ and PM_{10} mass	SKC® PEM with Teflon filter	Gravimetric analysis	LBNL
Air	Real-time $PM_{2.5}$	TSI DusTrak	Optical detector	-
Air	Real-time ultrafine particles	TSI Condensation particle counter	Optical detector	-
Air	PBDE flame retardants	PUF cartridge	GC/MS/MID	Battelle
Air	Phthalates, pesticides, and other flame retardants	PUF cartridge	GC/MS/MID	Battelle
Dust	Phthalates, pesticides, and other flame retardants	Vacuum sample	GC/MS/MID	Battelle
Dust	PBDE flame retardants	Vacuum sample	GC/MS/SIM	NERL
Dust	Perfluorinated compounds	Vacuum sample	UPLC-MS/MS	NERL
Dust	Metals	Vacuum sample	ICP-MS	UCSC

GC = gas chromatography; LBNL = Lawrence Berkeley National Laboratory; ICP = inductively coupled plasma; MID = modified isotope dilution; MS = mass spectroscopy; U.S. EPA's NERL = National Exposure Research Laboratory; PEM = personal environmental monitor; PUF = polyurethane foam; SIM = selective ion monitoring; TD = thermally desorbed; UCSC = University of California Santa Cruz; UPLC = ultra performance liquid chromatography.

Given the relatively small study sample size (n=40 ECE facilities), statistical analyses were limited. Data analyses focused on the computation of descriptive statistics of contaminant levels, summarizing questionnaire and inspection data such as building type and quality, pest infestations, pesticide use, types of furniture, and socio-demographic characteristics of the populations served by participating ECE facilities. Correlations of individual target analytes measured in both air and dust (i.e., pesticides, flame retardants and phthalates) were examined. Differences in contaminant levels stratified on geographic location, license type (center versus home-based), and indoor versus outdoor samples were compared. The association between contaminant levels and other appropriate variables such as building type and quality, age of furnishings, cooking, ventilation, local land use, and nearby traffic density were also evaluated. Finally, indoor and outdoor temperature and relative humidity and air exchange rates were compared to standards promulgated by the American Society of Heating, Refrigerating and Air-conditioning Engineers (ASHRAE).

The screening risk assessment involved several steps. Measured concentrations of indoor air pollutants were compared to CAL EPA Office of Environmental Health Hazard Assessment (OEHHA) Reference Exposure Levels (RELs) and U.S. EPA Reference Concentrations (RfCs)

or, for particulate matter, to the levels of the 24-hour California Ambient Air Quality Standard (CAAQS) and the National Ambient Air Quality Standard (NAAQS). Child exposure-dose estimates were calculated based on air concentrations, assumptions about inhalation and absorption, dust concentrations and non-dietary ingestion from house dust. For non-cancer causing compounds, exposure-dose estimates were compared to appropriate health-based benchmarks, such as U.S. EPA reference doses (RfDs). Because the health-based reference values include safety factors, exposures exceeding these levels are not necessarily likely to result in adverse health effects. For potentially carcinogenic compounds, the report authors computed child-specific "No Significant Risk Levels" (NSRLs) based on OEHHA's guidelines to define Safe Harbor Levels that account for the increased sensitivity of very young children. Age-adjusted NSRLs were calculated for four distinct age groups (i.e., birth to <1 year; 1 to <2 years; 2 to <3 years; and 3 to <6 years). The NSRL is defined as the daily intake level posing a one in 100,000 excess risk of cancer assuming lifetime exposure. To determine whether exposures exceeded the Safe Harbor Level, child exposure estimates were compared to the age-specific NSRL benchmarks. It was beyond the scope of this study to develop detailed, statistically representative exposure-dose estimates. The risk assessment presented in this final report provides preliminary information on the potential cancer and non-cancer health risks associated with documented exposures. Suggested areas for further investigation and risk mitigation are presented.

Results

Environmental Quality: The average indoor temperature and relative humidity were within ASHRAE standards. The air exchange rates measured in ECE facilities were higher than those reported in a recent California study of new homes (median = 1.4 versus 0.26 air changes per hour, respectively), and only 3 facilities (7.5%) were below the California Building Code assumed minimum ventilation level of 0.35 air changes per hour for residences. Carbon monoxide levels (median = 2.2 ppm, max = 4.0 ppm) were well within health-based guidelines. Pest problems were common (90% reported at least one pest), and 58% reported using pesticides, with 45% using broadcast application methods (e.g., sprays). Mold, rotting wood, or water damage was present in 23% of facilities, but no serious problems were observed. Overall, although pest problems (mainly ants) were common, the ECE child care environments were in good physical condition and well-maintained.

The VOCs measured in the highest concentrations in indoor air were d-limonene and decamethylcyclopentasiloxane with medians (range) = 33 (0.8-82) and 51 (2.6-88) $\mu g/m^3$, respectively. D-limonene is a cyclic terpene often used as a solvent in cleaning products that gives a "citrus smell", and decamethylcyclopentasiloxane is often used as a lubricant in personal care products. Levels of d-limonene were higher in the ECE facilities compared to levels measured in recent studies in homes. D-limonene, a terpene, may be a respiratory irritant, and can, along with other VOCs, react with ozone to form secondary air contaminants. Median (range) formaldehyde and acetaldehyde levels were 17.8 $\mu g/m^3$ (0.7 to 48.8 $\mu g/m^3$) and 8.5 $\mu g/m^3$ (0.7 to 23.3 $\mu g/m^3$), respectively. Formaldehyde levels exceeded the California 8-hour REL and chronic REL in 87.5% of facilities (35 of 40). Acetaldehyde concentrations were lower than the California RELs, but exceeded the U.S. EPA RfC in 30% of facilities (12 of 40). Formaldehyde and acetaldehyde are known respiratory irritants and carcinogens. Child inhalation exposure estimates for five VOCs (benzene, chloroform, ethylbenzene, acetaldehyde, or formaldehyde) exceeded age-specific NSRL Safe Harbor Levels for carcinogenicity, based on Proposition 65 guidelines computed by the report authors, in most facilities. For formaldehyde, the ratio of age-adjusted child dose estimates to the age-specific NSRLs ranged

from 12.0 to 107.5 for the four age groups assessed (i.e., birth to <1 year; 1 to <2 years; 2 to <3 years; and 3 to <6 years). Overall, VOCs were detected more frequently and at significantly higher levels indoors compared to outdoors. The indoor VOC levels were also inversely related to ventilation rates (for example, the correlation of air exchange rates and formaldehyde concentrations was -0.59), confirming that indoor sources were important determinants of the VOC levels. Potential adverse health effects from VOC exposure depend on the particular VOC. The principal health concerns of VOC exposure are respiratory tract irritation and cancer.

In addition to the target VOCs, the evaluation of unknown VOCs using the NIST mass spectral libraries indicated that over 100 additional VOCs were likely present in the facilities. Ranking the toxicological significance and relative importance of each of the chemicals identified by the analysis is beyond the scope of this study, but the results highlight the importance of expanding the number of VOCs considered in indoor air quality studies and the need to determine if any of the compounds have potential health impacts.

Phthalates are widely used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity). Phthalate compounds, detected in 100% of the air and dust samples, have been shown to disrupt normal hormone function in animals. There are no health-based benchmarks to evaluate phthalate levels in air. Of all compounds measured in dust, the highest were the phthalates di(2-ethylhexyl) phthalate (DEHP) and butyl benzyl phthalate (BBP), with medians of 172.2 and 46.8 µg/g, respectively. Estimated exposures to two phthalates that have been evaluated by OEHHA for cancer (DEHP) or reproductive risk (dibutyl phthalate [DBP]) were below levels of concern. Additionally, exposures to four of the phthalates (BBP, DBP, diethyl phthalate [DEP], and DEHP) with U.S. EPA oral references doses were also below levels of concern. Potential adverse health effects from phthalate exposure, including effects on reproduction and development, depend on the particular phthalate.

Flame retardants have relatively low vapor pressures. Detection frequencies in air ranged from 0-95%. There are no health-based benchmarks to evaluate any of the flame retardant levels in air. In this study, levels of organophosphate flame retardants in dust were higher than levels of penta- and octa-polybrominated diphenyl ether (PBDE) flame retardants, which were recently banned from use in California due to concern about their environmental persistence and potential adverse health effects (i.e., endocrine disruption and neurodevelopmental effects). Median levels of brominated flame retardants in dust were lower than levels in other studies focusing on residential environments, possibly due to the frequent cleaning and vacuuming that occurs in child care facilities. Maximum flame retardant levels were similar to the upper-bound levels measured in other California studies. Currently, of flame retardants measured in this study, only four (BDE-47, -99, -153, and -209) have an oral reference dose. Based on measurements of contaminants in dust, child dose estimates for two brominated flame retardants (BDE-47 and BDE-99) exceeded their respective non-cancer U.S. EPA RfDs in 10.3% (4 of 39) of facilities, for the birth to <1 year age group. RfDs for these PBDE congeners were established based on adverse neurobehavioral effects in animals.

Pyrethroid pesticides were detected in all ECE facilities and the levels were higher than levels of other measured pesticides. Pyrethroids are neurotoxicants, but less toxic to humans compared to organophosphate (OP) pesticides. Diazinon and chlorpyrifos, OP pesticides that are no longer approved for indoor use due to their potential neurotoxicity in humans (i.e., acetylcholine esterase inhibition), were frequently detected in dust (>90% of facilities). Because residues of these pesticides persist for long periods indoors due to low levels of light, moisture, and biological activity, it is likely that indoor residues of diazinon and chlorpyrifos were due to historical use. Agricultural OP pesticide use may result in indoor contamination; however, levels

of diazinon and chlorpyrifos were not higher in ECE facilities located in agricultural compared to non-agricultural areas. Dust and air levels of the herbicide dacthal were significantly higher in ECE facilities located in agricultural communities. No pesticide exposures exceeded health-based benchmarks.

Median indoor and outdoor air levels of PM_{10} were 47.6 and 28.9 µg/m^3, respectively, and median indoor and outdoor air levels of $PM_{2.5}$ were 15.0 and 16.2 µg/m^3, respectively. Indoor PM_{10} concentrations were higher than the level of the 24-hour CAAQS in 46% of ECE facilities. In four of 35 (11%) of the ECE facilities, indoor $PM_{2.5}$ concentrations were higher than the level of the 24-hour NAAQS standard of 35 µg/m³. Indoor ultrafine particle (UFP) levels were generally stable during sampling periods except when cooking with gas stoves occurred; in these cases, peak UFP levels increased by up to three orders of magnitude. Median indoor UFP levels in center-based facilities (11,997/cubic centimeter [ccm]) were much lower compared to median levels in home-based facilities (39,071/ccm), where more cooking near child activity areas occurred. The average indoor UFP levels (22,327/ccm) were higher than those reported in a recent study of six northern California elementary schools (average = 10,800/ccm indoors). In addition, the average indoor UFP levels in the ECE facilities were somewhat higher compared to those reported in a study of seven northern California residences (17,000/ccm). There are no health-based standards for UFPs. The primary health concerns of fine and ultrafine PM exposure are decreased lung function and exacerbation of pre-existing respiratory conditions such as asthma.

Perfluorinated compounds (PFCs) have low vapor pressures, and measurements of PFCs in air were not successful. Ten PFC compounds were measured in dust collected from the ECE facilities. The most common PFC breakdown compounds, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), were detected in 72% and 54% of facilities, respectively. PFOA has been associated with increased incidence of liver, Leydig cell and pancreatic tumors in rodent bioassays. The compound is currently being tested by the National Toxicology Program (NTP) and is under review for possible listing by the OEHHA Carcinogen Identification Committee. Currently, there are no health-based benchmarks to evaluate the risk of PFC exposures.

Lead, a ubiquitous metal, was frequently detected in dust (95% of samples), and child lead exposure estimates exceeded child-specific cancer NSRL benchmarks computed for this report in 95% of facilities. Although lead has been evaluated for cancer risks, the primary concern for children's exposure is developmental toxicity. U.S. EPA has defined a threshold of lead loading at 40 µg/square foot for indoor contamination. However, this threshold is based on a wipe sample, and therefore is not comparable to the vacuum sampling methods used for this study. No U.S. public health agency has defined a threshold for acceptable concentrations of lead in house dust. More than 95% of the dust samples in this study were below 400 parts per million, the threshold for lead in soil that children directly play in. Because U.S. EPA believes there is no safe level of exposure to lead, there is no defined reference dose.

Potential Sources of Indoor Chemical Contaminants: Sources of many of the measured chemicals in air include building materials, furnishings, and consumer products. For example, the primary sources of formaldehyde are believed to be composite wood products such as medium density fiberboard, particle board, and plywood. Other sources include certain types of foam insulation, textiles, paints and sealants, and indoor combustion sources such as unvented gas stoves.[1] Several VOCs with relatively high levels, such as d-limonene and decamethyl-cyclopentasiloxane, are often used in cleaners or personal care products. Sources of benzene, ethylbenzene and several related VOCs are likely nearby traffic and vehicle fuel evaporation, as well as indoor combustion sources, paints, and cleaners containing petroleum distillates.

Sources of chloroform include vaporization from chlorinated tap water and consumer products containing bleach for sanitization purposes.

Many of these sources were present in the ECE facilities tested. For example, 88% (35 of 40) of the facilities contained pressed wood or plywood; 28% of the facilities had indoor gas stoves located in child care areas; and two home-based facilities had gas stoves with no functioning exhaust fan. Bleach (sodium hypochlorite) was a component of cleaners or sanitizers in 26 (65%) of the facilities. Other sources of measured VOCs include consumer products used or stored in the facilities. For example, 135 chemical ingredients were identified in a variety of consumer products, including personal care products (hand soaps), cleaners, sanitizers, air fresheners, paints, pesticides, etc.

Indoor sources are also important for the less volatile chemicals measured in air, including phthalates, flame retardants, and pesticides, all of which were commonly detected in indoor air and dust. Phthalates have historically been used in plastics, toys, certain building products, and personal care products. Flame retardants are heavily used in furnishings and electronics to comply with the California Bureau of Electronic and Appliance Repair, Home Furnishings, and Thermal Insulation flammability standards defined in Technical Bulletin 117. Pyrethroid pesticides are the most common class of pesticides used indoors since most residential and structural uses of diazinon and chlorpyrifos were phased out between 2002 and 2004. It is likely that indoor residues of diazinon and chlorpyrifos were due to historical use. Finally, the higher levels of dacthal in ECE facilities located in agricultural areas suggest contamination from nearby agricultural pesticide use.

Implications for Regulatory Programs: This study has several implications for regulatory programs. Although the levels of formaldehyde and acetaldehyde were slightly lower than levels reported in recent studies in California homes and elementary school classrooms, they frequently exceeded health-based benchmarks. Regulatory steps have been taken to reduce emissions of formaldehyde from composite wood materials (Section 93120-93120.12, Title 17, California Code of Regulations), but more action may be needed. In addition to formaldehyde and acetaldehyde, exposures to benzene, chloroform, and ethylbenzene in air exceeded the child-specific NSRLs computed by the report authors for carcinogenicity.

Indoor PM_{10} concentrations were higher than the level of the 24-hour CAAQS in 46% of ECE facilities, and indoor $PM_{2.5}$ levels exceeded the level of the 24-hour NAAQS in 11% of the facilities. It should be noted that the measurements in this study were over an 8-10 hour period, and do not necessarily represent the levels children were exposed to for a full 24-hour period, the duration of the exposure period defined in the air quality standards. However, the monitoring suggests that many young children are experiencing a significant portion of total PM exposures in child care facilities and that exposure mitigation may be warranted. As noted earlier, UFP levels increased dramatically when gas stoves were used for cooking, especially when no functioning fan was present. If these high levels are shown to cause respiratory or other health problems in young children, CARB may want to consider recommending steps to mitigate these exposures.

Conclusions

For this study, extensive environmental monitoring in 40 ECE facilities in northern California was performed and dozens of toxicants were measured in the air and dust. Overall, levels of contaminants were similar to levels in other indoor environments and most exposures were below health-based benchmarks when such levels were available. The screening risk assessment identified five VOCs (benzene, chloroform, ethylbenzene, acetaldehyde, and

formaldehyde) and one metal in dust (lead) that exceeded OEHHA Safe Harbor guidelines for cancer. Formaldehyde levels also exceeded the OEHHA 8-hour and chronic RELs for non-cancer health endpoints and acetaldehyde levels, while lower than the California RELs, exceeded the U.S. EPA reference concentration. In addition, estimated exposures to two brominated flame retardants (BDE-47 and BDE-99) exceeded the U.S. EPA non-cancer RfD. Given the overriding interest in providing safe and healthy environments for young children, additional research is needed to identify strategies to reduce indoor sources of these chemicals. Additional research is also needed to assess the health risks of elevated UFPs and define standards to prevent exposures, if warranted. This information will be important for targeted education and outreach efforts to successfully improve the environmental and public health of young children receiving child care in California's ECE facilities.

Body of Report

1 Introduction

Young children spend up to 90% of their time indoors, mostly at home.[2-4] However, many infants and young children spend as much as ten hours per day, five days per week, in child care and preschool centers.[5,6] Nationally, 13 million children, or 65% of all U.S. children, spend some portion of the day in child care or preschool.[6] California, where approximately 1.1 million children five years or younger attend child care or preschool,[7] has the largest number of licensed child care centers in the United States[8] (49,000), 80% of which are family-based centers located in homes.[9] By the time they enter kindergarten, over 50% of all California children have attended some type of licensed child care facility.[10] Additionally, 146,000 staff work in California's licensed child care facilities.[10]

Collectively, early childhood education (ECE) facilities are varied and include home-based child care providers, centers operated like private schools, and programs run by government agencies (e.g., preschool in school districts or Head Start) or religious institutions. These facilities are located in a variety of building types, including homes, schools, private commercial buildings, and portable classrooms. Information on potential pollutant exposures in these environments is necessary to assess the potential health risks to children and adult staff, and, if warranted, to develop and implement policies to mitigate these exposures.

Recent studies indicate that ECE environments may contain lead, pesticides, allergens, and other contaminants hazardous to children's health.[3,6,11] Because children exhibit exploratory behaviors that place them in direct contact with contaminated surfaces, they are likely to be exposed to any contaminants present.[12,13] Children have higher exposures because they breathe more air, eat more food, and drink more water per unit of body weight compared to adults. For example, children ages 0-5 years breathe 1.7-2 times more air per unit of body weight than adults.[14] They are also less developed immunologically, physiologically, and neurologically and therefore may be more susceptible to the adverse effects of chemicals and toxins.[12,13,15]

Child care facilities may be contaminated from multiple sources and media. Until now, research concerning exposures of children has been primarily focused on exposures occurring in the home, but a larger percentage of children are spending more time in child care.[16] Thus, children who attend these facilities on a daily basis may be chronically exposed to potentially harmful chemicals during critical periods of development.

To address data gaps in environmental quality data for child care environments, we measured several classes of pollutants in indoor air and dust from 40 ECE facilities located in two California counties (Alameda and Monterey). Compounds measured in indoor air include volatile organic compounds (VOCs), carbonyls, phthalate esters, brominated and chlorinated flame retardants, pesticides and particulate matter. Compounds measured in indoor dust include lead and other metals, phthalate esters, brominated and chlorinated flame retardants, perfluorinated compounds (PFCs), and pesticides. Many of these chemicals have been shown to have indoor sources and are potentially associated with health effects in children.

1.1 Relevant Research

Limited information is available on environmental contaminants present in ECE environments. However, school environments are known to contribute to children's exposures to several contaminants, including mold, lead, pesticides, and VOCs.[6,10,17] These exposures can exacerbate asthma and other respiratory illnesses or impair the neurological development of children. Beyond preventing children's exposure to lead, few states have programs or licensing regulations that address children's exposures to environmental contaminants such as VOCs, pesticides, and other emerging pollutants in ECE facilities.

California has examined indoor environmental exposures to contaminants in school settings for school-aged children. For example, the 2003 California Portable Classroom Study sponsored by the California Air Resource Board (CARB) investigated conditions inside traditional and portable classrooms in California public schools.[6,10,17] Aldehydes and other carbonyls, VOCs, pollens, culturable microorganisms, and indoor-air particles were measured over a school day in classrooms. Dust samples were collected for analyses of pesticides, metals, polycyclic aromatic hydrocarbons (PAHs), and allergens. Of 15 aldehydes and other carbonyls measured in air, formaldehyde and acetaldehyde were detected most often (detection frequency >75%). Mean air concentrations of formaldehyde in both portable classrooms (15 ppb) and traditional (12 ppb) classrooms were higher than outdoor measurements (3.5 ppb). Higher mean formaldehyde levels were also associated with warmer months (spring/summer vs. fall/winter), age of classroom, and presence of pressed wood products in the classroom. Mean VOC concentrations were similar between portable classrooms and traditional classrooms and were also higher than outdoor levels. Particle counts for both $PM_{2.5}$ and PM_{10} were higher in portable classrooms compared to traditional classrooms, possibly because of the usual proximity of portable classrooms to roads and parking lots and the more frequent use of carpets in the classrooms. Of the twenty pesticides analyzed in dust samples, six were detected in over 80% of samples, and the insecticide esfenvalerate, a pyrethroid, had the highest mean dust concentration and median loading overall, at 4.5 µg/g and 0.3 ng/cm^2, respectively. Dust PAH levels were observed to be fairly low. Of 18 metals analyzed, 15 were detected in all dust samples. Higher lead levels were observed in traditional classrooms, while portable classrooms had higher levels of arsenic.

Nationally, the First National Environmental Health Survey of Child Care Centers was conducted by the U.S. Department of Housing and Urban Development (HUD), the U.S. Environmental Protection Agency (U.S. EPA), and the Consumer Products Safety Commission (CPSC). The study assessed children's exposures to lead, allergens, and pesticides in licensed U.S. child care centers.[18] Twenty-two percent of the facilities had detectable levels of allergens. Sixty-three percent reported recent pesticide applications, and an estimated 75% of centers reported at least one pesticide application in the last year.[6] Pyrethroid and OP pesticides were detected in 80% of the centers. However, this survey was limited for several reasons. First, no testing was done in home-based child care programs, which in California make up the majority of licensed child care facilities. Second, regional data was not available for specific states or smaller regions to allow for local projection of exposures. Finally, no testing was conducted for other potentially significant pollutants, including VOCs, aldehydes, phthalate esters, PFCs, brominated flame retardants, and particles.

In a pilot study of nine child care centers located in North Carolina, Wilson et al.[19] detected OP pesticides, pyrethroids, phthalates, and persistent organochlorine compounds in air and dust and suggested that exposures in day care environments may constitute a significant portion of total child exposures to these chemicals. In a survey of 637 California child care

centers, about half reported using sprays or foggers that could leave pesticide residues on surfaces and in air.[20] Another study found that problems with mold, cockroaches, and other factors potentially associated with respiratory disease problems were common.[10] In a 2009 report, The Environmental Working Group [21] described 21 cleaners used in 13 large K-12 California school districts that, when used as directed, released 457 chemicals; six of which are known to trigger asthma (formaldehyde, styrene, methyl methacrylate, ethanolamine, alkyl dimethyl benzyl ammonium chloride, and didecyl dimethyl benzyl ammonium chloride); 11 that are known, probable, or possible cancer-causing substances in humans (formaldehyde, styrene, chloroform, trichloroethylene, benzene, 1-chloro-2,3-epoxypropane, acetaldehyde, N-methyl-N-nitroso-ethanamine, 2-butoxyethanol, ethylbenzene, and quartz); and hundreds of other compounds for which there is little or no hazard information.

Overall, these studies suggest that ECE facilities may be contaminated from multiple sources and media. Until now, research concerning exposures of children has been primarily focused on exposures occurring in the home, but a large percentage of children are spending more time in child care. Thus, children who attend these facilities on a daily basis may be chronically exposed to environmental contaminants during critical periods of development.

1.2 Health Effects from Environmental Contaminants

To address data gaps in environmental quality data for child care environments, we measured indoor air and dust levels of several classes of pollutants in a sample of California ECE facilities, including VOCs, carbonyls, phthalate esters, brominated and chlorinated flame retardants, PFCs, lead and other metals, and particulate matter. Many of these chemicals have been shown to have indoor sources and are potentially associated with health effects in children. These health effects are summarized below.

A growing body of evidence suggests that indoor exposures are determinants of asthma prevalence and morbidity in children.[3] In addition to allergens from dust mites, mold, and cockroaches, known environmental triggers of asthma include VOCs, combustion by-products, and some common home-use pesticides and cleaners and sanitizers.[22-38] Exposure to VOCs in indoor air, from sources such as newly painted surfaces; cleaning, sanitizing and disinfecting products; and room fresheners, has been associated with increased risk of asthma in children[39,40] and respiratory symptoms including decreased lung function, inflammation, and airway obstruction.[32,38,41,42] Carbonyls (formaldehyde, acetaldehyde, and acetone) are VOCs present in pressed wood and laminated products like shelving, paneling, and furniture and are of particular concern in new buildings and homes. Formaldehyde is listed as a Class B1 compound (probable human carcinogen) by U.S. EPA[43] and a Group 1 compound (carcinogenic to humans) by the International Agency for Research on Cancer (IARC).[44] Acetaldehyde is listed by U.S. EPA as a Class B2 (probable human carcinogen) compound[45] and by IARC as a Group 2B (possibly carcinogenic to humans) compound.[46] Numerous rodent studies have reported adenocarcinomas and squamous cell carcinomas subsequent to aldehyde exposure[47-50] while occupational cohort studies have reported associations between formaldehyde exposure and lung, nasal, and nasopharyngeal cancer mortality.[51-53] Additionally, exposure to aldehydes has been associated with adverse respiratory outcomes, including increased risk of childhood asthma[54] and nocturnal breathlessness.[32,55] ARB's recently completed "new home" study found that concentrations of both formaldehyde and acetaldehyde exceeded accepted cancer and chronic non-cancer health benchmark levels in nearly all homes studied and exceeded benchmarks for acute health effects in most homes.[56,57] In the ARB's study of portable classrooms, indoor concentrations of formaldehyde were elevated above

OEHHA's 8-hour REL for acute eye, nose, and lung irritation in 4% of the classrooms. Levels in all classrooms exceeded OEHHA's chronic REL for irritant effects.[17]

Exposures in young children to particulate matter ($PM_{2.5}$ and PM_{10}) have been shown to increase allergen sensitization, decrease lung function, and exacerbate pre-existing respiratory conditions like asthma.[58,59] Prenatal and early-life exposures to PM_{10} may also adversely affect pulmonary function in asthmatic children up through ages of puberty.[58,59] Increases in respiratory disease of up to 22% and a 5% increase in post neonatal mortality for all causes has also been associated with increasing PM_{10} levels.[60] Increases in respiratory disease of up to 22% and a 5% increase in post neonatal mortality for all causes have also been associated with increasing PM_{10} levels.[60]

Three classes of environmental contaminants receiving increasing attention are brominated flame retardants (BFRs), phthalate esters, and PFCs. This is the first study to report levels of BFRs, phthalates, PFCs, and replacement fire retardants in child care environments. One class of BFRs, polybrominated diphenyl ethers (PBDEs), are endocrine disruptors that are persistent in the environment. These compounds have been detected in human tissue, serum, and breast milk from North America at much higher levels than those reported from Europe, Asia or Australia.[61-67] Within North America, the body burden of PBDEs has been found to be especially high in California, where furniture flammability standards have been among the strictest in the U.S.[67,68] Measurements of PBDEs in house dust indicate widespread contamination in residential environments.[69,70] A recent report from the Center for Environmental Research and Children's Health (CERCH), suggests PBDE levels in dust from Oakland and Salinas homes are similar to each other but are much higher than levels found elsewhere in the U.S.[70] Further, children's PBDE levels in blood have been found to be higher compared to adults, a difference likely due to a child's increased time spent indoors in proximity to house dust containing PBDEs.[71]

The manufacture, distribution, and processing of products containing two classes of PBDEs, pentabrominated and octabrominated diphenyl ethers, is now banned in California as of June 1, 2006.[68] Replacement furniture fire retardants such as chlorinated tris (tris[1,3-dichloro-2-propyl] phosphate [TDCPP]) and Firemaster 550 (a proprietary phosphorus-bromine blend formulation consisting of bis(2-ethylhexyl)tetrabromophthalate [BEHTBP] and 2-ethylhexyl tetra-bromobenzoate [EHTBB]) have come into wider use.[72] Although TDCPP was used prior to 1977 in children's sleepwear as a fire retardant, manufactures voluntarily stopped using it in these products after it was found to be mutagenic.[73,74] Chlorinated tris (TDCPP) was recently listed as a carcinogen on the Proposition 65 list.[75] Today TDCPP is a widely used flame retardant, commonly detected in furniture foam as well as infant products.[76,77]

Phthalate esters are plasticizers used in plastics and personal care products. Phthalate compounds are on the Proposition 65 list as developmental toxins and have been found to contaminate indoor environments.[78-81] Studies have associated phthalate exposures with bronchial obstruction, allergies, and asthma in young children, and they are likely endocrine disruptors in humans.[18,82-86]

PFCs are chemicals used to confer stain- and degradation-resistant properties to a variety of products. Such compounds include perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). Occupational studies have suggested an association between exposure to perfluorinated compounds and cancer incidence.[87,88] Currently, there are no health-based benchmarks to evaluate the risk of PFC exposures.

1.3 Importance of Air and Dust in Children's Exposures

Contaminants in indoor environments can expose children through inhalation, inadvertent non-dietary ingestion of dust on surfaces or hands, or dermal absorption through the skin.[89] Inhalation is the primary route of exposure for highly volatile VOCs that outgas from building materials and furnishings or volatilize rapidly from cleaners, paints, and other indoor consumer products. VOCs can also diffuse into buildings from outdoor sources such as vehicle fuel evaporation. Chemicals which are less volatile, known as semi-volatile compounds (SVOCs), also enter the air and expose children. A portion of SVOCs such as pesticides may volatilize quickly after an application, but then accumulate in dust and persist indoors where there is little sunlight, moisture, or biological activity.[90,91] Other SVOC compounds, such as phthalates in toys, may volatilize slowly or also accumulate in dust as the product breaks down.[92] Thus, dust acts as a reservoir for many toxicants, exposing young children directly when they mouth hands and surfaces contaminated by dust, or indirectly by contributing to contaminants in indoor air.[93] Studies of lead and BDE flame retardant level have conclusively shown that dust is a key pathway for children's exposures.[94,95] For this study, we conducted extensive sampling of air and dust to characterize contaminants in these key exposure media.

1.4 Research Objectives

Objective 1: Complete environmental measurements in California ECE facilities, including:

a. Conduct comprehensive environmental quality assessments and characterize levels of specified contaminants in air and dust in ECE facilities located in Monterey (n=20) and Alameda (n=20) Counties, California.

b. Identify factors associated with poorer environmental quality and higher levels of contamination.

Objective 2: Estimate potential health risks associated with indoor contaminant exposures.

2 Materials and Methods

The following sections describe the research approach used to understand environmental exposures and potential health risks from indoor contaminants in ECE facilities.

2.1 Research Approach Summary

We enrolled 40 ECE facilities located in Alameda and Monterey Counties, CA to participate in this study. We stratified regions in each county to ensure representation by geographic area within each county and type of licensure (center or home-based). Upon enrollment into the study, a questionnaire was administered to a site supervisor and a detailed inspection was conducted by field staff. Questionnaire and inspection forms were developed to assess environmental quality in the facility, particularly as it relates to potential sources of target analytes inside the facility. Additional data was collected on a variety of demographic and socioeconomic factors along with ECE provider knowledge and attitudes about environmental health.

Indoor dust and air samples were collected from enrolled ECE facilities. Dust samples were tested for phthalates, PFCs, flame retardants, pesticides, and metals. On a separate day, indoor air samples were collected when children were present. Integrated samples were collected over the entire school day and tested for VOCs, carbonyls, flame retardants, pesticides, phthalates, $PM_{2.5}$, and PM_{10}. Real time sampling devices measured $PM_{2.5}$, ultrafine particles (UFPs), temperature, relative humidity, carbon monoxide (CO), and carbon dioxide (CO_2). Outdoor integrated and real time air samples were collected at subsets of the facilities. The number of outdoor measurements ranged from 12 to 31 depending on the pollutant sampled.

Medical grade CO_2 was released as a tracer gas to enhance CO_2 levels in each facility, so that decay rate and mass-balance equations could be used to estimate facility air exchange rates. Logs were kept throughout the day documenting occupancy and changes in building ventilation including opening windows or doors. The sampling period was from May 2010 to May 2011 and thus included all four seasons.

Summary statistics were compiled for all analytes measured in ECE facilities. Comparisons between county (Alameda vs. Monterey) and ECE type (center vs. home-based) were calculated with appropriate tests for differences. Indoor and outdoor particle measurements correlated with proximity to traffic intensity. Additional chemical specific analysis was performed to test for characteristics associated with presence or levels of the contaminant in the child care environment. A screening risk assessment was performed for the compounds measured in the facilities that had appropriate health-based benchmarks.

Because results from the measurements of VOCs in air indicated that a large number of unknown chemicals were also present, we used National Institute of Science and Technology mass spectral libraries to identify these chemicals which were then semi-quantitatively estimated by comparing the instrument response to a toluene-based calibration curve.

2.2 Phases of Study

There were three phases of this research project: the study development stage, the pilot stage, and the full sampling stage. For the development stage, questionnaires and inspections

were completed and reviewed by CARB. A "Quality Assurance Project Plan" was prepared and reviewed by CARB in September 2010. Within the quality assurance and quality control (QA/QC) plan, study methodology was outlined and full sampling and analytical standard operating procedures (SOPs) for all analytes measured were provided (see Appendix G).

For the pilot stage, first and second visits were completed at seven ECE facilities. Seven sets of air samples were collected and analyzed by the Lawrence Berkeley National Laboratory (LBNL) and Battelle Memorial Laboratories for VOCs, carbonyls, pesticides, phthalates, flame retardants, PFCs, and particulate matter. Seven dust samples were analyzed for PFCs and BDEs by the U.S. EPA's National Exposure Research Laboratory (NERL). Pilot facilities were sampled from May 2010 to August 2010. Findings were reported in a pilot report prepared for CARB in December 2010. Changes to the study protocol included:

- Increased use of 4 l/pm PM_{10} and $PM_{2.5}$ samplers instead of 2 l/pm units to reduce error;
- Due to analytical problems caused by saturation of combined Tenax-TA® and carbosieve sorbent tubes from use of alcohol-based hand sanitizers, final protocols used separate Tenax-TA® and CarboTrap™ sorbent tubes to sample VOCs;
- PFCs were not detectable in air and were removed as air target analytes;
- Protocols to estimate air exchange rates were modified to include introduction of medical-grade CO_2 as a tracer gas.

Additional information about these protocol changes are described below. Once the pilot report was approved by CARB, full sampling was implemented at the remaining 33 ECE facilities. Full scale sampling occurred between November 2010 and May 2011. Throughout the study period, analytical samples were shipped to and analyzed by LBNL, NERL and Battelle Laboratories per study protocol. All study data were reviewed and compiled into datasets for statistical analysis.

2.3 Child Care Recruitment

There are two types of child care licenses issued by the California Department of Social Services (CDSS) Community Care Licensing Division: (1) center-licensed programs located in non-residential buildings, and (2) family-licensed programs located in homes. Family-licensed programs include Small Family Child Care Homes (SFCCH) and Large Family Child Care Homes (LFCCH). Family child care homes must be licensed in the licensee's own home with SFCCH facilities providing care for no more than 8 children and LFCCH facilities providing care for no more than 14 children. In this report, SFCCH and LFCCH are grouped together for analysis and referred to as home-based child care facilities. Center-licensed facilities are usually located in schools, converted homes, or commercial buildings and can range in size. In California, approximately 60% of children attend Center-based facilities and 40% attend home-based facilities. Thus, in each county, we targeted 12 (60%) centers and 8 (40%) homes.

Using publicly available databases accessed on January 10, 2010, from the CDSS, we geographically coded center and large home-based child care facilities by zip code. The center-licensed facilities were divided into 12 geographical units with approximately equal population in each county while the home-based facilities were divided into 8 geographical units. Publicly available databases were not available for small child care homes. See below for methods we used to enroll this group. See Appendix B for recruitment maps of Alameda and Monterey Counties.

For center-licensed facilities, a recruitment flyer was mailed to 15 randomly selected child care centers per geographical group in Alameda County (n=160). Recruitment flyers were sent to every child care center in our database in Monterey County (n=130). All letters were mailed to the attention of the contact named in the available CDSS database. Since SFCCH names are not publicly available, to comply with confidentiality requirements, we provided stamped envelopes to child care resource and referral agencies including the Community Child Care Council of Alameda County and Monterey County Child Care Resource and Referral. These agencies printed mailing labels and sent out recruitment flyers (n=100 in each county) with a description in English and/or Spanish to providers. If interest in response to a letter was not received in a geographic region, study staff made follow-up calls to child care centers and LFCCH homes in Alameda and Monterey County regions. Further recruitment of SFCCHs required word of mouth contacts. Overall, rates were low, with about 20 contacts necessary to recruit a child care center into the study, and 40 contacts necessary to recruit a home-based child care facility. Early in the study we completed background checks and fingerprinting to comply with licensing rules about working with children in child care centers. Obtaining these certificates significantly improved recruitment for the study.

All study activities were reviewed and approved by the University of California, Berkeley Committee for the Protection of Human Subjects. Written informed consent was obtained from the site director or other administrative personnel for each participating child care facility.

Forty ECE facilities were recruited to participate in our study with 20 each in Alameda and Monterey Counties. We enrolled 28 child care centers and 12 home-based facilities (Table 2). Upon enrollment, each child care facility received a unique two-digit ECE Identification Number or “ECE ID” that identifies the ECE facility. This ECE ID links all paper and electronic records including questionnaires, inspections, sample collection forms, laboratory data, etc., to the appropriate center or home.

Challenges in recruitment were a limitation of this study. The participation rate among child care centers was less than 5% of those contacted, and the recruitment rate of home-based child care facilities was even lower. Low recruitment rates may have resulted in selection bias in the study. In general, directors of the enrolled ECE facilities were interested in environmental risks to children’s health and may have previously implemented policies to minimize the use of contaminant sources. Despite these limitations, the participating centers represent a broad cross-section of institutions providing child care in California, including Head Start facilities, public school districts, private centers, and child care homes; the children were also typical of California populations, representing low-income, immigrant, and middle class families. Increasing the number of participating ECE facilities and expanding the geographic distribution would improve generalizability of the findings to the state as a whole.

Table 2. Child Care Facilities by County and License Type

	Alameda	Monterey	Totals
Child Care Center	13	15	28
Home-based	7	5	12
Totals	20	20	40

2.4 Site Visits

Typically, field technicians visited an ECE facility two times. The first visit included administering the consent form and questionnaire, conducting the inspection, and collecting dust samples, and the second visit involved air sample collection. Site visit dates occurred from May 2010 to May 2011. See Appendix A, Table 103 for dates of each site visit.

2.4.1 First Site Visit

For the first site visit, study staff met with the facility director or supervisor. The study staff described the study in full, read through the consent form, and answered any questions. If the site supervisor agreed s/he would sign one copy of the consent form and fill out contact information. In some cases consent forms were signed by senior administrative staff. However, all study information (described below) was collected from site supervisors and staff. Consent forms and contact information were later downloaded into an encrypted electronic database and paper copies were locked in a filing cabinet. A copy of the consent form was left with the site supervisor.

After consent, a questionnaire was administered to the site supervisor. If any information was not known, a note was made on the questionnaire and, if necessary, other staff members were contacted to obtain as much information as possible. Following the questionnaire, an inspection was conducted to collect information about the building and identify acceptable sampling locations. Dust samples were collected after the inspection. See Section 2.4.2 and Table 3 for a description of the information collected by questionnaire and inspection.

2.4.2 Questionnaire and Inspection Forms

Questionnaire and inspection forms were developed to collect information about each ECE facility, including demographic characteristics of children, factors in the building potentially related to air quality (e.g., presence of pressed wood furniture, carpets, air fresheners), and information about building quality, such as mold, water damage, and pest infestations (Table 3). Chemicals in the child care facilities (Figure 1) were inventoried in the inspection form. See Appendix F for copies of the questionnaire and inspection forms.

Table 3. Subject Areas for Study Instruments

Pest infestations (insect, rodent, other) Pesticide use and storage Mold, water damage, rotting wood Peeling paint Carpeting Age of structure Building type Building materials Press board furniture Floor type Cleaning products use /storage Sanitizer use	Air and/or carpet freshener use Computers present Age of upholstered furniture Air quality and ventilation Demographics of children/community Environmental policies Staff training/education Environmental health knowledge, attitudes, behaviors GPS coordinates Local land use

Figure 1. Typical products recorded in the inspection chemical inventory form, including pesticides, cleaners, metal polishers, paints, and other items that could affect indoor air quality.

2.4.3 Second Site Visit

Air samples and measurements were collected during the second Site Visit. Technicians typically arrived at the ECE facility 45 minutes before the children to set-up the sampling devices. The indoor samplers (Figure 2) were usually started at the beginning of the school day when children arrived. The indoor and outdoor samples were run for the whole child care day (typically 8 hours). Samplers were deployed around the height of a child's breathing zone (0.6 m to 1 m). Indoor and outdoor samplers were protected by a "kiddie-corral" made of untreated wood. After setting up equipment, all extra boxes or carrying cases were removed to limit the amount of foreign materials in the room. Sampling technicians were instructed to not wear or apply any personal care products with noticeable scents. To improve air exchange rate calculations, supplemental CO_2 was added to the indoor sampling location when children were not present (see Section 3.1.2, below).

Figure 2. Indoor equipment set-up at an ECE facility. Left image includes the flowmeters and integrated samplers. Right image shows real-time devices.

Outdoor measurements were collected at a subset of locations. The number of outdoor measurements varies by the pollutant measured. Due to feasibility and costs, we collected more outdoor measurements from real-time devices than integrated samples which require laboratory preparation and analysis. For example, we collected outdoor gravimetric $PM_{2.5}$ and PM_{10} at 12

facilities and DustTrak $PM_{2.5}$ measurements at 31 facilities. The majority of outdoor measurements were collected in the children's outdoor play area. However, due to electrical power constraints or teacher preferences, some outdoor locations were in other areas adjacent to the ECE facility. Outdoor collection area was occasionally covered by a portable gazebo to protect sampling devices from sunlight and rain.

A field technician was always present during the air sampling to log room conditions and ensure proper function of the equipment. Observational information collected included the number of children (0-6 years old), additional children (7-18 years old), child care staff, and CERCH staff (see Visit Materials Packet - Appendix F). Field technicians also tracked changes in ventilation conditions such as the number and area of outdoor or passage windows and doors and the duration they were kept open. Every two hours, flow rates from flow meters were recorded to ensure accurate sample volumes. Additional events that could have affected sampling results like cooking, heater use, or chemical use were also recorded.

2.5 Environmental Sampling and Laboratory Analysis Summary

Environmental sampling was performed by CERCH study staff. VOC, carbonyl, and gravimetric PM air sample analysis and air exchange rate modeling were conducted by Dr. Randy Maddalena in the Environmental Energy Technologies Division at LBNL. Semi-volatile organic compounds, including flame retardants, phthalate esters, and pesticides in air; and pesticides, phthalates, and non BDE-flame retardants in dust were measured by Battelle's Memorial Laboratory in Columbus, Ohio. Measurements of PFCs and PBDEs in dust were conducted at U.S. EPA's NERL in Research Triangle Park, North Carolina. Finally, measurements of lead and other metals in dust were performed in the laboratory of Dr. Donald Smith at University of California, Santa Cruz. Sampling collection and analytical methods (Table 4) are described in the following sections. Full sampling and analytical method Standard Operating Procedure (SOP) documents are in Appendix G.

Table 4. Sample Collection and Analytical Methods Summary

Media	Analyte	Sampling Method	Analytical Method	Analytical Laboratory
Air	VOCs	Sample tube with Tenax-TA sorbent	TD-GC/MS	LBNL
Air	Aldehydes and acetone	XPoSure aldehyde sampler	HPLC	LBNL
Air	$PM_{2.5}$ and PM_{10} mass	SKC® PEM with Teflon filter	Gravimetric analysis	LBNL
Air	Real-time $PM_{2.5}$	TSI DusTrak	Optical detector	-
Air	Real-time ultrafine particles	TSI Condensation particle counter	Optical detector	-
Air	PBDE flame retardants	PUF cartridge	GC/MS/MID	Battelle
Air	Phthalates, pesticides, and other flame retardants	PUF cartridge	GC/MS/MID	Battelle
Dust	Phthalates, pesticides, and other flame retardants	Vacuum sample	GC/MS/MID	Battelle
Dust	PBDE flame retardants	Vacuum sample	GC/MS/SIM	NERL
Dust	Perfluorinated compounds	Vacuum sample	UPLC-MS/MS	NERL
Dust	Metals	Vacuum sample	ICP-MS	UCSC

GC = gas chromatography; LBNL = Lawrence Berkeley National Laboratory; ICP = inductively coupled plasma; MID = modified isotope dilution; MS = mass spectroscopy; NERL = National Exposure Research Laboratory; PEM = personal environmental monitor; PUF = polyurethane foam; SIM = selective ion monitoring; TD = thermally desorbed; UCSC = University of California Santa Cruz; UPLC = ultra performance liquid chromatography.

2.5.1 Air Sampling and Laboratory Analysis

Air samples were collected over an entire school day (6 to 10 hours) and tested for VOCs, aldehydes and acetone, flame retardants, phthalates, pesticides, and particulate matter at cut points of 2.5 and 10 microns. The air sampling system used a single rotary vane pump installed in a stainless steel box lined with foil-faced fiberglass sound insulation to reduce noise. The pump was cooled by a fan. The pump's exhaust system included a muffler to reduce noise and a HEPA and carbon filter to eliminate emissions. Air was pulled through a manifold with 10 taper-tube flowmeters (Key Instruments part #10110_R6, #10310_R5, #10510_R5, and #10710_R3 for VOC, Carbonyls, Particle Mass, and SVOCs sampling, respectively). The flowmeters selected cover the range of flow rates needed for the target analytes. Calibration curves were determined for each flowmeter with sampling cartridges or tubes in-line using a Gilibrator® air flow calibrator. Calibration curves were checked at the end of the sampling campaign and were consistent with results prior to sampling.

Air samples were collected indoors at 40 child care facilities. An extra air PBDE measurement was collected at a revisit for ECE 40. The number of valid samples for each analyte is presented in Table 5 and indicates how many samples passed quality assurance measures.

Table 5. Integrated Air Sample Counts

Media	Analyte	Number of Valid Samples Collected[1]		
		Field	Duplicates	Outdoor
Air	VOCs	34	3	20
Air	Aldehydes and acetone	40	12	19
Air	PBDEs	41	2	16
Air	Phthalates, pesticides, and other flame retardants	40	2	14
Air	$PM_{2.5}$ mass	35	4	12
Air	PM_{10} mass	35	4	12

[1]Number of valid results include all samples that met QA/QC criteria.

Table 6 presents average flow rates and total sample volumes for integrated air samples although sample volumes and rates varied by facility. Indoor air samplers were set-up and deployed prior to outdoor samplers which resulted in a longer sample collection time than outdoor samples (473 minutes versus 429 minutes, respectively). Outdoor VOC and carbonyl sample rates were collected at a higher rate than indoors to decrease the number of samples below the detection limits.

Table 6. Indoor and Outdoor Average Integrated Air Sample Flow Rates and Sample Volumes

	Indoors[1]		Outdoors[2]	
	Average Flow Rate (l/min)	Average Total Volume (l)	Average Flow Rate (l/min)	Average Total Volume (l)
VOCs	0.015	7	0.019	8
Carbonyls	0.25	120	0.29	125
2 LPM PEMs[3]	2	946	2	858
4 LPM PEMs	4	1892	4	1716
SVOCs	4	1892	4	1716

[1]Averge Collection Time = 473 minutes
[2]Averge Collection Time = 429 minutes
[3] LPM = liters per minute; PEMs = personal environmental monitors

"Real-time" measurements of particles in air and of environmental conditions as a function of time were collected over the entire school day. In this study, concentrations of $PM_{2.5}$, UFPs, carbon monoxide (CO), carbon dioxide (CO_2), temperature, and relative humidity were measured in real-time. All real-time machines logged data at 60- second intervals. At a subset of facilities, outdoor and duplicate real time measurements were collected (Table 7). While the original intention was to collect at least 2 duplicates indoors for both the Condensation Particle Counter (CPC) and DustTrak, duplicates for these machines were only collected at our office

building for QA/QC purposes to limit the amount of noise our equipment contributed to the child care environment. See Appendix A, Table 104 for a list of the real-time devices deployed at each facility.

Table 7. Real-time Sample Count Breakdown

TYPE	Indoor	Outdoor	Indoor Duplicate
CPC	39	28	1
DustTrak $PM_{2.5}$	40	31	0
QTrak	40	30	3

2.5.1.1 Volatile Organic Compound Sampling and Laboratory Analysis

Initial sampling methods used sorbent tubes containing both Tenax-TA® and carbosieve. However, during pilot tests, analytical problems related to alcohols released by hand sanitizers interfered with the analysis (described in Appendix C). Final protocols used separate Tenax-TA® and CarboTrap™ sorbent tubes (P/N 012347-005-00; Gerstel or equivalent) to sample VOCs. Prior to use, the sorbent tubes were conditioned by helium purge (approximately 10 cc/min) at 275 °C for 60 minutes and sealed in Teflon capped tubes. VOC samples were collected onto the sample tubes directly from the room air or outdoor air. Approximately 7 liters of air were collected per sample over an 8-hour period (flow rate of 0.015 liters per minute [lpm]). After sample collection, the sorbent tubes were re-sealed with Teflon-lined caps and stored on blue ice for transportation. Samples were stored in a -20°C freezer until analysis.

VOC samples were analyzed at LBNL following U.S. EPA Methods TO-17.[96] Sorbent tubes were thermally desorbed for analysis by gas chromatography/mass spectrometry (TD-GC/MS) using a thermodesorption auto-sampler (Model TDSA2; Gerstel), a thermodesorption oven (Model TDS3, Gerstel), and a cooled injection system (Model CIS4; Gerstel). The cooled injection system is fitted with a Tenax-packed glass liner (P/N 013247-005-00; Gerstel). Desorption temperatures of 25 °C with a 0.5-minute delay followed by a 60 °C/min ramp to 250 °C and a 4-minute hold time were used. The cryogenic trap is held at -10 °C and then heated within 0.2 minutes to 270 °C at a rate of 12 °C/s, followed by a 3-minute hold time. Analytes were resolved on a GC (Series 6890Plus; Agilent Technologies) equipped with a 30 meter HP-1701 14% Cyanopropyl Phenyl Methyl column (Model 19091U-233; Agilent Technologies) at an initial temperature of 1 °C for 0.5 minutes then ramped to 40 °C at 25 °C/min, to 115 °C at 3 °C/min and finally to 250 °C at 10°C/min, holding for 10 minutes. The resolved analytes were detected using an electron impact MS system (5973; Agilent Technologies). The MS was operated in scan mode. All compounds over the MDL (< 1 to several ng) were evaluated by library search using the NIST spectral library followed by comparison to reference standards, where available. Multipoint calibrations were prepared from pure standards for common indoor pollutants and used to quantify target compounds (Table 8). All pure standards and analytes were referenced to an internal standard (~120 ng) of 1-bromo-4-fluorobenzene. During the pilot study, where a pure standard was not available, or the compound couldn't be positively identified, the concentration was estimated based on the total-ion-current responses using toluene as a surrogate standard.

Thirty–nine VOCs were analyzed in this study (Table 8). VOC MDLs ranged from 0.03 µg/m³ to 1.80 µg/m³ (individual analyte MDLs are presented in Appendix C, Table 111). For four compounds (D4 and D5 siloxanes, d-limonene, and 2-butoxyethanol) in 29 cases, the VOC

levels were above the calibration high mass. The thermal desorption analysis used for VOCs does not allow for dilutions and re-analysis of samples that have chemicals above the calibration range because the entire sample is consumed during the analyses. In the cases where the mass exceeded the highest calibration point, we report the highest calibration concentration for the method.

Table 8. VOC Analytes Measured in Air

VOC Analytes			
1,2,3-Trimethylbenzene	Carbon tetrachloride	Hexadecane	Tetrachloroethylene
1,2,4-Trimethylbenzene	Chloroform	Hexamethylcyclotrisiloxane[3]	Tetradecane
2-Butoxyethanol	Decamethylcyclopentasiloxane[3]	Hexanal	Toluene
2-Ethyl-1-hexanol	Decanal	Hexane	Texanol[1]
3-Carene	Decane	m/p-Xylene	TXIB[2]
a-Pinene	d-Limonene	Methylene chloride	Undecane
a-Terpineol	Dodecane	Nonanal	
Benzaldehyde	Ethylbenzene	Octamethylcyclotetrasiloxane[3]	
Benzene	g-Terpinene	Octanal	
Butanal	Heptanal	Octane	
Butylbenzene	Heptane	o-Xylene	

[1]Texanol is the common name for 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, an additive used in latex paint.
[2] TXIB is the common name for 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, a plasticizer used in vinyl flooring.
[3] Hexamethylcyclotrisiloxane (D3), Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5).

2.5.1.2 Carbonyl Sampling and Laboratory Analysis

Carbonyl samples were collected on silica gel cartridges coated with 2,4-dinitrophenyl-hydrazine (XPoSure Aldehyde Sampler; Waters corporation) with ozone scrubbers (P/N WAT054420; Waters) upstream. Approximately 120 liters of air were drawn through the sample cartridge over an 8-hour period (0.25 lpm). After use, the sample cartridges were capped, sealed individually in foil bags, and stored on blue ice during transport and stored in a -20°C freezer until analysis at LBNL. The target analytes in the low molecular weight carbonyl analysis include formaldehyde, acetaldehyde, and acetone.

Samples for formaldehyde, acetaldehyde, and acetone were analyzed by LBNL following U.S. EPA Method TO-11.[97] Cartridges were extracted by eluting with 2 ml of high-purity acetonitrile into 2-ml volumetric flasks. Extracts were analyzed by high-performance liquid chromatography (HPLC) (1200 Series; Agilent Technologies) using a C_{18} reverse phase column with 65:35 H_2O:acetonitrile mobile phase at 0.35 ml/minute and UV detection at 360 nm. Multipoint calibrations were prepared for the target aldehydes using commercially available hydrazone derivatives of formaldehyde, acetaldehyde and acetone. The method detection limit (MDL) for formaldehyde, acetaldehyde, and acetone were 10, 0.98, and 2.5 ng, respectively. Formaldehyde, acetaldehyde, and acetone MDLs in µg/m³ calculated using the average total sample volume in this study (0.12 m³) were 0.08, 0.008, and 0.02 µg/m³, respectively.

2.5.1.3 Semi-Volatile Organic Compound Air Sampling and Laboratory Analysis

Semi-volatile organic compounds (SVOCs) have a boiling point in the range of 240-400°C.[98] Flame retardants, phthalates, and pesticides are considered SVOCs. Two identical cartridges, each containing a polyurethane foam (PUF) plug, were used to collect SVOCs (Figure 3). One cartridge was analyzed for selected phthalate esters, chlorinated tris phosphate flame retardants, pesticides, and brominated flame retardant constituents of Firemaster 550 and the second cartridge was analyzed for selected BDEs. All SVOC analytes analyzed are presented

in Table 9. Pre-cleaned (via Soxhlet extraction procedures), BDE-free PUF plugs 22 mm in diameter and 76 mm in length were used. A stainless steel punch was used to prepare 19-mm filters from Pall A/E glass fiber filter media. The filters and glass cartridges were baked in a muffle furnace at 450 °C overnight for cleaning and then assembled (filter, support screen and PUF) and sealed with high density polyethylene (HDPE) covers at each end. SVOC samples were collected at 4 lpm for the duration of the child-care day. After use, PUF samples were capped with aluminum foil and transported on blue ice for storage in a -20°C freezer. PUF samples were shipped on dry ice in 5 batches to Battelle Laboratory for analysis.

Table 9. SVOC Air Analytes Measured with PUF Cartridges

BDEs	Other Flame Retardants
BDE-47	Tris (2-chloroethyl) phosphate (TCEP)
BDE-99	Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)
BDE-100	2-Ethylhexyl tetrabromobenzoate (EHTBB)
BDE-153	Bis(2-ethylhexyl)tetrabromophthalate (BEHTBP)
BDE-154	
BDE-209	

Phthalate Esters	Pesticides
Diethyl phthalate (DEP)	Chlorpyrifos
Dibutyl phthalate (DBP)	Diazinon
Diisobutyl phthalate (DIBP)	Dacthal
Butyl benzyl phthalate (BBP)	Cis-/trans-permethrin
Di(2-ethylhexyl) phthalate (DEHP)	Cypermethrin
	Cyfluthrin
	Bifenthrin
	Imiprothrin
	Sumithrin
	Piperonyl butoxide

Figure 3. PUF cartridge used to sample SVOCs with corresponding sample label affixed to cartridge.

2.5.1.3.1 Brominated Diphenyl Ether Flame Retardant PUF Analysis

BDE analytes analyzed in the PUFs are listed in Table 9. Blank and spike samples were analyzed prior to sampler deployment to verify integrity of the sampling matrix and method extraction efficiency. The PUFs were placed in a 22-mL ASE cell, spiked with the surrogate recovery standards (SRSs) BDE 126 and 13C12 BDE 209, and extracted at 2000 psi and 100 °C through three 20-minute cycles using DCM. The extract was concentrated to 10 ml and treated with 1 g of 44% acid silica for 2 hours. The extract was combined with three washes of the acid silica and concentrated to 1 ml; this concentrate was applied to an alumina SPE cartridge that is eluted with 1:1 hexane:DCM. The extract was concentrated to a final volume of 0.2 ml, spiked with the internal standard, and analyzed using GC/MS/MID in the negative chemical ionization (NCI) mode for the BDEs.

The extracts were analyzed using an Agilent HP 6890 GC interfaced to an Agilent 5973 MS detector with negative chemical ionization source and operated using automated ChemStation data acquisition and processing software. The extracts were analyzed with a six-point calibration curve spanning the linear range of the instrument. Sample extracts with analyte concentrations exceeding the calibration range by 15% were diluted and reanalyzed for the specific high concentration analyte. The internal standard method of quantification was used. The same analysis protocols and checks as described above were applied to these analyses. BDE 209 was an original target analyte for air analysis. However, after the first set of PUF analysis, the calibration curves and/or its C13-labelled analogue did not meet laboratory QA/QC standards. Therefore, only BDE-209 values for the first set of analysis are presented in this report. Method detection limits for BDEs were 0.02 ng. Using the average indoor air volume for SVOCs (1.9 m^3), BDE MDLs as a concentration was 0.01 ng/m^3.

2.5.1.3.2 Phthalate Esters, Pesticide, and Non-BDE Flame Retardant PUF Analysis

Phthalate esters, pesticides, and non-BDE flame retardants analyzed in PUFs are listed in Table 9. The PUFs were placed in a 22-ml accelerated solvent extractor (ASE) cell, spiked with the SRS 13C4-di-n-hexyl phthalate and extracted at 2000 psi and 100° C through two 5-minute cycles using dichloromethane (DCM). The extract was concentrated to 10 ml, and 1 ml was removed, spiked with the internal standard dibromobiphenyl, and analyzed using GC/MS in the multiple ion detection (MID) mode for the phthalate esters. MDLs for all phthalate analytes were approximately 1 ng, which includes a field matrix blank correction of three times the standard deviation. Using the average indoor air volume for SVOCs (1.9 m^3), phthalate MDL as a concentration was 0.5 ng/m^3.

After phthalate analysis, the remaining 9 ml of extract was applied to an aminopropyl solid phase extraction (SPE) cartridge and eluted with additional DCM. The eluent was concentrated to 0.2 ml, spiked with the internal standard, and analyzed using GC/MS/MID for the tris phosphate flame retardants and the brominated Firemaster 550 flame retardant constituents (BEHTBP and EHTBB). In the MID mode, two ions were monitored per analyte, the quantification ion and the confirmation ion.

The extracts were analyzed using an Agilent HP 6890N GC interfaced to an Agilent 5975 MS detector and operated using automated ChemStation data acquisition and processing software. The unknowns were quantified using a six-point calibration curve spanning the linear range of the instrument. Sample extracts with analyte concentrations exceeding the calibration range by 15% were diluted and re-analyzed for the specific high concentration analyte. The internal standard method of quantification was used, where the ratio of the analyte signal to

internal standard signal was used for quantification. The calibration data was fitted using linear least squares regression analysis. A regression fit of r^2>0.99 was required for use of a linear calibration curve. Factors used to confirm analyte identification included: correct retention time (± 0.02 min), co-maximized quantification and confirmation ions, and the correct ratio of the ion intensities for the quantification and confirmation ion (±30% variance). MDLs ranged from 0.2 to 0.5 ng for the non-BDE flame retardants (See Appendix C, Table 127). Using the average indoor air volume for SVOCs (1.9 m³), non-BDE flame retardant MDLs had a range of 0.1 to 0.3 ng/m³.

Pesticides in PUFs were analyzed with the same general GC/MS/MID approach described for non-BDE flame retardants, above. The extracts were analyzed with a six-point calibration curve that spans the linear range of the instrument. Sample extracts with analyte concentrations that exceed the calibration range by 15% were diluted and reanalyzed for the specific high concentration analyte. The internal standard method of quantification was used. Pesticide MDLs were calculated by subtracting three times the standard deviation of field matrix blanks and ranged from 0.05-0.5 ng. Using the average indoor air volume for SVOCs (1.9 m³), the MDL as a concentration for pesticides ranged from 0.03 to 0.26 ng/m³.

2.5.1.4 Real-Time Particle and Environmental Measurements

Real time monitors were deployed at each child care facility. Real-time instruments measure parameter of interest (i.e., PM, CO_2, temperature) through time. Monitors were set to store one-minute averages, counts, or concentrations.

Texas Science Instrument (TSI) 8554 QTraks were used to measure CO_2, CO, relative humidity, and temperature. The TSI 8554 CO_2 sensor uses non-dispersive infrared and has a range of 0 to 5000 ppm. The accuracy is ± 3% of reading + 50 ppm) at 25°C with a resolution of 1 ppm. The CO is read by an electro-chemical sensor with a range of 0-500 ppm. The accuracy is ± 3% of reading or 3 ppm, whichever is greater. The resolution is 1 ppm with a response time <60 seconds to 90% of final value. The temperature sensor is a thermistor with a range of 0 to 50°C. A thin-film capacitive sensor measures humidity with a range of 5-95% RH.[99] QTraks were calibrated in the Spring of 2010 by Texas Science Instruments.

Ultrafine particles were measured using two TSI 3781 water CPCs. The TSI 3781 detects total particle number concentration in the size range of > 3µm down to 6 nm (D_{50} –detection of 50% of particles) and concentration of 0 to 5 x 10^5 particles/cm^3. The particle concentration accuracy is ± 10% at 5 x 10^5 particles/cm^3. The response time is <2 seconds to 95% in response to concentration step change. The device has an aerosol flow rate of 0.12+/-0.012 lpm and inlet flow rate of 0.6+/-0.12 lpm.[100] Comparison tests were performed between both CPCs used prior to deployment in the field. See Appendix C for additional QA/QC information for these instruments.

Real time fine particulate matter was measured with a TSI DustTrak 8520. The DustTrak 8520 used a 2.5 µm size selective inlet to measure $PM_{2.5}$ concentrations based on the light scattering properties of Arizona Road Dust. The DustTrak 8520 was compared to CARB's Monitoring and Laboratory Division (MLD) ambient air $PM_{2.5}$ samples collected on Teflon filters in Sacramento, California, prior to sampling (See Appendix C for additional QA/QC information). The DustTrak 8520 uses a 90° light scattering sensor and has a concentration range of 0.001 to 100 mg/m³. The resolution is ± 0.1% of reading or 0.001 mg/m³, whichever is greater. The factory set flow rate of 3.0 lpm was used.[101] An additional DustTrak 8530 was rented from Ashtead Technology with a 2.5 µm size selective impactor. The TSI 8530 has an aerosol

concentration range of 0.001 to 400 mg/m³. The resolution is +/-0.1% of reading or 0.001 mg/m³, whichever is greater. The factory set flow rate of 3.0 lpm was used.[101] The DustTrak 8530 was calibrated in June 2010 by TSI. Devices were "zeroed" prior to each day of sampling.

2.5.1.5 Gravimetric Particle Sampling and Weighing

Gravimetric $PM_{2.5}$ (particles with a diameter less than or equal to 2.5 micrometers) and PM_{10} (particles with a diameter less than or equal to 10 micrometers) were collected using SKC® Personal Environmental Monitors (PEMs) onto 37mm Teflon filters. The integrated $PM_{2.5}$ and PM_{10} particle mass concentrations were determined following EPA Method IP-10A.[102] Flow rates of 2 lpm and 4 lpm were set per the manufacturer's recommendations, and samples were integrated over the period when children were present, typically 8 hours. Each Teflon filter used for mass analysis was weighed on two separate occasions both before deployment and after recovery using a Sartorius SE-2F balance to confirm accurate weighing and reporting. Because Teflon filters do not readily absorb water, they are generally much less sensitive than quartz filters to variations in ambient relative humidity. Nevertheless, filters were equilibrated for a minimum of 24 hours at temperature = 21±3 °C and relative humidity= 30-40% for at least one weighing before and one weighing after sampling. A 100 µg certified standard weight was weighed with each group of sample filters to confirm consistent operation of the balance. An MDL of 14.4 µg was calculated by computing three times the standard deviation of blank filters. Reported data was blank corrected by subtracting the mean blank mass (2.3 µg) from weighed particle masses.

2.5.2 Dust Collection and Laboratory Analysis

With the exception of one facility where no carpets or floor dust was present, dust samples were collected from carpets centrally located in the primary child care room where air sampling would take place during the second site visit (n=39). The dust sampling methods followed procedures described in the American Society for Testing Materials (ASTM) Standard Practice D 5438-05.[103,104] These methods have been validated for house dust from carpets, bare floors, and furniture by the U.S. EPA[105] using the High Volume Surface Sampler (HVS3) (Envirometrics Inc.).[105] The HVS3 vacuums were thoroughly checked for leaks and normal air flow was verified prior to use. The entire sampling train was cleaned with laboratory grade detergent, de-ionized water, and isopropanol between each use. Dust samples were collected from at least 1m² into cleaned, 250 ml amber glass bottles (I-CHEM, item# 341-0250). Bulk dust was shipped on dry ice to Battelle Laboratory where it was sieved to 150 µm using a stainless steel sieve and aliquotted. One aliquot was sent to U.S. EPA for PFC and BDE analysis in dust and another sent to UCSC for lead analysis. A total of 39 dust samples were collected (Table 10). Dust samples were analyzed for pesticides, phthalate esters, PBDE flame retardants, tris phosphate flame retardants and Firemaster 550 flame retardants, PFCs, and metals (Tables 11 and 12). For QA purposes, SVOC dust samples were also analyzed in duplicate. Both dust concentrations (i.e., ng/g) and dust loading (i.e., ng/m²) are presented in this report. Dust concentration is the analyte weight of interest (i.e., pesticide) in relation to amount of sieved dust analyzed. Dust loading is the analyte weight of interest in relation to the surface area vacuumed (m²) by the HVS3. Therefore, dust loading was calculated by multiplying dust concentration by total weight of sieved dust and dividing by the area vacuumed.

Table 10. Sample and Analysis Counts for Dust

Media	Analyte	Number of Valid Samples for Analysis	Analytical Duplicates[1]
Dust	PBDEs	39	1
Dust	Phthalates, pesticides, and other flame retardants	39	2
Dust	PFCs	39	3
Dust	Heavy Metals	38[2]	4

[1] Analytical duplicates are repeat analyses of dust sample
[2] ECE 45 sample mass too low for metals analysis

Table 11. BDE, Other Flame Retardants, and Phthalate Esters Dust Sample Target Analytes

BDEs	Other Flame retardants	Phthalate esters
BDE-47	Tris (2-chloroethyl) phosphate (TCEP)	Diethyl phthalate (DEP)
BDE-99	Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)	Dibutyl phthalate (DBP)
BDE-100	2-Ethylhexyl tetrabromobenzoate (EHTBB)	Diisobutyl phthalate (DIBP)
BDE-118	Bis(2-ethylhexyl)tetrabromophthalate (BEHTBP)	Butyl benzyl phthalate (BBP)
BDE-153		Di(2-ethylhexyl) phthalate (DEHP)
BDE-154		
BDE-183		
BDE-190		
BDE-197		
BDE-203		
BDE-205		
BDE-206		
BDE-207		
BDE-209		

Table 12. Pesticide, Metals, and PFCs Dust Sample Target Analytes

Pesticides	Metals	PFCs
Diazinon	Aluminum (Al)	Perfluorobutyric acid (PFBA)
Chlorpyrifos	Cadmium (Cd)	Perfluoropentanoic acid (PFPeA)
Dacthal	Chromium (Cr)	Perfluorohexanoic acid (PFHxA)
Imiprothrin	Copper (Cu)	Perfluoroheptanoic acid (PFHpA)
Piperonyl butoxide	Iron (Fe)	Perfluorooctanoic acid (PFOA)
Bifenthrin	Manganese (Mn)	Perfluorononanoic acid (PFNA)
Sumithrin	Lead (Pb)	Perfluorodecanoic acid (PFDA)
cis-Permethrin	Zinc (Zn)	Perfluorobutane sulfonate (PFBS)
trans-Permethrin		Perfluorohexane sulfonate (PFHS)
Cyfluthrin		Perfluorooctane sulfonic acid (PFOS)
Cypermethrin		

2.5.2.1 Brominated Diphenyl Ether Dust Analysis

U.S. EPA conducted measurements of 14 BDE congeners in dust samples (Table 129). Prior to sample extraction, surrogate recovery standards of ^{13}C-labeled BDE 209 (2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether, BDE 209L) a ^{13}C-labeled chlorinated diphenyl ether (2,2',3,4,5-pentachlordiphenyl ether [Cambridge Isotope Laboratories, Andover, MA]) and BDE 181 were added to each sample. One gram of dust sample was extracted using pressurized fluid extraction with hexane:dichloromethane (80:20). All samples and blanks were extracted at 75 degrees C heat time for 5 minutes, static time for 5 minutes, and pressure at1500 psi or 10.34 MPa for two cycles. The extract was reduced to 2 ml. The extract was cleaned using two 3 ml Silica SPEs, modified and used in tandem. For the 1st SPE, alumina and sodium sulfate was added atop the silica. The second was modified by the addition of sulfuric acid to the silica bed. After concentration to 1 ml, internal standards were added prior to analysis. Three analytical internal standards were used, F-BDE 69 (4'-fluoro-2,3',4,6-tetrabromodiphenyl ether), F-BDE 160 (4'-fluoro-2,3,3',4,5,6-hexabromodiphenyl ether), and F-BDE 208 (4'-fluoro-2',3,3',4,5,5',6,6'-nonabromodiphenyl ether). All chemicals were $\geq$ 98.5% purity and were obtained in stock solutions of 50 ng/ml in isooctane from either Cambridge Isotope Laboratories or ChironAS (Trondheim, Norway).

After concentration, extract was measured for BDEs using an Agilent 6890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC/MS). Quantification of BDE congeners were performed with negative chemical ionization operated in SIM mode. PBDEs were analyzed by the U.S. EPA at two different time points. ECEs 10-16 were analyzed on August 2010 and ECEs 17-49 were analyzed September 2011. BDE MDLs ranged from 6.9 to 31.0 ng/g. See Appendix C, Table 127 for individual BDE MDL and analytical recoveries.

2.5.2.2 Phthalate Ester, Pesticides, and Non-BDE Flame Retardant Dust Analysis

Battelle Laboratory quantified analytes for phthalate esters, pesticides, and non-BDE flame retardants in dust. A 0.5-g aliquot of the dust was spiked with the SRSs listed in the analytical methods section for air samples. The dust was sonicated in a solution of 1:1 hexane:acetone. The mixture was then centrifuged, and the extract withdrawn. A 1-ml aliquot of the extract was spiked with internal standards and analyzed using GC/MS/MID for the phthalate esters without further processing (to limit laboratory contamination). The remaining aliquot was cleaned up on an SPE cartridge and concentrated to 1 ml for analysis. After addition of the internal standard, the extract was analyzed for tris phosphate flame retardants, pesticides, and brominated flame retardant constituents of Firemaster 550 using the same GC/MS/MID method used for the air samples. Phthalates had a MDL of 20 ng/g and non-BDE flame retardants had a MDL of 1 ng/g. Pesticides had a MDL range of 0.3 to 20 ng/g. See Appendix C more information.

2.5.2.3 Perfluorinated Compound Dust Analysis

U.S. EPA measured PFC analytes in dust. To analyze these compounds, 100 mg of dust were centrifuged with methanol containing carbon-13 labeled internal standards ($^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_2$−PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{18}O_2$-PFHxS, and $^{13}C_4$−PFOS). After vortexing for 30 seconds, the samples were shaken on a horizontal shaker for 10 minutes and then placed in an ultrasonic bath. The tubes were centrifuged and the entire extract was passed through an SPE cartridge pretreated with methanol. The supernatant passing through the SPE cartridge was evaporated to 1.0 ml. An aliquot of the supernatant was combined with 2 mM of ammonium-acetate:methanolic sample in an autosampler vial for liquid chromatography-mass spectrometry (UPLC-MS/MS) analysis. The analysis was carried out using a Waters Acquity

UPLC equipped with a Quatro Premier XE triple quadrupole mass spectrometer operated in negative electrospray ionisation (ESI) mode. Analytes were separated chromatographically using an ethylene bridged hybrid C18 column (2.1 mm i.d. × 50 mm, 1.7 mm; Waters, Milford, MA, USA). Ionization and collision cell parameters were optimized for each individual analyte. Extracted standard curves were constructed using solvent standards prepared to give a 9-point calibration to determine analytes in unknowns. Analytical runs included extracted method blanks, duplicate measurement of 10% of the unknown samples and inclusion of standard reference materials (SRMs) from NIST equal to 10% of the unknown samples. MDLs for PFCs in dust were 5 ng/g.

2.5.2.4 Metals Dust Analysis

Sieved dust samples were shipped to Dr. Donald Smith at the University of California Santa Cruz. The dust samples were processed based on EPA method 3050b. All plastic ware was cleaned using trace metal cleaning procedures, and trace metal grade reagents. 0.5 grams of dry dust samples were combined with 50% nitric acid (HNO_3) and the samples were shaken thoroughly to ensure mixing. The slurries were heated in a water bath at 95^{o}C for 15 minutes. The samples were cooled to room temperature and 2.5 ml concentrated HNO_3 was added, and the mixtures were heated again at 95^{o}C for 2 hours. The samples were cooled and 30% H_2O_2 was added. The samples were heated again at 95^{o}C for 2 hours.

The samples were then cooled to room temperature and centrifuged. The supernatants were decanted into a pre-weighed 60 ml Nalgene bottle. 10 ml of water was mixed with the residues, and the mixtures were centrifuged again. The supernatants were added to the previous volumes, and the total volumes were brought to 50 ml with water. The final solutions were weighed. Samples were analyzed on a Perkin Elmer 4300 DV ICP-OES. Standards contained 0.5 ppm Cd, Cr, Cu, Mn, Pb, and Zn and 40 ppm Al and Fe (low standard) or 2 ppm Cd, Cr, Cu, Mn, Pb, and Zn, and 80 ppm Al and Fe (high standard). Internal standards of 100 ppm Y and Sc were used to normalize count rates. Concentrations obtained at multiple wavelengths for a given element were averaged for the reported concentration.

Blanks were analyzed 6 times and the method detection limit is (MDL) 3x the standard deviation of the blank. MDLs are in µg/ml (ppm) as analyzed. MDLs ranged from 0.1 to 7.5 µg/g assuming 0.5 grams of dust sampled extracted into a final volume of 50 ml. See Appendix C for additional QA information.

2.5.3 Ventilation Measurements

The ventilation rate or air exchange rate (AER, air changes per hour) is an important factor for interpretation of indoor sources of pollutants and the relationship between indoor and outdoor pollutant levels. Ventilation measurements were estimated using both continuous indoor CO_2 measurements and the release of CO_2 as a tracer gas. The use of continuous indoor CO_2 measurements to estimate air exchange rates is a standard method.[106-109] However, when piloting the continuous indoor CO_2 measurement method for estimating AER, study staff found high variability and relatively low CO_2 levels indoors at the first facilities. In addition, tracking the number of people inside some ECE facilities proved difficult because of the frequency with which people entered and exited the child care room being monitored. To address these concerns, we released medical grade CO_2 (Praxair, Part Number CD M-10, United States Pharmacopeia grade) to temporarily increase indoor CO_2 levels and use the subsequent decay curve as a tracer gas to compute the AER. CO_2 was chosen as the tracer gas due to its low toxicity, “natural” presence in the existing environment, and acceptability to ECE facility

directors. CO_2 was added to the room when children were not present (usually at lunch or the end of the day) and CO_2 levels were increased to approximately 2500 ppm. We then compared AER estimates based on the CO_2 decay and a continuous mass-balance model. The tracer gas decay method uses the following equations:[110,111]

$$C_t - C_{input} = [C_{orig} - C_{input}]e^{(-Qt/V_r)}$$

Where,

C_t = Concentration of tracer at elapsed time, ppm
C_{input} = Concentration of tracer from inlet air and occupant emissions, ppm
C_{orig} = Concentration of tracer at start of test, ppm
Q = Effective ventilation rate, m³/hour
T = Time of test duration, hour
V_r = Volume of child care room, liters

We accounted for both CO_2 input from outdoors and occupant emissions in our model. Total CO_2 input into the child care room was calculated using the formula:

$$C_{input} = \frac{C_{out}}{1{,}000{,}000} * V_r * ACH + C_e$$

Where,

C_{input} = Total CO_2 input into the child care room, $\left(\frac{l}{h}\right)$
C_{out} = Average outdoor CO_2 concentration, ppm
V_r = Volume of child care room, liters
ACH = Air changes per hour, $hour^{-1}$
C_e = Emission CO_2 concentration of occupants, $\left(\frac{l}{h}\right)$

Using occupancy logs, CO_2 input from occupants in the ECE facility were calculated using per person emission rates from Persily et al., 1997.[109] Changes of three different age groups were recorded minute-by-minute in the occupancy logs. Children 0-5 years old were assumed to have CO_2 emission rate of 10.44 l/h and adults 18.72 l/h.[110] Adult emission rates were used for additional children between the ages of 5-18 who were often present in home ECE facilities.

$$C_e = \left[\varepsilon_{0-5} * 10.44\frac{l}{h}\right] + \left[\varepsilon_{5-18} * 18.74\frac{l}{h}\right] + \left[\varepsilon_{adults} * 18.74\frac{l}{h}\right]$$

Where,

ε_{0-5} = # of children between ages 0-5 years
ε_{5-18} = # of children between ages 5-18 years
ε_{adults} = # of adults

The emission profile combined with measured indoor and outdoor CO_2 concentrations was used to fit the mass balance to the data by optimizing the estimated ventilation rate. QTrak indoor CO_2 concentrations, ventilation, and occupancy logs were matched together by minute-by-minute time measurements. Changes in ventilation, including opening/closing of exterior/passage windows or doors were recorded minute-by-minute in ventilation logs. If a change in the indoor environment was observed, a separate AER for that time period was calculated. Average outdoor CO_2 throughout the day was used in the models. If outdoor CO_2 concentrations were not measured at the ECE facility, the average outdoor CO_2 concentration from all facilities was used (371 ppm). When the occupancy changed, the mass balance

equation was calculated with a new CO_2 input (l/h) and predicted CO_2 before occupancy change was used as C_{orig}. Predicted CO_2 was calculated using an adapted equation:

$$C_{pred} = C_{Pred,Occ\,\Delta} * e^{[-ACH*(T_i - T_{ACH})]} + \left[\frac{\frac{C_{input}}{V_r}}{ACH} * 1000000\right] * \left[1 - e^{[-ACH*(T_i - T_{ACH})]}\right]$$

Where,

C_{pred} = Predicted CO_2 from model, ppm

$C_{Pred,Occ\,\Delta}$ = Predicted CO_2 before occupancy change, ppm

T_i = Elapsed time, hours

T_{ACH} = Elapsed time at start of new air change rate, hours

Initial "predicted CO_2" concentrations were based on the QTrak CO_2 concentration. When the CO_2 was released as a tracer gas, the predicted CO_2 concentration was the peak QTrak concentration for the corresponding minute. To produce the best fit between the predicted CO_2 concentrations and QTrak generated CO_2 concentrations, the mean squared error (MSE) between the model and QTrak generated values was minimized by the "Solver" function in Microsoft Excel by changing the AER for each time period the AER was predicted to be distinct based on the ventilation logs. The Solver function adequately reduced the MSE in most instances. For occasional periods, Solver reduced the AER to zero. Therefore, a constraint of limiting the AER to ≥0.15 hour^{-1} was implemented. 0.15 hour^{-1} is the 5th percentile of a sample of 2844 U.S. residences[112] and is a reasonable lower limit on indoor ventilation, including office buildings. The model optimization approach provided a daily average ventilation rate and ventilation rates during distinct time periods when ventilation would be different (open versus closed windows). The indoor environment was constantly changing along with the air exchange rates throughout the day. The use of both the mass balance and tracer gas method is appropriate since the air exchange rates calculated just during the CO_2 release may not be generalized across the entire day, and provided a means to compare the tracer gas and mass balance methods to ensure estimated AERs were in a similar range for both methods.

2.6 Quality Assurance and Quality Control Procedures

A quality assurance and quality control plan was reviewed and approved by CARB before study activities were initiated. All participating institutions including CERCH, LBNL, Battelle Laboratories, and U.S. EPA contributed and reviewed the QA/QC plan for the study along with providing sampling and analysis SOPs. QA/QC documentation strives to meet the following objectives:

- Ensure high quality measurements;
- Provide a means to assess the quality of the data;
- Ensure accuracy of questionnaire data and inspection measurements;
- Outline the project's organizational and management structure;
- Detail operating procedures for collection and analysis of analytes;
- Outline data generation, transfer, protection, and storage procedures.

2.7 Data Management and Analysis

All data was extensively reviewed. For all survey instruments, the performing field technician reviewed questionnaire or inspection forms immediately after completing the forms to ensure all questions were answered. At the field office, an additional review was completed by a second reviewer to ensure consistency and completeness. Fifteen percent of data forms were double data entered and range checks were performed using SAS Version 8. If any out-of-scale values were present, the forms were individually inspected to confirm recorded information. When needed, and approved by Dr. Bradman, participants were contacted to resolve any data problems.

Statistical analysis was performed with STATA statistical software Version 11.2 to calculate the descriptive statistics and tests of association (e.g., Spearman Rank Correlation Coefficients, Mann-Whitney test, Wilcoxon test). Individual data sets were merged by ECE identification numbers to create comprehensive data sets for statistical analysis. Values below the MDL are presented as "<MDL" in results tables. Mean, standard deviations (SD), and indoor to outdoor ratios are calculated using the MDL divided by square root of 2 for values below the MDL.[113] Non-parametric tests of associations are used in this report due to the small sample size. The MDL /√2 for values below the MDL was also used in the tests for associations and to calculate relative standard deviations, as described below. R Version 2.13.2 was used to graph Figures 5, 7, 8, and 10.

To compare duplicate measurements, the percent relative standard deviation (RSD) is used as a measure of precision.[114] When duplicate measurements were below the MDL, the RSD is the absolute value of coefficient of variation multiplied by 100.

$$RSD\ (\%) = \left|\frac{standard\ deviation}{mean}\right| * 100$$

3 Results

3.1 ECE Facility Characteristics

Forty facilities serving a total of 1,764 children were sampled. Table 13 describes individual characteristics of the ECE facilities. The average attendance was 44 children, with a maximum of 200 children and a minimum of four enrolled in a small child care home. Seventy-six percent of the children were 3+ years old, 19% were 2-3 years, and 5% were less than 2 years of age. Statewide, 6% of children less than 2 years are enrolled in child care,[115] suggesting no bias in the age structure of the population we sampled.

Table 13. ECE Facility Characteristics

ECE#	County	ECE Type	Number of Children	Building Type[1]	Building Age[2]	Neighborhood Type[3]
10	Alameda	Home	16	Home (SFD)	1942	Residential
11	Alameda	Center	20	Home (SFD)	1912	Residential
12	Monterey	Center	100	School	2008	Residential
13	Monterey	Center	15	School(P)	1970	Agricultural
14	Alameda	Center	119	School(P)	1976	Residential
15	Alameda	Center	58	Office	1940	Commercial
16	Alameda	Center	25	School	.	Commercial
17	Alameda	Center	42	School (P)	.	Commercial
18	Alameda	Center	40	Home (SFD)	1980	Residential
19	Alameda	Home	15	Home (SFD)	1926	Residential
20	Alameda	Center	20	Office	.	Residential
21	Alameda	Home	14	Home (SFD)	1903	Residential
22	Alameda	Center	97	School	1989	Commercial
23	Alameda	Home	8	Home (SFD)	1939	Commercial
24	Monterey	Center	90	Office	.	Residential
25	Monterey	Center	200	School	2000	Residential
26	Monterey	Center	31	School	.	Residential
27	Monterey	Center	40	School	2007	Residential
28	Monterey	Center	24	School	1990	Agricultural
29	Monterey	Center	15	Church	1953	Residential
30	Monterey	Center	24	School (P)	.	Residential
31	Monterey	Center	50	School (P)	.	Residential
32	Alameda	Center	85	School (P)	1955	Commercial
33	Monterey	Home	10	Home (SFD)	1950	Residential
34	Alameda	Center	70	School	.	Residential
35	Alameda	Home	20	Home (SFD)	1963	Residential
36	Monterey	Home	10	Home (SFD)	1977	Residential

Table 13 Continued. ECE Facility Characteristics

ECE#	County	ECE Type	Number of Children	Building Type[1]	Building Age[2]	Neighborhood Type[3]
37	Alameda	Center	120	School	.	Residential
38	Monterey	Home	13	Home (SFD)	2001	Agricultural
39	Monterey	Home	5	Home (SFD)	1999	Agricultural
40	Alameda	Home	11	Home (SFD)	1930	Residential
41	Monterey	Home	6	Home (SFD)	1998	Residential
42	Alameda	Center	77	School	1960	Residential
43	Alameda	Center	28	School (P)	1970	Residential
44	Monterey	Center	40	Home (SFD)	1955	Residential
45	Alameda	Home	4	Home (SFD)	1938	Residential
46	Monterey	Center	34	School (P)	1998	Residential
47	Monterey	Center	48	School	1995	Residential
48	Monterey	Center	55	Church	1971	Rural/Ranch
49	Monterey	Center	65	School (P)	1998	Agricultural

[1] SFD= single family detached; P= portable
[2] Some directors did not know building age
[3] Neighborhood was judged by study staff during inspection

In the facilities sampled, 95% of the children spent at least 1-2 hours outside, and with some spending up to 6 hours outside, depending on the weather (Table 14). Thirty-seven percent spent more than 8 hours per day in child care, 41% spent 5-8 hours, and 22% spent less than 5 hours. Overall, 50% of children received a government subsidy, compared to 39% statewide. Among the facilities sampled, 87% had at least one child receiving a government subsidy, with up to 100% of children in some facilities. On average, the child care staff working in the facilities had some college education. At two facilities, the average education achieved was a high school diploma, and at 17 facilities, the average education achieved was at least a college degree (Table 15).

Table 14. Average Time Children Spent Outdoors

Hours Children Spent Outdoors	Frequency	Percent
Less than one	2	5
One to two	13	32.5
Three to four	22	55
Five to six	3	7.5

Table 15. Average Education of Child Care Staff

Education	Frequency	Percent
High school diploma	2	5.0
Some college	21	52.5
College graduate	17	42.5

3.1.1 Building Characteristics

Half the facilities were in buildings constructed after 1970, with the oldest structure built in 1903 and the most recent built in 2008 (Table 16). Heating systems were on average 16 years old, and in one building was 80 years old. Child care building types included single family detached homes (37.5%), traditional school buildings (27.5%), portable school buildings (22.5%), office buildings (7.5%), and churches (5%) (Table 17). Twenty-six (65%) of the child care facilities were in residential neighborhoods, 8 facilities (20.0%) were in commercial areas, five facilities (12.5%) were adjacent to agricultural fields, and one facility (2.5%) was in a rural/ranch area.

Pest problems were common (90% reported at least one pest), and 58% of facilities reported using pesticides within the last year, with 45% using broadcast application methods, including foggers (n=3 facilities [7.5%]) and sprays (n=17 facilities [43%]). The most common unwanted pests reported inside were ants (73%) and then flies (50%). Table 18 shows the frequency of unwanted pests. Mold, rotting wood, or water damage was present in 23% of facilities, but no serious problems were observed. Overall, although pest problems (mainly ants) were common, the ECE child care environments were in good physical condition and well-maintained.

Table 16. Child Care Building Descriptive Statistics

	N[1]	Mean	Min	25th %	Median	75th %	Max
Year building originally constructed	31	1967	1903	1942	1970	1998	2008
Age of heating system (years)	28	16	1	4.5	10	20	80
Age of air conditioning system (years)	16	9.3	1	4.5	10	12	20

[1]Not all child care programs knew year of construction or age of heating/air conditioning system and only 17 facilities had air conditioning.

Table 17. Child Care Building Type

Building Type	Frequency	Percent
Single family detached home	15	37.5
School (traditional)	11	27.5
School (portable)	9	22.5
Office building	3	7.5
Church	2	5.0

Table 18. Unwanted Pests Observed Inside Facility

Unwanted Pest Reported	Frequency	Percent
Ants	29	72.5
Flies	20	50.0
Spiders	14	35.0
Mice or rats	14	35.0
Head lice	13	32.5
Termites[1]	3	7.5
Cockroaches	2	5.0
Fleas	2	5.0
Other pests[2]	8	21.1

[1]One facility did not know if termites were present in facility

[2]Other pests included pincher bugs (2), bees (1), mites (1), mosquitos (1), skunks/raccoons/deer (1), snakes (1), and yellow jackets (1)

3.1.2 Building Parameters

Environmental parameters were measured using the TSI QTrak 8553 which logs real-time CO_2, CO, temperature, and relative humidity (RH). Indoor environmental parameters were collected at all 40 ECE facilities, while outdoor environmental parameters were collected at 30 ECE facilities. Duplicate QTrak measurements were averaged together for the final data set. Since QTrak measurements were taken every minute, average CO_2, CO, temperature, and RH statistics were generated for each facility. Indoor CO_2 results are not presented due to addition of medical grade CO_2 for ventilation measurements. Table 19 presents the distribution of average indoor CO, temperature, and RH and Table 20 presents average outdoor CO_2, CO, temperature, and RH.

Table 19. Summary of Average Indoor Environmental Parameters (n=40)

	Mean	SD	Min	25th %	Median	75th %	Max
CO (ppm)	2.4	0.7	1.3	1.8	2.2	2.7	4.0
Temperature (°F)	70.0	3.0	60.8	67.8	70.2	71.6	76.2
RH (%)	49.3	6.9	34.5	44.4	48.2	54.6	62.6

Table 20. Summary of Average Outdoor Environmental Parameters (n=30)

	Mean	SD	Min	25th %	Median	75th %	Max
CO_2 (ppm)	370.5	20.8	336.5	357.4	365.5	384.2	420.4
CO (ppm)	1.4	0.3	0.9	1.2	1.3	1.5	2.1
Temperature (°F)	66.3	10.9	51.8	57.6	63.7	73.3	89.1
RH (%)	49.4	12.0	21.6	41.5	49.4	57.0	74.7

ASHRAE's standard 55-1992 provide guidelines for thermal comfort and relative humidity.[116] Under typical humidity and airflow conditions, ASHRAE 's acceptable temperature range is 68.5-74.5°F in the heating season and 73.0-79.0°F in the cooling season. ASHRAE's standard for relative humidity is set at 60% to control mold growth. Average indoor temperature (70.0°F) over all child care facilities was within ASHRAE's standard for acceptable temperature. Relative humidity exceeded ASHRAE standards in 5% of facilities.

3.1.3 Child Care Air Exchange Rates

Ventilation measurements were estimated using both continuous indoor CO_2 measurements and the release of CO_2 as a tracer gas. This approach allowed estimation of the full-day average air exchange rate (AER) based on the full day of continuous CO_2 monitoring which was then compared to the shorter term AER computed after the release of CO_2 as a tracer gas. We used CO_2 emission profiles combined with measured indoor and outdoor CO_2 concentrations fit to a mass balance equation to estimate ventilation rate. The 40 ECE facilities had an average AER of 2.01 per hour with a range from 0.28 to 5.63 per hour (Table 21). The air exchange rates measured in ECE facilities were higher than rates reported in a recent California study (median=1.4 versus 0.26 air changes per hour, respectively), and only 3 facilities (7.5%) were below the California Building Code assumed minimum ventilation level of 0.35 air changes per hour.[117] Due to the moderate climate in Alameda and Monterey Counties, natural ventilation such as windows were often used in the ECE facilities measured, especially on warm, often breezy, afternoons.

Table 21. Summary of Average Air Exchange Rates during Air Sampling

	N	Mean	SD	Min	25th %	Median	75th %	Max
AER (h^{-1})	40	2.01	1.41	0.28	0.92	1.43	2.96	5.63

The following is an example of an AER calculation for ECE 29 (Figure 4). During air sampling, a change in the indoor environment (such as a window opened or closed) was noted four times and AERs were calculated for these time periods (Table 22) by minimizing the mean-squared error between the predicted and measured CO_2 concentrations. The time-weighted average AER was calculated over the sampling period.

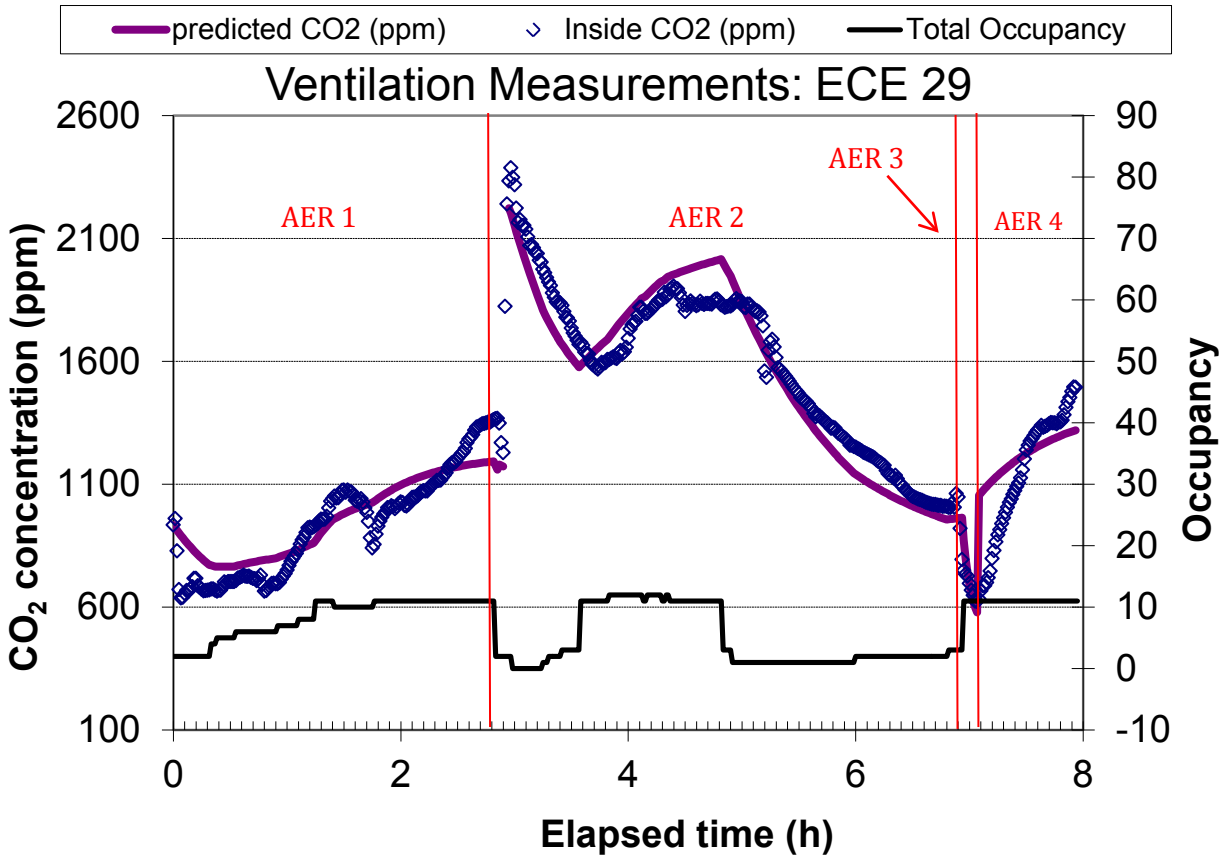

Figure 4. Figure showing measured and predicted CO_2 concentrations at ECE 29. By fitting the predicted CO_2 model with the measured CO_2 levels, air exchange rates were calculated for the different time periods when a field technician noted a change in the ECE environment (i.e., open window or door).

Table 22. Calculated AER for Four Time Periods at ECE 29

	AER (h^{-1})	Ventilation Notes
AER 1	1.83	One passage door open
AER 2	0.87	CO_2 release, one passage door open
AER 3	13.05	One entry and passage door open
AER 4	1.48	One passage door open
Time-Weighted Average	**1.49**	

3.1.4 Chemical Inventory

Stored chemical products were inventoried during the inspection. Products included pesticides, cleaners, paints, solvents, etc. Bleach (sodium hypochlorite) was a component of cleaners or sanitizers in 26 (65%) of the facilities. Excluding pesticides (see Section 3.6.5), a total of 135 active ingredients were recorded. Note, that the presence of a product does not necessarily mean it was used recently or inside. Additionally, some products do not list ingredients on the label. Some of the chemicals found in the products were monitored in air or dust, but many of the chemicals were not measured. The chemical inventory provides information on the presence of different chemicals that a child may be exposed to in a child care facility. The range of active ingredients also indicates the need for education about product safety and use around children. See Appendix E, Table 153 for an inventory of the active ingredients recorded.

3.2 Volatile Organic Compound Results and Discussion

As described in Section 2.5.1, a total of 34 VOC measurements were available for analysis. Two sorbent tubes (P/N 012347-005-00; Gerstel or equivalent) were used to sample common VOCs using separate Tenax-TA® and CarboTrap™ tubes in all facilities except ECE 11. ECE 11 was sampled during the pilot stage of the project when sorbent tubes with a primary bed of Tenax backed with Carbosieve were used (See VOC QA/QC for further information). Silica gel cartridges coated with 2,4-dinitrophenyl-hydrazine (XPoSure Aldehyde Sampler; Waters corporation) with an ozone scrubber (P/N WAT054420; Waters) upstream were used to measure low-molecular weight carbonyls- formaldehyde, acetaldehyde, and acetone. For the results presented below, the 39 target VOC analytes are collectively named VOCs and low molecular weight carbonyls are collectively named carbonyls. Table 23 provides a description of the VOCs and potential sources.

Table 23. VOC Analytes and Sources

Analyte	Sources
Hexane[118]	• Gasoline evaporative emissions • Cleaning agent in printing, textile, automotive and furniture industries • Quick-drying glues for crafts and in consumer products (shoes, leather)
Methylene chloride[118]	• Paint stripper • May be found in some aerosol and pesticide products
Carbon tetrachloride[118]	• Dry cleaning solvent • Previously used as a refrigerant
Chloroform[118]	• Water contaminant released during water use
Benzene[118]	• Cigarette smoke • Gasoline evaporative emissions
Butanal[119]	• Used in production of resins, rubber, solvents, plasticizers and high molecular weight polymers • Naturally occurring in some foods and plants
Heptane, Octane, Butylbenzene[118]	• Gasoline evaporative emissions
Toluene[118]	• Consumer products including paint, paint thinners, lacquers, adhesives and rubber • Cigarette smoke • Gasoline evaporative emissions
Hexamethylcyclotrisiloxane, Octamethylcyclotetrasiloxane, Decamethylcyclopentasiloxane[120]	• Manufacturer of silicones • Personal care products • Carriers, lubricants and solvents in commercial applications
Tetrachloroethylene[118]	• Dry cleaning solvent • Some consumer products
Hexanal, Heptanal, Octanal, Nonanal, Decanal, Benzaldehyde[118]	• Flavors and perfumes • Product of secondary reactions between ozone and unsaturated compounds
Ethylbenzene[118]	• Inks and paints • Gasoline evaporative emissions
m/p-Xylene, o-Xylene[118]	• Consumer products including cleaning agents, paint thinners and varnishes • Cigarette smoke • Gasoline evaporative emissions
a-Pinene[118]	• Fragrance in cleaning products, air fresheners, and personal care products
Decane, Undecane, Dodecane, Tetradecane, Hexadecane[121,122]	• Kerosene, diesel and home heating oil evaporative emissions • Solvent • Component of paints and varnishes • Used in the rubber and paper industry

Table 23 Continued. VOC Analytes and Sources

Analyte	Sources
2-Butoxyethanol[118]	• Paint thinners and strippers, varnish removers, and herbicide • Liquid soaps, cosmetics, commercial and household cleaners, and dry cleaning compounds • Some ink and spot removers
3-Carene, g-Terpinene[123]	• Cologne, perfume, soap, shaving cream, deodorant, air freshener
1,2,3-Trimethylbenzene[124]	• Fuel evaporative emissions • Paints • Cleaners
d-Limonene[123]	• Fragrance in air fresheners, insecticides, and personal care products (hand sanitizers) • Solvent for cleaning products
2-Ethyl-1-hexanol[125]	• Cleaning products • Insecticides • Paint related products • Rugs and bathmats • Sheet vinyl flooring
a-Terpineol[123]	• Insecticides • Solvents • Plasticizers • Perfumes • Synthetic pine oil
Texanol[126]	• Additive to latex paint
TXIB[123]	• Plasticizer in resilient vinyl flooring
Formaldehyde[127]	• Pressed-Wood Products • Urea-formaldehyde foam insulation • Combustion sources and environmental tobacco smoke • Glues
Acetaldehyde[128]	• Incomplete combustion • Industrial emissions • Environmental tobacco smoke
Acetone[129]	• Nail polish remover • Paints, varnishes, lacquers • Cleaning products

3.2.1 Volatile Organic Compound QA/QC

The VOC sampling method initially used dual sorbent sampling tubes containing both Tenax-TA® and carbosieve, but high levels of a low molecular weight alcohol caused problems with the chromatography during several of the pilot facility tests. We determined that the interference was likely due to periodic hand sanitizer use in the facilities, which caused shifts in retention times and reduction in the instrument response such that the results from those

samples were not valid. To address the problem we switched to a single sorbent sampling tube containing Tenax-TA® and a second tube containing a carbon molecular sieve material (CarboTrap) for the remainder of the study (See Appendix C for more information).

For three duplicate VOC samples, the mean relative standard deviation was 11.8% (SD=8.3), showing a relatively small error between measurements. Seventeen travel blanks were analyzed for possible contamination. Results show little contamination during travel and analysis. Of the 39 analytes measured, only two had median blank masses above the method detection limit (Hexamethylcyclotrisiloxane - 4.1 ng and benzaldehyde - 1.5 ng). Three Tenax travel spikes were used to quantify recovery. For all 39 analytes, average recovery for the travel spikes was 96.2% (SD=7.9).

At five facilities, a second Tenax-TA tube was placed "downstream" from the field sample to quantify the amount of an analyte that passes through one Tenax tube, referred to as breakthrough. Overall, average breakthrough was minimal, with analyte concentrations below 1μg/m³. In one sample (ECE 28), the measured VOCs on the breakthrough tube were significant. Breakthrough is a function of both contaminant concentration and sample volume and occurs when the absorption capacity of a media is exceeded.[130] We ruled out breakthrough because the breakthrough tube concentrations did not coincide with the primary tube concentrations (in some cases the contaminants were higher on the breakthrough tube than the primary tube and some chemicals were present on the breakthrough tube that were not on the primary tube which is impossible if breakthrough occurred). The tube was used after facility 28 and the results for subsequent uses were valid (including one breakthrough experiment, one indoor measurement and one trip spike). We also ruled out contamination of the tube from the home or from another facility. Except for the D3 siloxane, the majority of the contaminants on the tube in question are of higher molecular weight so they were not likely taken up by diffusion. The elevated D3 siloxane relative to the other two siloxanes is unusual for an environmental sample and the chromatogram had a number of other higher order siloxanes not quantified in the sample. This was the first time this tube was used in the field; however, when Tenax sorbent tubes are purchased they are pre-conditioned, plus all new tubes were conditioned in the lab before deployment. From the evidence presented, the elevated breakthrough was either because the tube was not originally purged or contaminated by contact with a substance like silicone grease. We believe this anomaly does not invalidate any other sample results. Please see Appendix C for additional VOC QA/QC information.

3.2.2 Volatile Organic Compound Air Results

Thirty-four indoor VOC measurements were available for analysis (six early samples were invalid due to alcohol contamination from hand sanitizer use – see above). VOCs concentrations were calculated when the analyte mass was above the method detection limit. When the mass was not above the MDL, "<MDL" is reported. When duplicate samples were collected, an average of the duplicate and field concentrations was computed for final analysis. Concentrations above the MDL are reported in Table 24. The two most prominent target VOCs measured were d-limonene and decamethylcyclopentasiloxane. Both d-limonene and decamethylcyclopentasiloxane analytes were detected in all facilities and had median (range) concentrations of 33.1 (0.8-82) and 51 2.6-88) μg/m^3, respectively. D-limonene is a cyclic terpene often used as a solvent in cleaning products that gives a "citrus smell". Decamethylcyclopentasiloxane is a siloxane often used in cosmetic products. Outdoor VOC concentrations were measured at 20 ECE facilities. Outdoor concentrations (Table 25) were lower than indoor concentrations and VOCs measured generally had a higher detection frequency indoors than outdoors.

Table 24. Summary of Indoor VOC Analyte Concentrations (µg/m³)

Analyte	N	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Hexane	34	58.8	0.9	0.9	<MDL	<MDL	0.6	1.0	2.5	2.9	3.6
Methylene chloride	34	2.9	0.3	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.5
Carbon tetrachloride	34	2.9	0.6	0.3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.1
Chloroform	34	38.2	1.3	2.6	<MDL	<MDL	<MDL	0.8	2.9	7.7	12.6
Benzene	34	70.6	0.9	0.5	<MDL	<MDL	0.9	1.0	1.4	2.0	2.6
Butanal	34	100.0	0.8	0.4	0.2	0.5	0.7	0.9	1.5	1.6	2.0
Heptane	34	100.0	3.0	4.1	0.2	0.5	1.5	3.5	8.9	10.9	19.8
Octane	34	100.0	0.8	0.8	0.3	0.5	0.6	1.1	1.7	1.8	4.3
Toluene	34	100.0	4.1	3.0	1.0	1.7	3.1	5.5	9.0	11.2	12.4
Hexamethylcyclotrisiloxane	34	47.1	3.0	2.3	<MDL	<MDL	<MDL	4.6	6.7	8.0	9.3
Tetrachloroethylene**	33	51.5	0.4	1.3	<MDL	<MDL	0.1	0.2	0.4	1.0	7.8
Hexanal	34	100.0	7.7	5.4	1.9	3.9	5.7	10.0	16.8	20.9	22.5
Ethylbenzene	34	100.0	0.7	0.6	0.1	0.3	0.6	1.0	1.6	2.0	2.0
m/p-Xylene	34	100.0	2.2	1.9	0.3	0.7	1.6	3.0	5.5	6.7	7.1
a-Pinene	34	100.0	6.4	10.0	0.4	1.7	3.6	6.4	11.4	19.9	57.7
o-Xylene	34	100.0	1.0	0.8	0.2	0.4	0.8	1.6	2.2	2.7	2.9
Octamethylcyclotetrasiloxane**	33	90.9	7.4	18.1	<MDL	0.5	0.9	2.9	17.8	70.9*	78.5*
Heptanal	34	97.1	1.1	0.5	<MDL	0.8	1.0	1.3	1.6	2.1	2.7
Decane**	33	90.9	0.8	0.9	<MDL	0.4	0.6	1.0	1.3	3.0	4.5
2-Butoxyethanol	34	100.0	10.9	19.4	1.1	1.8	2.9	8.6	29.9	64.0*	92.4*
3-Carene	34	82.4	0.5	0.7	<MDL	0.1	0.2	0.6	1.4	1.8	3.0
Trimethylbenzene (1,2,4)	34	97.1	0.7	0.6	<MDL	0.3	0.5	0.9	1.6	2.3	2.7
d-Limonene	34	100.0	37.3	28.1	0.8	9.1	33.1	68.7*	72.8*	74.9*	81.5*
Trimethylbenzene (1,2,3)	34	64.7	0.2	0.2	<MDL	<MDL	0.1	0.3	0.6	0.7	1.0
g-Terpinene	34	61.8	0.7	1.4	<MDL	<MDL	0.3	0.4	1.5	4.8	7.1
Benzaldehyde	34	100.0	3.0	1.7	1.2	2.0	2.4	3.8	5.1	5.7	9.4
Octanal	34	100.0	2.3	1.0	1.1	1.7	2.1	2.5	3.4	5.3	5.7

Table 24 Continued. Summary of Indoor VOC Analyte Concentrations (µg/m³)

Analyte	N	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Undecane	34	85.3	0.9	1.0	<MDL	0.3	0.6	0.9	1.5	3.3	4.6
Butylbenzene	34	17.7	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.2
Decamethylcyclopentasiloxane	34	100.0	46.4	28.2	2.6	17.4	51.4	70.8*	76.9*	83.6*	88.2*
2-Ethyl-1-hexanol	34	100.0	1.9	1.0	0.6	1.1	1.6	2.8	3.5	3.9	3.9
Nonanal	34	100.0	9.1	3.5	3.9	6.5	8.5	10.3	15.0	15.6	16.0
Dodecane	34	91.2	1.1	1.1	<MDL	0.4	0.7	1.6	2.6	2.8	5.0
Decanal	34	94.1	4.3	4.7	<MDL	1.6	2.6	4.7	8.6	18.2	22.0
a-Terpineol	34	85.3	1.8	4.2	<MDL	0.3	0.4	1.9	3.6	6.4	24.1
Tetradecane	34	100.0	3.1	3.3	0.3	1.1	1.9	4.0	7.0	7.7	17.3
Texanol	34	100.0	8.7	12.0	0.9	2.4	4.6	8.6	24.0	32.7	60.7
Hexadecane	34	100.0	1.0	0.7	0.3	0.6	0.8	1.2	2.0	2.4	4.1
TXIB	34	100.0	7.7	13.8	0.9	2.3	4.7	7.9	13.0	14.1	82.8

*Denotes when high calibration range used as analyte mass to calculate sample concentration. Values underestimate the true air concentrations.

**Analytes not measured in pilot study.

Table 25. Summary of Outdoor VOC Analyte Concentrations (µg/m³) (n=20)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Hexane	25.0	0.4	0.3	<MDL	<MDL	<MDL	<MDL	0.7	1.0	1.3
Methylene chloride	0.0	0.2	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Carbon tetrachloride	0.0	0.5	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Chloroform	0.0	0.3	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Benzene	75.0	0.7	0.3	<MDL	<MDL	0.6	0.9	1.1	1.2	1.2
Butanal	25.0	0.1	0.1	<MDL	<MDL	<MDL	<MDL	0.2	0.2	0.2
Heptane	85.0	0.6	0.6	<MDL	0.2	0.4	0.9	1.6	1.8	1.9
Octane	60.0	0.2	0.1	<MDL	<MDL	0.1	0.2	0.4	0.5	0.5
Toluene	100.0	1.5	1.2	0.2	0.7	0.9	2.1	3.7	4.1	4.1
Hexamethylcyclotrisiloxane	25.0	1.6	0.9	<MDL	<MDL	<MDL	<MDL	2.6	3.9	4.6
Tetrachloroethylene	30.0	0.1	0.1	<MDL	<MDL	<MDL	0.1	0.2	0.3	0.4
Hexanal	80.0	0.2	0.1	<MDL	0.1	0.2	0.2	0.3	0.5	0.6
Ethylbenzene	65.0	0.2	0.3	<MDL	<MDL	0.1	0.3	0.7	0.8	0.9
m/p-Xylene	95.0	0.9	1.0	<MDL	0.3	0.4	1.1	2.2	3.0	3.8
a-Pinene	45.0	0.2	0.3	<MDL	<MDL	<MDL	0.3	0.5	0.9	1.1
o-Xylene	80.0	0.4	0.4	<MDL	0.1	0.2	0.5	0.9	1.3	1.7
Octamethylcyclotetrasiloxane	35.0	0.2	0.1	<MDL	<MDL	<MDL	0.2	0.2	0.3	0.3
Heptanal	15.0	0.1	0.0	<MDL	<MDL	<MDL	<MDL	0.1	0.1	0.2
Decane	30.0	0.2	0.1	<MDL	<MDL	<MDL	0.2	0.4	0.4	0.4
2-Butoxyethanol	20.0	0.1	0.1	<MDL	<MDL	<MDL	<MDL	0.3	0.4	0.5
3-Carene	0.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Trimethylbenzene (1,2,4)	60.0	0.2	0.3	<MDL	<MDL	0.1	0.3	0.6	1.0	1.3
d-Limonene	5.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.2
Trimethylbenzene (1,2,3)	25.0	0.1	0.2	<MDL	<MDL	<MDL	<MDL	0.2	0.5	0.7
g-Terpinene	0.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Benzaldehyde	100.0	2.4	1.1	1.2	1.8	2.3	2.7	3.2	4.8	6.3
Octanal	55.0	0.1	0.1	<MDL	<MDL	0.1	0.2	0.2	0.3	0.3

Table 25 Continued. Summary of Outdoor VOC Analyte Concentrations (µg/m³) (n=20)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Undecane	5.0	0.1	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.2
Butylbenzene	0.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Decamethylcyclopentasiloxane	95.0	0.4	0.4	<MDL	0.2	0.3	0.6	1.0	1.2	1.3
2-Ethyl-1-hexanol	5.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.1
Nonanal	95.0	0.4	0.3	<MDL	0.2	0.2	0.5	0.7	0.9	1.2
Dodecane	0.0	0.1	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Decanal	55.0	0.1	0.1	<MDL	<MDL	0.1	0.2	0.3	0.4	0.5
a-Terpineol	0.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Tetradecane	10.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	0.1
Texanol	10.0	0.1	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	0.2	0.2
Hexadecane	5.0	0.0	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.1
TXIB	10.0	0.1	0.2	<MDL	<MDL	<MDL	<MDL	<MDL	0.5	0.9

Thirty-four of the VOC analytes had significantly higher (Wilcoxon $p<0.05$) concentrations indoors than outdoors (See Appendix A, Table 105). In addition, we calculated indoor to outdoor (I/O) concentration ratios (indoor concentration/ outdoor concentration) for each facility. Table 26 presents mean and median I/O ratios from the twenty facilities where both measurements were collected. The I/O ratios ranged from 1.1 for benzene to 1,604 for d-limonene. Results indicate that indoor sources were the primary determinants of VOCs within the ECE facilities.

Table 26. VOC Indoor to Outdoor (I/O) Concentration Ratios (n=20 ECE facilities)

Analyte	Mean	SD	Min	25th %	Median	75th %	Max
Hexane	2.0	2.0	0.6	1.1	1.3	1.9	8.4
Methylene chloride	1.2	0.2	0.6	1.1	1.1	1.3	1.4
Carbon tetrachloride	1.2	0.2	0.6	1.1	1.1	1.3	1.4
Chloroform	6.2	11.1	0.9	1.1	1.3	2.7	38.1
Benzene	1.1	0.5	0.5	0.8	1.1	1.2	2.7
Butanal	13.6	9.6	3.9	7.0	11.5	17.2	45.8
Heptane	4.2	4.3	1.0	1.5	2.2	5.6	17.0
Octane	8.2	6.1	1.4	3.0	6.9	11.8	21.1
Toluene	3.4	2.4	1.3	1.9	2.4	3.8	9.7
Hexamethylcyclotrisiloxane	1.4	1.1	0.4	0.9	1.1	1.4	5.3
Tetrachloroethylene	1.9	1.6	0.4	1.0	1.3	2.0	6.5
Hexanal	44.3	31.7	9.3	24.6	35.0	55.1	119.1
Ethylbenzene	6.7	7.1	1.0	1.6	3.8	8.9	25.4
m/p-Xylene	5.0	6.6	0.8	1.4	2.0	5.1	27.9
a-Pinene	59.9	62.8	5.6	13.3	39.9	71.3	230.6
o-Xylene	5.3	5.7	0.9	1.7	3.5	5.6	21.6
Octamethylcyclotetrasiloxane	67.3	177.6	0.7	2.3	4.7	40.5	785.5
Heptanal	26.0	10.2	7.4	21.7	26.9	33.0	43.3
Decane	9.0	11.5	1.1	2.8	5.6	9.8	48.8
2-Butoxyethanol	88.4	85.7	23.1	35.3	53.7	121.0	375.0
3-Carene	24.8	31.5	1.1	6.7	9.0	41.1	126.4
Trimethylbenzene (1,2,4)	5.5	4.5	0.7	2.3	4.1	7.3	15.5
d-Limonene	1,603.9	1,481.2	81.7	359.1	708.6	3,119.0	4,015.5
Trimethylbenzene (1,2,3)	7.1	11.1	0.3	1.0	1.3	7.8	37.6
g-Terpinene	16.6	24.1	0.9	1.1	4.0	20.7	84.0
Benzaldehyde	1.3	0.6	0.3	0.9	1.2	1.8	2.5
Octanal	25.0	13.2	8.8	15.2	18.5	32.9	54.1
Undecane	6.1	7.3	0.6	1.9	3.9	7.3	29.1
Butylbenzene	1.4	1.3	0.6	1.1	1.1	1.3	6.7
Decamethylcyclopentasiloxane	159.8	129.9	28.7	60.5	99.1	279.0	457.0
2-Ethyl-1-hexanol	41.6	22.9	15.0	28.0	35.8	46.5	101.2
Nonanal	42.9	36.7	5.6	15.4	37.1	55.2	167.8
Dodecane	7.7	8.2	0.6	2.7	4.4	10.7	35.0
Decanal	39.3	35.3	2.7	14.4	22.8	58.6	140.3
a-Terpineol	34.3	51.1	1.1	3.2	10.7	47.7	172.8
Tetradecane	59.4	47.2	17.5	23.5	39.1	102.1	164.9
Texanol	278.7	435.8	6.6	63.2	128.8	240.0	1,832.3
Hexadecane	19.8	14.6	5.2	10.8	16.4	21.2	62.2
TXIB	116.6	83.5	11.2	52.0	101.0	143.4	324.5

3.2.3 Determinants of Volatile Organic Compounds

To explore the relationship between indoor and outdoor air pollution in ECE facilities, we obtained traffic statistics within a one kilometer (km) radius buffer from the California Environmental Health Tracking Program (CEHTP) traffic linkage service (Table 27). The values are computed from data recorded in the CalTrans Highway Performance Monitoring System (HPMS) 2004.[131] The following traffic summary statistics were abstracted: sum of all length-adjusted traffic volumes (∑LATV), sum of all Gauss-adjusted traffic volumes (∑GATV), and length-adjusted traffic volume of the highest segment (heaviest used road; LATV-HS) were obtained on July 19th, 2011.[131] Length-adjusted traffic volumes are the length of a road segment (km) multiplied by the average daily traffic volume (vehicles per hour). Gauss-adjusted traffic volumes assume a Gaussian dispersion of airborne exhaust pollution from the traffic segment and traffic counts are weighted by a 500 meter (half 1-km total radius) Gaussian curve measured from the ECE facility to the center of street.[132] Participating programs had a wide range of nearby traffic density (Table 27). Differences in traffic metrics between Alameda and Monterey County are presented in Table 28. Overall, nearby traffic levels were significantly higher in Alameda County, consistent with the higher population and density.

Table 27. Summary Traffic Metric Statistics (n=40)

	Min	25th %	Median	75th %	90th %	95th %	Max
∑LATV (vehicle-km/hr)	31	4,294	7,708.5	14,397	28,063	35,622	52,018
∑GATV (vehicles/day*)	0	29.5	3,879.5	14,218	29,250	51,817	324,498
∑LATV -HS (vehicle-km/hr)	30	1,741.5	2,777.5	6,277	16,479	18,401	20,065

*Average annual daily traffic

Table 28. Summary of Traffic Metric Statistics by County

	Monterey			Alameda		
	∑LATV (vehicle-km/hr)	∑GATV (vehicles/day*)	∑LATV - HS (vehicle-km/hr)	∑LATV (vehicle-km/hr)	∑GATV (vehicles/day*)	∑LATV - HS (vehicle-km/hr)
N	20	20	20	20	20	20
Min	31	0	30	4,824	0	1,692
25th %	1,134	3	689.5	8,376	2,636	2,125
Median	4,420	1,808	1,980	11,256	11,643	4,045
75th %	6,665	5,259	3,439	24,366	27,177	15,769
Max	16,004	15,686	7,351	52,018	324,498	20,065

*Average annual daily traffic

A number of VOCs are products of gasoline evaporative emissions. We hypothesized that indoor and outdoor concentrations of these VOC may be associated with proximity to traffic. Benzene and heptane levels indoors and outdoors were significantly associated ($p<0.05$) with all traffic metrics (Table 29). Overall, outdoor VOC concentrations were more strongly associated with proximity to traffic than indoor VOC concentrations.

Table 29. Association between Indoor and Outdoor VOC Concentrations and Nearby Traffic Intensity Tested with Spearman Correlations (rho)

	Indoor (n=34)			Outdoor (n=20)		
	∑ LATV	∑ GATV	LATV -HS	∑ LATV	∑ GATV	LATV -HS
Hexane	0.33	0.32	0.32	0.41	0.71*	0.25
Benzene	0.39*	0.42*	0.40*	0.52*	0.55*	0.54*
Heptane	0.38*	0.34*	0.46*	0.52*	0.53*	0.60*
Octane	0.23	0.25	0.27	0.35	0.62*	0.38
Toluene	0.25	0.34*	0.29	0.48*	0.44	0.56*
Ethylbenzene	0.24	0.30	0.29	0.53*	0.57*	0.54*
m/p-Xylene	0.25	0.28	0.31	0.53*	0.40	0.60*
o-Xylene	0.25	0.32	0.30	0.49*	0.47*	0.57*
Decane	0.16	0.53*	0.15	0.46*	0.58*	0.39
Trimethylbenzene (1,2,4)	0.34	0.37*	0.34	0.44	0.39	0.49*
Trimethylbenzene (1,2,3)	0.25	0.26	0.30	0.34	0.61*	0.25
Undecane	-0.01	0.20	0.08	-0.06	0.37	-0.23
Butylbenzene	-0.05	-0.07	0.08	NC	NC	NC
Dodecane	-0.07	0.15	0.10	NC	NC	NC
Tetradecane	0.07	0.11	0.26	-0.08	0.25	-0.38
Hexadecane	0.44*	0.52*	0.53*	-0.30	0.09	-0.52*

*Significant, $p<0.05$
NC-Values not calculated. Outdoor concentrations below MDL for these analytes.

We also hypothesized that air freshener use was associated with increased indoor VOC concentrations of analytes found in fragrances. Twenty-two facilities (55%) reported air freshener use, seventeen (42.5%) reported no air freshener use, and one facility did not know about air freshener use. Of the thirty-four valid VOC measurements, twenty reported no air freshener use and fourteen reported air freshener use. Indoor concentrations of hexanal and decanal were significantly higher (Mann-Whitney $p<0.05$) in facilities reporting air freshener use compared to facilities not reporting air freshener use (Table 30).

Table 30. Difference in VOC Concentrations between Facilities Reporting No Air Freshener Use and Air Freshener Use

	Air Fresheners Not Used (n=20)					Air Fresheners Used (n=14)				
	>MDL (%)	25th % (µg/m³)	Median (µg/m³)	75th % (µg/m³)	Maximum (µg/m³)	>MDL (%)	25th % (µg/m³)	Median (µg/m³)	75th % (µg/m³)	Maximum (µg/m³)
Hexanal*	100	3.5	4.6	7.8	20.9	100	4.8	9.3	13.7	22.5
a-Pinene	100	1.8	4.0	6.2	57.7	100	1.7	3.5	6.9	15.7
Heptanal	92.9	0.7	1.0	1.4	2.7	100	0.9	1.0	1.2	1.6
3-Carene	85.7	0.1	0.2	0.3	3.0	80.0	0.1	0.4	0.8	1.8
d-Limonene	100	8.2	17.7	57.2	81.5	100	20.1	54.5	71.3	74.9
g-Terpinene	71.4	<MDL	0.3	0.5	7.1	55.0	<MDL	0.2	0.4	1.6
Benzaldehyde	100	2.0	2.4	3.8	9.4	100	2.1	2.5	3.4	5.7
Octanal	100	1.5	2.1	2.6	5.7	100	1.8	2.3	2.5	3.9
Nonanal	100	5.8	8.3	11.9	15.6	100	7.3	9.0	9.8	16.0
Decanal*	100	1.3	2.3	3.9	8.6	90.0	2.4	4.0	7.6	22.0
a-Terpineol	92.9	0.1	0.3	1.5	6.4	80.0	0.4	0.7	2.3	24.1

*Significant, $p<0.05$

3.2.4 Identification and Quantification of Unknown VOCs

In this section, we describe a semi-quantitative approach used to identify and quantify unknown peaks in the VOC GC/MS chromatograms using a mass spectral library search and a modified toluene equivalent mass calibration. Toluene equivalent mass has long been used in reporting total volatile organic compounds (TVOC) for unidentified chemicals.[133] To use toluene equivalent mass for individual compounds, the peaks in the total ion chromatogram (TIC) must be well resolved so that the area under the chromatographic response for the specific compound can be related to the mass of toluene using a toluene response factor. However, for complex chromatograms that have large numbers of unresolved or partially resolved peaks, identifying the area under the TIC that is related to a specific chemical is more challenging. For these chemicals, we use a dominant and/or unique fragment ion chromatogram in the mass spectra, referred to here as the extracted ion chromatogram (EIC).

To identify compounds for quantification, we first reviewed a chromatogram from each of the facilities tested in the main part of the study. To get an initial estimate of the different chemical classes present in the samples, we screened the samples for five ions generally related to a specific chemical class. These included siloxanes (m/z = 73), terpenes (m/z = 93), alkyl-aromatics (m/z = 91), alkoxy (m/z = 45) and alkanes (m/z = 57). Using this information, we selected several samples with a wide variety of chemical classes represented to develop the compound list for the method.

For each of the selected chromatograms, each peak was identified using a mass spectral library search with the NIST08 database. The chemical name and retention time for each peak with a match quality greater than ~80% was added to the compound list in the quantification method and used to quantify the next data file. After the next file was quantified and each identified peak reviewed to confirm that it was a good match, the chromatogram was carefully reviewed for additional unidentified peaks. The mass spectrum from each remaining unidentified peak was searched using the NIST08 database and if a good quality match was found, the additional chemical was added to the compound list in the method along with the associated retention time. This process was repeated with each data file until all peaks greater than about 5 ng toluene equivalent were identified. The approach resulted in the identification of 173 unique chemicals, including overlap with the *a priori* target analytes where standard calibration curves were used.

To provide a first estimate of the mass of the compounds we started by assigning each compound to a chemical class. The relationship between the extracted ion for the particular chemical class and that of toluene was determined using surrogate compounds from the calibration data collected over the course of the project. For each calibration data file, we determined the area of the extracted ion (EI_x) and the total ion (TI_x) for each chemical (x) and for toluene. This was only done when the TIC peaks were separated from other peaks. The chemical class, surrogate compounds, individual EI_x/TI_x ratios and overall surrogate specific class EI_s/TI_s ratio are presented in Appendix D, Table 150. We assume that the TIC response for the surrogate compound (toluene) is equal to the TIC response for all chemicals in the analysis. With this assumption, the extracted ion response for toluene ($EI_{toluene}$) was transformed to surrogate category response (EI_s) and assigned to each chemical (EI_x) by,

$$EI_{toluene} \times \frac{TI}{EI_{toluene}} \times \frac{EI_s}{TI} = EI_x$$

The EI_x values were then used to quantify the estimated mass of individual chemicals based on the chemical class assignment and the conversion factor determined by the five-point toluene calibration curve. Using the final quantification method, each data file was analyzed a final time including a careful review of peak identification and integration. There was no attempt to distinguish between isomers or confirm the NIST identification with pure standards beyond what was included with the initial set of target chemicals.

In total, 129 additional VOC analytes were determined through the NIST library. To assess the quality of the estimated values, we examined the association of the measured versus estimated values for those compounds that were included *a priori* in the standard calibration curve (Appendix D, Table 150). The measured and estimated values for all compounds were strongly correlated (R^2=0.75, $p<0.05$) (Figure 5). More than 60% of the individual compounds had a Spearman correlation >0.8 and more than 70% had a Spearman correlation >0.7 (See Appendix D, Table 151). As seen in Figure 5, the semi-quantitative model generally underestimated VOC analytes (slope=0.69). Overall, these results indicate that the estimated values are a good indicator of the likely concentrations on the NIST identified compounds and that the information can be used to identify likely VOC contaminants warranting further study. The distributions of the concentrations of the semi-quantitative VOCs are presented in Appendix D, Table 152.

Over 100 unique VOCs were identified in at least 50% of the facilities and/or at levels greater than 1 $\mu g/m^3$. Ranking the toxicological significance and relative importance of each of the chemicals identified is beyond the scope of this study but the results highlight the importance of expanding the number of VOCs considered in indoor air samples. The list of compounds should be screened to determine how many of the compounds have relevant health-based exposure guidelines.

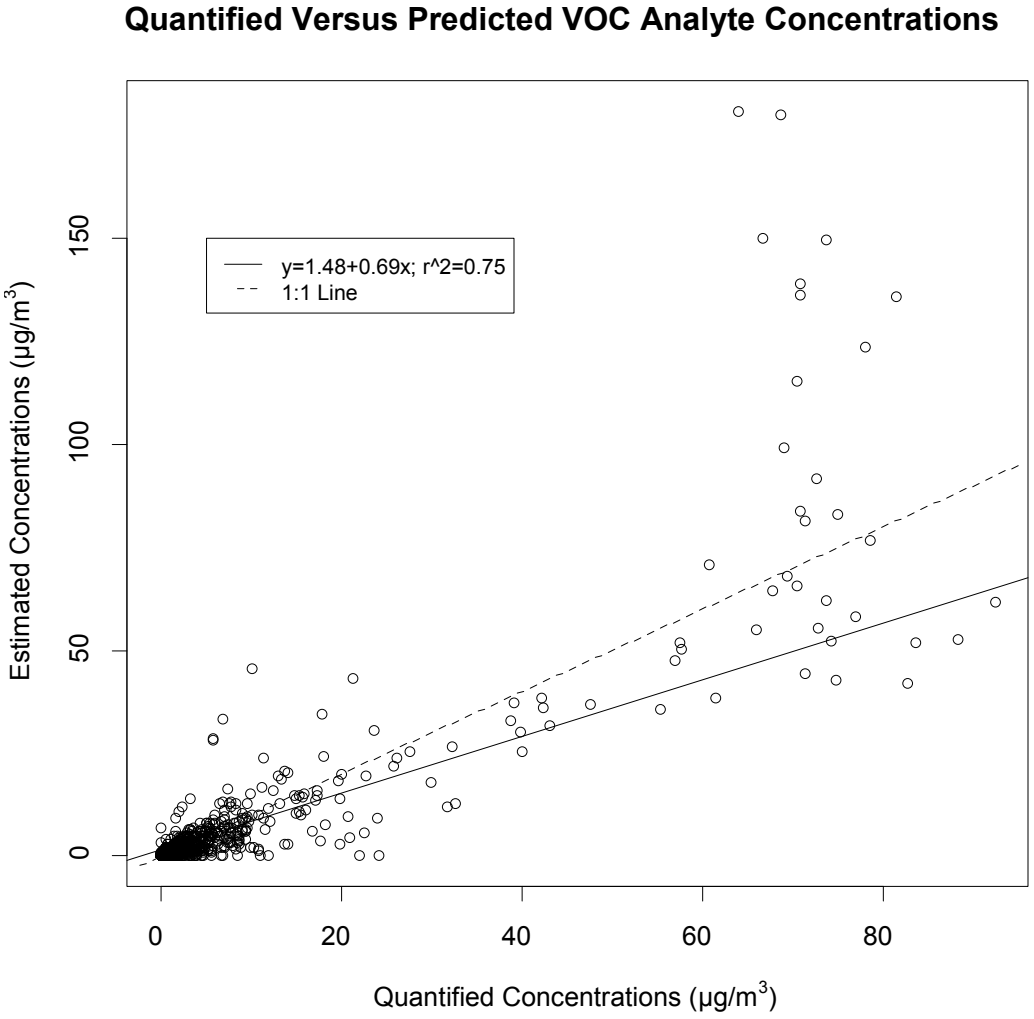

Figure 5. Relationship between VOC analyte concentrations measured with standard calibration curves versus estimated concentrations from semi-quantitative method. Lines in graph are the linear regression and one to one slope.

3.2.5 Carbonyl QA/QC

Nine field blanks were collected from the 40 ECE facilities (~23%). Median formaldehyde, acetaldehyde, and acetone field blank masses were 40.6, 36.6, and 108.6 ng, respectively. Overall, levels are very low compared to the measured concentrations, suggesting minimal background contamination. Twelve duplicate indoor carbonyl samples were collected for QA/QC purposes. The mean RSDs were 3.5% (SD=4.3), 3.2% (SD=3.2), and 3.7% (SD=4.3) for formaldehyde, acetaldehyde, and acetone duplicate samples collected, respectively. These values indicate good precision for field duplicates. See Appendix C for additional carbonyl QA/QC.

3.2.6 Carbonyl Air Monitoring Results

Valid carbonyl measurements were collected from all 40 ECE facilities. Tables 31 and 32 summarizes results for indoor (n=40) and outdoor (n=19) measurements. In facilities where duplicates were collected, we averaged the two measurements to obtain a single concentration. Figure 6 compares the distribution of indoor and outdoor carbonyl levels. Wilcoxon matched data test was used to assess difference in indoor and outdoor carbonyl concentrations. Overall, levels were significantly higher indoors than outdoors ($p<0.05$) for all three carbonyls, indicating that indoor sources are primary contributors to carbonyl concentrations. There were no significant differences (Mann-Whitney $p>0.05$) when carbonyl concentrations were stratified by county or ECE type (Table 33).

Table 31. Summary of Indoor Carbonyl Concentrations (µg/m³) (n=40)

Analyte	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Formaldehyde	18.9	10.1	0.7	10.6	17.8	25.0	33.2	37.3	48.8
Acetaldehyde	8.5	5.4	0.7	4.7	7.6	10.5	17.1	20.2	23.3
Acetone	58.5	172.4	1.0	11.5	19.9	43.3	70.9	155.7	1,100.9

Table 32. Summary of Outdoor Carbonyl Concentrations (µg/m³) (n=19)

Analyte	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Formaldehyde	2.5	0.8	1.5	1.9	2.3	3.1	3.9	4.0	4.0
Acetaldehyde	2.5	1.5	1.1	1.6	1.8	3.4	4.9	6.5	6.5
Acetone	4.3	2.4	0.0	3.0	3.9	4.7	8.8	9.9	9.9

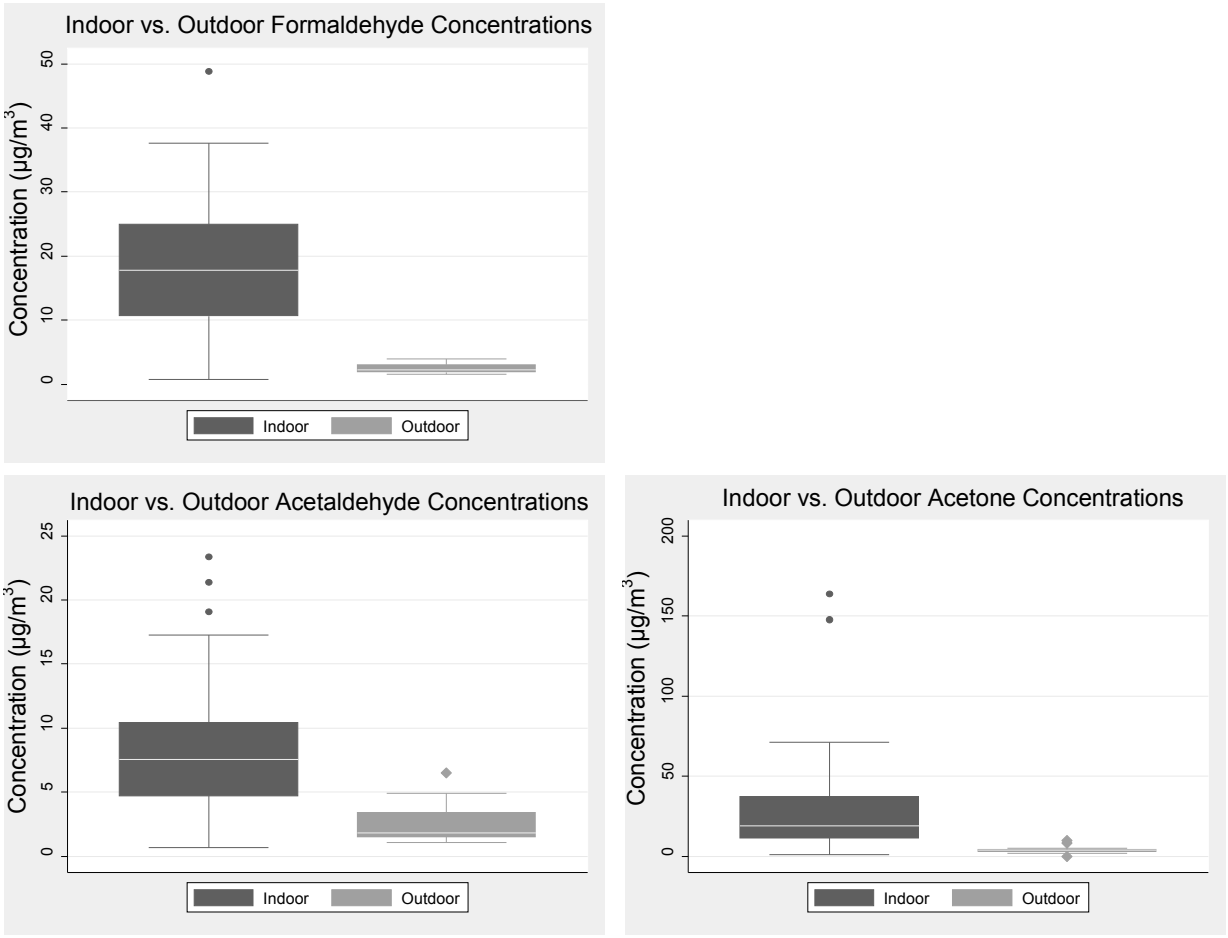

Figure 6. Box plots of indoor (n=40) vs. outdoor (n=19) formaldehyde, acetaldehyde, and acetone concentrations. Acetone box plot does not include ECE 17 as it was an extreme outlier.

Table 33. Summary of Carbonyl Concentrations (µg/m³) by ECE Type

	Formaldehyde		Acetaldehyde		Acetone	
	Center	Home	Center	Home	Center	Home
N	28	12	28	12	28	12
Mean	16.5	24.6	7.9	9.8	74.3	21.8
SD	7.5	13.2	5.6	5.1	205.0	14.3
25th %	9.9	13.4	4.3	6.8	10.8	14.4
Median	17.3	22.6	5.7	8.1	22.0	16.4
75th %	21.1	35.5	9.5	11.8	53.0	23.8
Max	30.3	48.8	23.3	21.3	1,100.9	62.1

3.2.7 Formaldehyde Concentration Determinants

Due to off-gassing from pressed wood products, recently constructed buildings have been associated with higher formaldehyde concentrations.[134] We collected formaldehyde measurements from all 40 child care programs but only 31 child care programs knew the age of their building. The correlation between formaldehyde concentrations and building age was not significant ($r=-0.08$, $p=0.67$), however, formaldehyde levels were strongly inversely associated with air exchange rates ($rho=-0.59$, $p<0.05$). We tested for differences in formaldehyde concentrations between portable/manufactured buildings (portable/manufactured buildings, n=9) and all other buildings and found no significant differences between building types (Mann-Whitney, $p>0.05$). Renovations within the last year (n=23) were not associated with increased formaldehyde concentrations (Mann-Whitney, $p>0.05$). Installing new floor coverings within the last year (n=6) was not associated with increased formaldehyde concentrations (Mann-Whitney, $p>0.05$). Pressed-wood furniture present inside thirty-five child care facilities (87.5%) but was also not associated with increased formaldehyde concentrations (Mann-Whitney, $p>0.05$).

3.2.8 Volatile Organic Compound Discussion

Thirty-nine VOC compounds were measured in indoor air samples collected from 34 ECE facilities. The two highest VOCs measured were d-limonene and decamethyl-cyclopentasiloxane. Both d-limonene and decamethylcyclopentasiloxane were detected in all facilities and had median concentrations of 33 and 51 $\mu g/m^3$, respectively. D-limonene is a cyclic terpene often used as a solvent in cleaning products that gives a “citrus smell”. Decamethylcyclopentasiloxane is a siloxane often used in cosmetic products. The mean indoor/outdoor (I/O) ratios for d-limonene and decamethylcyclopentasiloxane were 1,603 and 160 $\mu g/m^3$, respectively, highlighting indoor consumer product use as the likely source of these compounds in ECE facilities. The d-limonene levels in the ECE facilities were significantly higher than levels reported in a recent study in California homes (33 vs. 11 $\mu g/m^3$), likely due to frequent use of cleaning products in child care. D-limonene is a potential respiratory irritant and can also react with ozone to form formaldehyde and other secondary contaminants.[1]

Eighteen other VOC compounds were measured in 100% of indoor air samples with median concentrations ranging from a high of 10.9 $\mu g/m^3$ for 2-butoxyethanol to a low of 0.7 $\mu g/m^3$ for ethylbenzene. The average I/O ratios for these compounds ranged from a high of 279 for Texanol and a low of 1.3 for benzaldehyde. Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) is a commonly used additive in latex paint.[126]

Traffic is a known source of benzene. Indoor and outdoor benzene, hexane, and heptane levels measured at ECE facilities were positively associated with proximity to traffic. Three of the 4 BTEX volatile aromatic compounds typically found in petroleum (benzene, toluene, ethylbenzene, and xylenes)[135] were detected in 100% of indoor samples; the exception was benzene, detected in 70.6% of samples. Average indoor air concentrations of the BTEX compounds ranged from 0.7 to 4.1 $\mu g/m^3$, levels very similar to those reported in previous studies of portable classrooms in California.[17]

Many VOCs, including the carbonyls formaldehyde, acetaldehyde and acetone, were present indoors due to numerous common indoor sources at levels similar to or lower than those in other indoor environments. The median indoor air formaldehyde and acetaldehyde concentrations (18 $\mu g/m^3$ and 8.5 $\mu g/m^3$) were lower in ECE facilities than the levels found in a recent study of 103 new single family homes in California (median = 36 $\mu g/m^3$ and 20 $\mu g/m^3$).[1] In that study, nearly all homes had formaldehyde concentrations that exceeded guidelines for

cancer and chronic irritation, while 59 percent exceeded guidelines for acute irritation.[1] Average formaldehyde levels (18.9 µg/m³) in ECE facilities were slightly higher than average levels measured in studies of classrooms in California (Phase 2 averages = 15 µg/m³ for portable classrooms); 12 µg/m³ for traditional classrooms; and 13 µg/m³ for all classrooms).[17] Pressed wood materials with urea-formaldehyde resins are likely to be the dominant source of formaldehyde indoors.[136]

All measured VOC concentrations were below acute (immediate effects) risk levels. Two carbonyl compounds, acetaldehyde and formaldehyde, were measured at concentrations exceeding chronic benchmarks for respiratory irritation. Thirty-five out of 40 ECE facilities (87.5%) had formaldehyde concentrations above OEHHA's 8-hour REL and cREL (9 µg/m³), with the highest concentration 5.4 times the RELs. Twelve out of 40 ECE facilities (30%) had acetaldehyde concentrations above the chronic RfC (9 µg/m³), with the highest concentration 2.6 times the RfC.[45]

Child inhalation exposure estimates for five potentially carcinogenic VOC compounds (benzene, chloroform, ethylbenzene, acetaldehyde, and formaldehyde) exceeded age-specific NSRL Safe Harbor Levels computed by the report authors. Thus, many facilities would exceed the one in 100,000 excess lifetime cancer risk level for one or more of these compounds if the exposures continued for a lifetime. However, the much shorter exposure in ECE facilities presents a lower risk. The average indoor air concentrations for these five compounds ranged from a high of 18.9 µg/m³ for formaldehyde and a low of 0.7 µg/m³ for ethylbenzene. For formaldehyde, a known human carcinogen,[137] the ratio of age-adjusted child dose estimates to the age-specific NSRL benchmarks ranged from 12.0 to 107.5 for the four age groups assessed (i.e., birth to <1 year; 1 to <2 years; 2 to <3 years; and 3 to <6 years).

The evaluation of unknown VOCs using the NIST mass spectral libraries indicated that ~130 additional VOCs were likely present in the facilities. Ranking the toxicological significance and relative importance of each of the chemicals identified by the analysis is beyond the scope of this study but the results highlight the importance of expanding the number of VOCs considered in indoor air quality studies and the need to determine if any of the compounds have potential health impacts.

Overall, VOCs were detected more frequently and at significantly higher levels indoors compared to outdoors. The indoor VOC levels were also inversely related to ventilation rates (for example, the correlation of air exchange rates and formaldehyde concentrations was -0.59), confirming that indoor sources were important determinants of the VOC levels.

3.3 Phthalate Results and Discussion

We analyzed indoor and outdoor air and dust samples collected from ECE facilities for five phthalate esters (diethyl phthalate [DEP], diisobutyl phthalate [DIBP], dibutyl phthalate [DBP], butyl benzyl phthalate [BBP], and di(2-ethylhexyl) phthalate [DEHP]).

3.3.1 Phthalate QA/QC

Indoor and Outdoor Air . For phthalate analysis in PUF, the average lab matrix spike recovery was 112.9% (SD= 14.1). Field matrix spike recoveries averaged 106.2% (SD= 28.5). Two duplicate indoor air phthalate measurements were collected at ECE#16 and #40 and analyzed for precision between measurements. The average RSD was 42.2% (SD=34.7).

Overall, the absolute differences were small, and the higher RSDs were associated with concentrations below the detection limit. The RSD for dibutyl phthalate, which was present in the air at the highest levels, was low (average=10.4%). For the other phthalates measured in air, the duplicate field concentrations were similar to the median levels reported, suggesting that reported upper-range values are more reliable.

Carpet Dust. For phthalate analysis in dust, the average lab matrix spike recovery was 98.6% (SD=5.4). Three phthalate dust samples were analyzed in duplicate. The average RSD was 5.73% (SD=1.4), showing strong precision in phthalate dust analysis. See Appendix C for more information.

3.3.2 Phthalate Air Results

A total of 40 indoor and 14 outdoor phthalate samples were valid for analysis. Final mass of phthalates were calculated by subtracting three-times the standard deviation of field matrix blanks. When duplicate samples were taken indoors, the average concentration between the two measurements was calculated and reported for that facility. Phthalates were detected more often in the indoor environment (Table 34) than the outdoor environment (Table 35). Concentrations of DEP, DIBP, and BBP were significantly higher indoors than outdoors (Wilcoxon $p<0.05$). The detection frequencies for DEP and DIBP were also significantly higher indoors versus outdoors (McNemar $p<0.05$). Interestingly, DIBP, a plasticizer often used in combination with other high molecular weight phthalates as a gelling aid, was found to be only present indoors. The phthalate indoor to outdoor air concentration ratios are summarized in Table 36.

Table 34. Summary of Indoor Air Phthalate Detection Frequencies and Concentrations (µg/m³) (n=40 ECE Facilities)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Diethyl phthalate	97.5	0.42	0.51	<MDL	0.14	0.21	0.57	0.85	1.34	2.81
Diisobutyl phthalate	87.5	0.23	0.45	<MDL	0.02	0.10	0.23	0.39	0.98	2.56
Dibutyl phthalate	100	0.87	0.75	0.05	0.29	0.52	1.43	2.03	2.40	2.65
Butyl benzyl phthalate	50.0	0.03	0.06	<MDL	<MDL	<MDL	0.03	0.12	0.19	0.23
Di(2-ethylhexyl) phthalate	52.5	0.12	0.43	<MDL	<MDL	0.01	0.06	0.23	0.38	2.71

Table 35. Summary of Outdoor Air Phthalate Detection Frequencies and Concentrations (µg/m³) (n=14 ECE Facilities)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	Max
Diethyl phthalate	14.3	0.05	0.13	<MDL	<MDL	<MDL	<MDL	0.25	0.43
Diisobutyl phthalate	0.0	0.00	0.00	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Dibutyl phthalate	71.4	4.36	11.21	<MDL	<MDL	0.10	0.16	23.40	36.78
Butyl benzyl phthalate	14.3	0.00	0.00	<MDL	<MDL	<MDL	<MDL	0.01	0.01
Di(2-ethylhexyl) phthalate	35.7	0.09	0.16	<MDL	<MDL	<MDL	0.14	0.32	0.52

Table 36. Summary of Indoor/Outdoor Air Concentrations Ratios for Phthalates (n=14 ECE Facilities)

Analyte	Mean	SD	Min	25th %	Median	75th %	Max
Diethyl phthalate	909.0	1,916.5	0.6	81.0	269.8	627.3	7,339.6
Diisobutyl phthalate	270.1	342.1	0.5	22.2	120.6	420.9	929.4
Dibutyl phthalate	124.2	242.8	0.1	1.9	3.1	67.5	759.1
Butyl benzyl phthalate	49.2	94.3	0.1	0.6	9.1	71.3	354.3
Di(2-ethylhexyl) phthalate	152.8	237.4	0.0	0.4	1.8	314.4	656.0

3.3.3 Phthalate Dust Results

Five phthalates, a constituent of plastics, personal care, and other consumer products, were measured in all 39 dust samples collected. The target analytes were diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), and di(2-ethyl hexyl) phthalate (DEHP). The median BBP and DEHP concentrations (46.8 and 172.2 µg/g) were substantially higher than DEP, DIBP, and DBP (medians = 1.4, 9.3, 13.7 µg/g, respectively (Table 37). Similarly, loadings of BBP and DEHP were also higher (medians = 135.7 and 361.7 µg/m^2, respectively) than DEP, DIBP, and DBP loadings (medians = 3.5, 26.8, and 51.1 µg/m^2, respectively; see Table 38).

Table 37. Summary of Phthalate Dust Concentrations (µg/g) (n=39)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Diethyl phthalate	100	2.1	1.5	0.5	1.0	1.4	2.7	4.3	4.6	7.9
Diisobutyl phthalate	100	16.2	25.0	3.5	5.9	9.3	14.4	23.2	81.4	145.8
Dibutyl phthalate	100	26.9	29.7	2.8	10.3	13.7	31.3	69.9	119.8	138.5
Butyl benzyl phthalate	100	208.3	343.6	7.1	22.7	46.8	236.9	815.7	1,194.1	1,435.5
Di(2-ethylhexyl) phthalate	100	221.6	182.8	51.6	113.0	172.2	265.4	408.4	543.9	1,088.1

Table 38. Summary of Phthalate Dust Loading (µg/m²) (n=39)

Analyte	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Diethyl phthalate	5.9	6.0	0.2	1.5	3.5	8.5	14.4	22.6	25.3
Diisobutyl phthalate	38.8	36.0	1.0	7.7	26.8	55.7	99.5	132.3	135.1
Dibutyl phthalate	72.0	76.3	1.4	13.2	51.1	97.3	201.6	253.4	338.5
Butyl benzyl phthalate	483.8	790.7	4.5	54.7	135.7	507.9	1,771.8	2,042.2	3,895.8
Di(2-ethylhexyl) phthalate	722.2	962.0	21.0	160.0	361.7	840.2	1,976.9	2,442.1	5,102.4

3.3.4 Phthalate Air and Dust Result Correlations

We computed Spearman's rank correlation coefficients to compare the concentrations in the air with the concentrations and loadings in dust. Concentrations of DIBP, DBP, and BBP in air and dust were moderately to strongly correlated (Spearman r=0.46-0.61, p<0.05; Table 39). DEP levels in air and dust were weakly correlated (0.24, p>0.05), whereas DEHP levels were not correlated. When examining contaminant loading and air levels, only BBP levels in air were significantly correlated.

Table 39. Spearman Correlation of Phthalate Concentrations in Air and Dust Concentrations and Loading (n=39).

	Air to Dust Concentration (rho)	Air to Dust Loading (rho)
Diethyl phthalate (DEP)	0.24	0.23
Diisobutyl phthalate (DIBP)	0.47*	0.05
Dibutyl phthalate (DBP)	0.46*	-0.06
Butyl benzyl phthalate (BBP)	0.61*	0.64*
Di(2-ethylhexyl) phthalate (DEHP)	-0.22	-0.14

*Spearman, p<0.05

3.3.5 Phthalate Discussion

Phthalate esters are semi volatile organic compounds used as plasticizers in plastics and personal care products. Phthalate compounds are on the California Proposition 65 list as developmental toxins, and have been found to contaminate indoor environments.[78-81] Studies have associated phthalate exposures with bronchial obstruction, allergies, and asthma in young children, and they are likely endocrine disruptors in humans.[18,82-86]

Levels of five phthalates were measured in air sampled from 40 ECE facilities located in Monterey (n=20) and Alameda (n=20) counties. Dibutyl phthalate was detected in 100% of indoor air samples, and was the phthalate measured at the highest concentrations in both indoor and outdoor air (median = 0.52 and 0.10 μg/m^3, respectively). All five phthalates were detected more frequently in the indoor compared to outdoor air. Indoor and outdoor air dibutyl phthalate levels were very similar to those measured in a pilot study of nine child care centers located in North Carolina (mean=0.49 and 0.07 μg/m^3).[138]

Of all the compounds measured in dust from ECE facilities, including flame retardants and pesticides, the phthalates DEHP and BBP (medians = 172.2 and 46.8 μg/g, respectively) were measured in the highest concentrations (n=39 ECE facilities). Air and dust concentrations of three phthalates (DIBP, DBP and BBP) were moderately to strongly correlated with each other (Spearman rho=0.46-0.71; p<0.05), suggesting deep carpet dust may be an ongoing source of phthalates indoors. Increased ventilation and vacuuming could reduce phthalate exposure in ECE facilities.

In the screening risk assessment, no phthalate compounds were found with dose estimates exceeding health-based reference values for any of the four age groups assessed (birth to <1 year; 1 to <2 years; 2 to <3 years; and 3 to <6 years).

3.4 Flame Retardant Results and Discussion

We analyzed indoor and outdoor air collected from ECE facilities for six polybrominated diphenyl ether (PBDE) (i.e., BDE-47, -99, -100, -153, -154, and 209) and four non-BDE flame retardants, including two constituents of Firemaster 550 (2-ethylhexyl tetrabromobenzoate [EHTBB] and bis[2-ethylhexyl]tetrabromophthalate [BEHTBP]), and two tris phosphate flame retardants (tris [2-chloroethyl] phosphate [TCEP] and TDCPP)(Tables 40-42).

In addition, we analyzed dust samples for 14 PBDE flame retardants (Table 43) and four non-BDE flame retardants (EHTBB, BEHTBP, TCEP and TDCPP).

3.4.1 Flame Retardant QA/ QC

Indoor and Outdoor Air . Two lab and field matrix spikes were analyzed for PBDE flame retardants in PUF by Battelle Laboratories. The average recovery for lab and field matrix spikes was 82.0% (SD= 9.2) and 86.2% (SD 16.9), respectively. For two duplicate flame retardant measurements in air, the average RSD was 42.1% (SD=41.7).

Carpet Dust. For flame retardants in dust, three lab spikes were analyzed for recovery. The average lab spike recovery was 85.5% (SD=12.6). One dust sample was analyzed in duplicate for PBDE flame retardants and two dust samples were analyzed in duplicate for Firemaster 550 and tris phosphate ester flame retardants. The average RSD for flame retardants analyzed in duplicates was 25.6% (SD=31.4). See Appendix C for additional QA/QC information.

3.4.2 Flame Retardant Air Results

A total of 40 indoor and 16 outdoor flame retardant results were available for analysis (Tables 40 and 41). Three times the standard deviation of the field matrix blank was subtracted out of sample masses before analysis. If duplicate indoor samples were collected, an average concentration was computed. Concentrations were reported when analyte mass was above the MDL. When below the MDL, values were flagged. BDE-209 was only reported from the first seven ECE facilities (#10-16) due to laboratory calibration issues (See methods in Section 2.5.1.3.1). Indoor BDE-209 values for the first seven facilities are reported but BDE-209 was excluded from further analysis and no outdoor measurements were analyzed for that congener. BDE-47 and BDE-99 were the most common congeners detected indoors and outdoors (%>MDL= 90 and 95%, respectively).

Indoor BDE-99 and TCEP concentrations were significantly higher ($p<0.05$) compared to levels in outdoor air (Wilcoxon $p<0.05$). Of the facilities where indoor and outdoor flame retardant air measurements were collected, the probability of detecting BDE-47 indoors was significantly higher than the probability of detecting the compound outdoors (McNemar's test $p<0.05$). The flame retardant indoor to outdoor air concentration ratios are summarized in Table 42.

Table 40. Summary of Flame Retardant Indoor Air Concentrations (ng/m³)

Analyte	N	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
BDE-47	40	90.0	0.52	0.67	<MDL	0.07	0.26	0.62	1.60	2.16	2.67
BDE-99	40	95.0	0.19	0.21	<MDL	0.06	0.12	0.24	0.46	0.67	0.93
BDE-100	40	37.5	0.01	0.02	<MDL	<MDL	<MDL	0.01	0.03	0.05	0.08
BDE-153	40	20.0	0.33	1.24	<MDL	<MDL	<MDL	<MDL	0.87	1.43	7.62
BDE-154	40	5.0	0.13	0.73	<MDL	<MDL	<MDL	<MDL	<MDL	0.09	4.60
BDE-209*	7	100	1.63	1.31	0.47	0.97	1.39	1.65	4.46	4.46	4.46
EHTBB	40	15.0	0.58	2.61	<MDL	<MDL	<MDL	<MDL	0.89	2.29	16.23
BEHTBP	40	17.5	0.23	0.87	<MDL	<MDL	<MDL	<MDL	0.56	0.99	5.39
TCEP	40	65.0	2.69	3.89	<MDL	<MDL	0.91	3.05	8.66	12.94	15.34
TDCPP	40	90.0	0.59	0.36	<MDL	0.40	0.53	0.72	0.96	1.25	1.99

* BDE-209 was only analyzed from the first seven ECE facilities sampled. See methods in Section 2.5.1.3.1.

Table 41. Summary of Flame Retardant Outdoor Air Concentrations (ng/m³)

Analyte	N	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	Max
BDE-47	16	56.3	1.16	2.67	<MDL	<MDL	0.09	0.60	4.08	10.20
BDE-99	16	75.0	0.06	0.05	<MDL	<MDL	0.05	0.09	0.14	0.15
BDE-100	16	12.5	0.01	0.01	<MDL	<MDL	<MDL	<MDL	0.01	0.03
BDE-153	16	37.5	0.25	0.60	<MDL	<MDL	<MDL	0.17	0.62	2.40
BDE-154	16	0.0	0.01	0.00	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
EHTBB	16	12.5	0.14	0.39	<MDL	<MDL	<MDL	<MDL	0.55	1.53
BEHTBP	16	12.5	0.30	1.00	<MDL	<MDL	<MDL	<MDL	0.62	4.02
TCEP*	14	50.0	0.72	0.54	<MDL	<MDL	0.19	1.17	1.59	1.60
TDCPP*	14	100	0.72	1.20	0.06	0.21	0.32	0.39	2.36	4.41

* Tris-chlorinated flame retardants analyzed in separate PUF cartridges from BDEs and were collected at 14 facilities.

Table 42. Summary of Indoor to Outdoor (I/O ratio) Flame Retardant Air Concentrations

Analyte	N	Mean	SD	Min	25th %	Median	75th %	Max
BDE-47	16	17.6	21.3	0.1	0.7	12.5	29.7	77.2
BDE-99	16	10.0	16.5	0.5	1.5	5.2	11.0	68.2
BDE-100	16	1.2	0.8	0.2	0.8	1.0	1.4	3.3
BDE-153	16	9.2	24.1	0.0	0.5	0.8	6.3	97.0
BDE-154	16	0.8	0.2	0.3	0.7	0.8	0.9	1.0
EHTBB	16	0.7	0.3	0.0	0.6	0.8	0.9	1.0
BEHTBP	16	2.5	7.2	0.0	0.6	0.8	0.9	29.5
TCEP	14	6.0	8.7	0.5	0.7	2.7	6.6	31.2
TDCPP	14	2.6	2.5	0.1	1.3	2.1	2.7	10.5

3.4.3 Flame Retardant Dust Results

Thirty nine dust samples were analyzed for PBDE congeners, TCEP, TDCPP, EHTBB, and BEHTBP. Where duplicate samples were measured, the average was used, except for one measurement duplicate on an aliquot with 0.25 g of dust.

Table 43 summarizes flame retardant dust concentrations in the ECE facilities. Total PBDEs were calculated by summing all PBDE congeners on a mass basis. PBDEs were detected in 100% of the dust samples. Median PBDE levels were somewhat lower than medians recently reported in California homes;[70,139] however, the maximum levels were in the same range. Overall, flame retardant levels were higher than levels found in other regions of the U.S., likely due to the strict flammability standards promulgated by the California Bureau of Electronic and Appliance Repair, Home Furnishings, and Thermal Insulation.[70,139] Figures 7a and 7b show the relative proportion of each PBDE congener mass in each facility. BDE-209, BDE-47, and BDE-99 comprised the bulk of the PBDE mass in the dust samples. BDE-47 and BDE-99 were banned in 2003; however, furniture and other long-lasting products containing these materials are still in use in many buildings. BDE-209 is currently used in plastic electronic casings. In many dust samples, BDE-209 is the dominant congener.

Use of tris phosphate flame retardants (TCEP and TDCPP) is increasing as a replacement for PBDEs. These tris phosphate compounds were detected in 100% of the dust samples (Table 43). The median concentrations of TDCPP (2,265 ng/g) and TCEP (319 ng/g) were similar to or higher than any of the median individual PBDE congener levels. Components of the Firemaster 550 flame retardant mixture (EHTBB and BEHTBP) were also detected in 100% of the dust samples, with median levels of 362 and 132 ng/g, respectively. Firemaster 550 is also used as a replacement for the banned PBDEs. Flame retardant loading values are presented in Table 44. The compounds TDCPP (median= 6,045.8 ng/m²) and BDE-209 (median = 2,923.6 ng/m²) had the highest loading values across the flame retardants measured.

Table 43. Summary of Flame Retardant Concentrations (ng/g) in Dust (n=39)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
BDE-47	100	1,717.0	3,085.7	139.6	263.8	768.9	1,326.5	5,786.6	11,699	15,116
BDE-99	100	2,351.0	4,637.4	225.9	393.5	1,031.1	1,584.7	4,832.4	13,230	25,522
BDE-100	100	471.2	945.0	53.3	86.8	211.5	330.9	1,047.6	2,010.6	5,525.0
BDE-118	76.9	25.0	24.3	<MDL	10.0	24.2	26.8	45.4	108.3	121.9
BDE-153	100	297.1	633.1	34.5	63.8	125.1	177.8	560.6	1,285.8	3,783.3
BDE-154	100	229.0	498.7	29.1	49.7	94.1	167.8	396.4	914.4	3,031.6
BDE-183	87.2	26.0	27.7	<MDL	12.4	17.3	27.1	41.6	113.2	139.2
BDE-190	2.6	14.3	17.2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	16.5
BDE-197	89.7	24.0	20.0	<MDL	16.1	17.3	20.9	26.4	33.7	70.8
BDE-203	20.5	16.9	22.5	<MDL	<MDL	<MDL	<MDL	20.1	36.8	69.2
BDE-205	0.0	15.7	19.4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
BDE-206	66.7	101.4	176.5	<MDL	<MDL	48.3	73.3	164.8	330.7	1,085.5
BDE-207	100	79.5	86.1	22.8	37.5	46.7	84.1	192.3	282.1	481.1
BDE-209	100	2,588.4	3,363.1	347.2	882.5	1,442.5	2,635.8	6,863.6	11,369	16,792
∑ BDE	100	7,956.6	10,671.0	1,225.4	2,197.4	4,205.7	9,455.9	20,981	32,598	55,155
TCEP	100	935.9	1,580.2	98.3	203.1	319.1	663.5	2,745.2	6,750.7	6,834.9
TDCPP	100	6,189.4	12,710.5	765.2	1,458.3	2,265.0	5,803.1	9,667.3	36,927	70,931
EHTBB	100	1,062.3	2,510.1	85.2	216.2	362.4	712.3	1,833.0	6,557.9	14,812
BEHTBP	100	431.1	1,191.9	28.8	80.6	132.9	327.6	745.2	1,299.3	7,489.7

Table 44. Summary of Flame Retardant Loading (ng/m²) in Dust (n=39)

Analyte	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
BDE-47	4,818.8	8,345.7	80.5	541.7	1,534.0	3,843.9	15,306	29,719	39,928
BDE-99	7,392.1	14,404	107.0	855.6	1,883.8	5,002.2	23,062	45,331	72,995
BDE-100	1407.1	2,646.7	30.1	172.2	406.6	969.9	3,866.5	7,588.4	13,873
BDE-118	88.4	99.9	<MDL	10.2	41.6	136.8	285.7	313.2	339.4
BDE-153	901.6	1,698.2	18.1	99.2	255.7	608.0	2,945.6	4,724.4	8,871.7
BDE-154	686.0	1,248.9	17.3	83.8	190.6	562.9	2,124.4	3,718.5	6,309.6
BDE-183	75.1	79.8	<MDL	15.7	38.0	121.3	229.9	268.8	276.7
BDE-190	41.9	42.4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	24.6
BDE-197	73.8	71.1	<MDL	15.2	38.5	102.3	203.7	232.0	241.1
BDE-203	48.6	55.4	<MDL	<MDL	<MDL	<MDL	71.7	162.8	179.8
BDE-205	44.8	45.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
BDE-206	274.1	443.6	<MDL	<MDL	60.0	179.1	675.9	1,545.8	2,281.8
BDE-207	254.9	372.4	11.5	60.3	104.1	350.9	614.3	1,386.3	1,804.1
BDE-209	8,437.2	14,569	280.6	1,234.4	2,923.6	8,260.5	28,538	35,882	78,443
∑ BDE	24,531	42,275	732.4	4,176.4	7,047.1	23,390	51,007	129,908	224,927
TCEP	5,311.1	15,175	96.7	244.8	837.9	1,590.2	19,669	31,757	88,535
TDCPP	13,128	21,697	730.7	2,566.0	6,045.8	11,017	37,960	89,044	90,756
EHTBB	4,216.3	13,989	57.4	396.2	682.8	1,788.0	9,978.1	18,952	86,007
BEHTBP	1,364.4	3,232.3	32.4	122.3	282.0	742.9	5,596.5	9,583.1	17,040

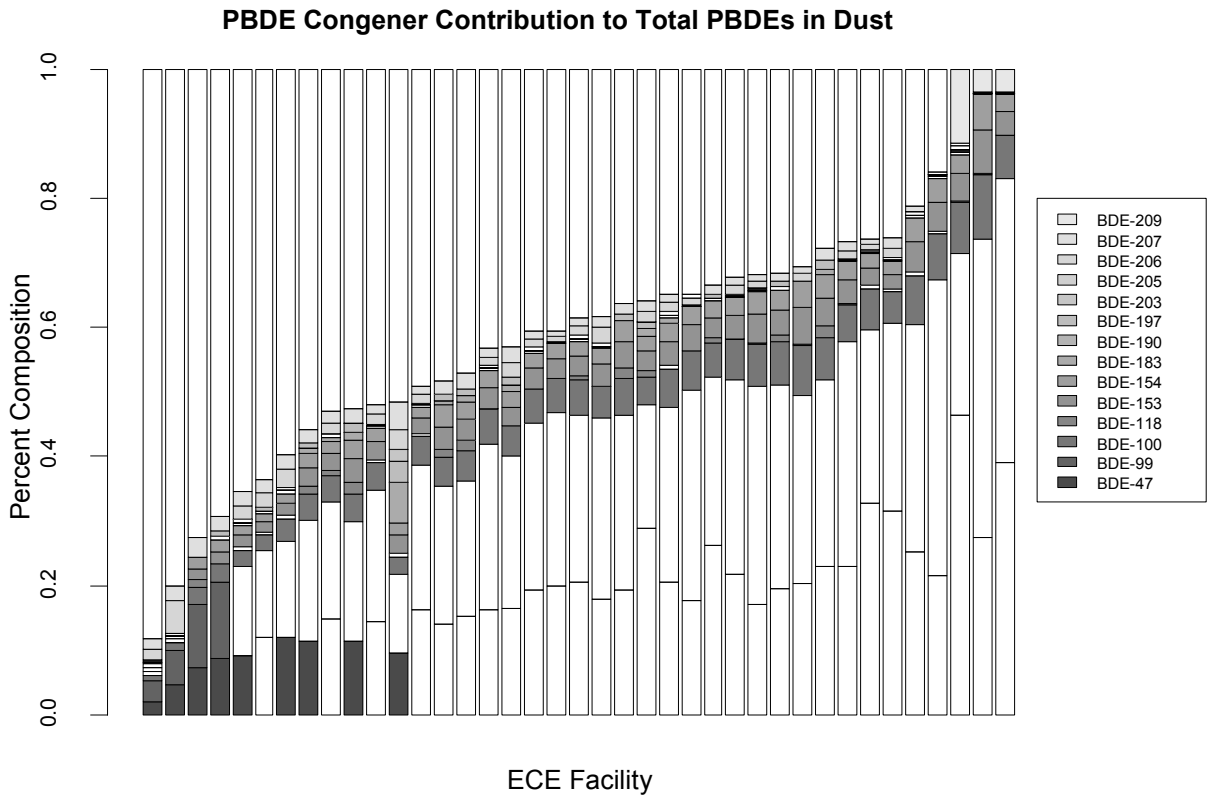

Figure 7a. PBDE congener proportion of total PBDE concentration sorted on BDE-209. Each "stacked" bar is a PBDE congener measurement from one ECE facility (n=39).

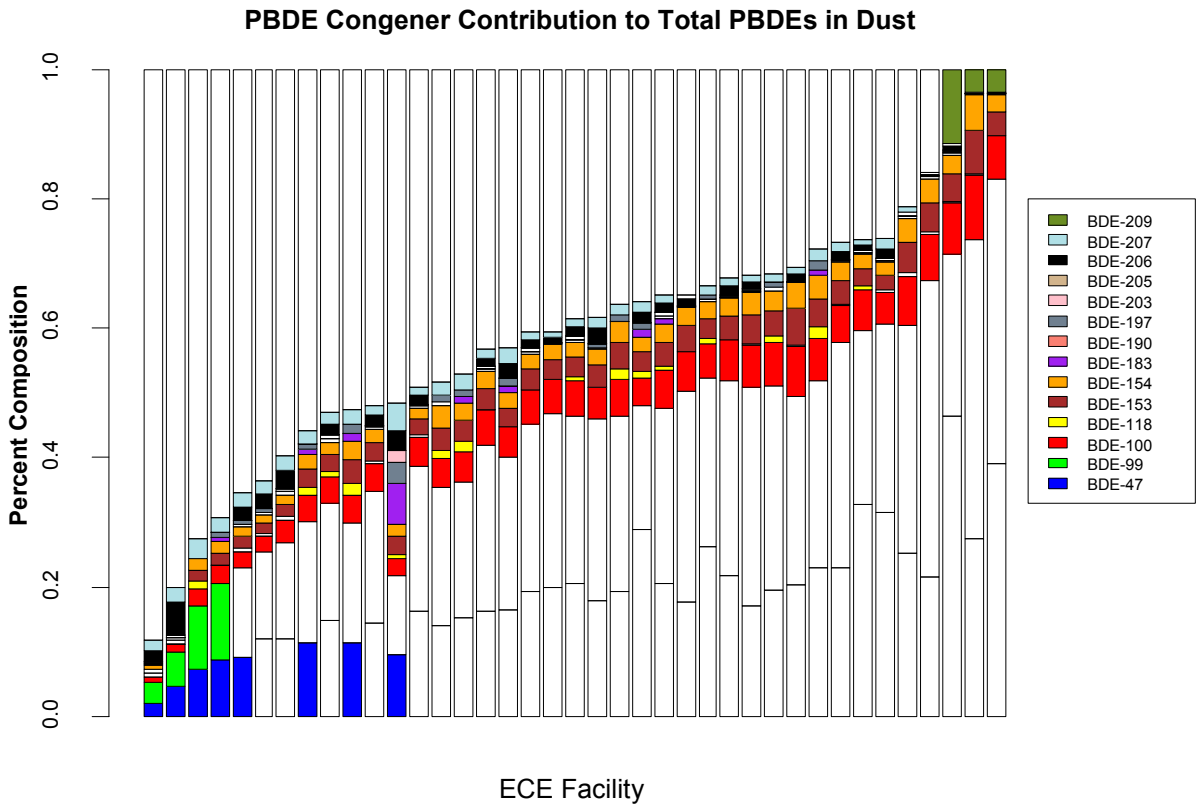

Figure 7b. Color version of the PBDE congener proportion of total PBDE concentration sorted on BDE-209. Each "stacked" bar is a PBDE congener measurement from one ECE facility (n=39).

3.4.4 Flame Retardant Air and Dust Result Correlations

Significant correlations between indoor air and dust concentrations were found for BDE-100, TDCPP, and BEHTBP (Table 45). The correlation between BEHTBP loading and air levels was the only significant correlation found between indoor air and dust loading. Overall, the correlations were weak, consistent with the low vapor pressure of these compounds.

Table 45. Spearman Rank Correlation Coefficients Testing the Relationship between Flame Retardant Air and Dust Concentrations and Loading in Dust

	Air to Dust Concentration (rho)	Air to Dust Loading (rho)
BDE-47	0.29	0.29
BDE-99	0.29	0.28
BDE-100	0.36*	0.10
BDE-153	0.12	0.13
BDE-154	-0.24	-0.18
TCEP	0.13	0.08
TDCPP	0.32*	0.09
EHTBB	-0.02	0.15
BEHTBP	0.30*	0.29*

*p<0.05.

3.4.5 Predictors of Flame Retardant Concentrations in Air and Dust

Due to California's strict flammability standards, foam furniture contains flame retardants. The manufacture, distribution, and processing of products containing pentaBDEs (BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183) was banned in California as of June 1, 2006.[68] Replacement furniture fire retardants such as chlorinated tris (tris[1,3-dichloro-2-propyl] phosphate [TDCPP]) and Firemaster 550 (a proprietary phosphorus-bromine blend formulation consisting of BEHTBP and EHTBB) have come into wider use.

Twenty-two facilities had upholstered furniture present in rooms where children spend time and 17 had napping equipment made out of foam. No significant differences in indoor air flame retardant concentrations were found between ECE facilities with and without upholstered furniture, or between ECE facilities with and without napping equipment made out of foam.

Dust concentrations of all of the individual pentaBDE congeners were higher in facilities with upholstered furniture present, but were not statistically significantly higher (Table 46). Similarly, concentrations of the pentaBDE and several individual and total PBDE flame retardants were higher in facilities where foam mattresses were present (Table 47), but the difference was not statistically significant. Concentrations of TCEP and TDCPP were significantly higher in facilities with napping equipment made out of foam (Table 47). While bromine levels in electronics have been associated with decaBDE (BDE-209) levels in dust,[140,141] we did not find significantly higher BDE-209 dust concentrations in rooms with a computer or television ($p>0.05$).

In summary, flame retardant concentrations in dust were higher in facilities where upholstered furniture or foam napping equipment was present. In many cases the individual differences were not statistically significant; however, the overall trend of higher levels, especially for the pentaBDE congeners, suggests that these furnishings were associated with increased pentaBDE contamination in dust. The lack of statistically significant differences for the individual congeners is likely due to the small sample size.

Table 46. Comparison of Flame Retardant Dust Concentrations between Facilities with and without Upholstered Furniture Present in Child Care Room

	No Upholstered Furniture Present (n=17)					Upholstered Furniture Present (n=22)				
	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)
BDE-47	100	292.5	658.0	946.0	11,699	100	263.8	837.3	1,638.6	15,116
BDE-99	100	412.3	691.7	1,222.2	13,230	100	362.2	1,160.3	3,070.9	25,522
BDE-100	100	87.6	134.0	257.3	1,983.7	100	80.2	254.9	475.2	5,525.0
BDE-118	76.5	12.6	23.9	25.9	31.8	77.3	5.1	24.3	28.8	121.9
BDE-153	100	61.7	85.4	145.1	1,124.4	100	64.1	148.4	299.3	3,783.3
BDE-154	100	49.7	65.8	104.6	779.5	100	60.1	116.6	251.0	3,031.6
BDE-183	94.1	14.0	15.2	20.4	43.8	81.8	8.7	19.1	28.1	139.2
TCEP	100	203.1	352.2	569.0	6,750.7	100	218.5	310.0	780.9	6,834.9
TDCPP	100	1,513.0	2,533.3	4,827.5	9,667.3	100	1,370.2	2,144.1	5,803.1	70,931
EHTBB	100	216.2	377.3	618.4	6,557.9	100	218.2	347.2	900.4	14,812
BEHTBP	100	82.5	132.9	340.4	1,299.3	100	80.6	130.3	259.4	7,490

Table 47. Comparison of Flame Retardant Dust Concentrations between Facilities with and without Foam Napping Equipment Present in Child Care Room

	No Foam Napping Equipment (n=18)					Foam Napping Equipment (n=17)				
	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)
BDE-47	100	232.6	510.6	852.0	2,870.0	100	288.6	939.0	1,175.2	15,116
BDE-99	100	322.0	677.0	1,260.1	3,909.5	100	395.2	1,118.9	1,631.4	25,522
BDE-100	100	72.9	140.9	271.5	758.1	100	86.8	257.3	366.2	5,525.0
BDE-153	100	63.8	85.5	165.4	435.9	100	61.7	145.1	270.9	3,783.3
BDE-154	100	40.5	67.3	119.9	348.3	100	49.7	106.9	199.0	3,031.6
BDE-183	100	14.4	17.7	23.8	139.2	70.6	<MDL	13.6	21.3	113.2
TCEP*	100	175.7	285.3	415.4	2,442.4	100	220.1	642.9	2,139.0	6,835
TDCPP*	100	1,336.4	1,510.6	3,202.5	70,931	100	2,051.5	2,836.7	6,789.5	36,927
EHTBB	100	216.2	383.4	712.3	14,812	100	232.9	354.0	656.0	6,557.9
BEHTBP	100	63.9	115.4	417.6	7,489.7	100	85.2	144.2	235.2	1,299.3

* Mann-Whitney p-value<0.05

3.4.6 Flame Retardant Discussion

Flame retardants are used in furnishings and electronics to comply with the California Bureau of Electronic and Appliance Repair, Home Furnishings, and Thermal Insulation flammability standards defined in Technical Bulletin 117. Brominated flame retardants are a class of compounds receiving increasing attention due to their persistence in the environment and potential adverse health effects. The manufacture, distribution, and processing of products containing two classes of polybrominated diphenyl ethers (PBDEs), pentabrominated (BDE-47, -99, -100) and octabrominated diphenyl ethers (BDE-153, -154, -183), is now banned in California as of June 1, 2006.[68] Replacement furniture fire retardants such as TDCPP and Firemaster 550 (a proprietary phosphorus-bromine blend formulation consisting of BEHTBP and EHTBB) have come into wider use. Prior to 1977, TDCPP was used in children's sleepwear as a fire retardant, however, manufacturers voluntarily stopped using it in these products after it was found to be mutagenic.[73,74] Chlorinated tris (TDCPP) was recently listed as a carcinogen on the Proposition 65 list.[75] Today TDCPP is a widely used flame retardant, commonly detected in furniture foam as well as infant products.[76,77]

This is the first study to report air and dust levels of PBDE flame retardants and non-BDE replacement fire retardants in child care environments. A total of 40 indoor and 16 outdoor ECE facility air samples were analyzed for flame retardant compounds. While only reported in 7 indoor air samples due to laboratory calibration issues, the deca-BDE compound, BDE-209, was measured at detectable levels in all 7 samples analyzed (median=1.4 ng/m^3). The penta-BDE congeners, BDE-47 and BDE-99, were commonly detected indoors (%>MDL = 90 and 95%, respectively) and outdoors (%>MDL = 56 and 75%, respectively). Levels of BDE-47 and BDE-99 were significantly higher indoors compared to outdoors (indoor/outodoor [I/O] ratio = 17.6 and 10.0, respectively).

The median levels of two tris phosphate compounds, TDCPP (2,265 ng/g) and TCEP (319 ng/g), in dust were similar to or higher than any of the individual PBDE congener levels. Overall, the median levels of PBDE flame retardants in dust were lower than levels reported in other studies focusing on residential environments in California, possibly due to the frequent cleaning that occurs in ECE facilities.[70,139] Maximum flame retardant levels in dust were similar to the upper-bound levels measured in other California studies.

Flame retardants have relatively low vapor pressures. Detection frequencies in air ranged from 0-95%. Exposure estimates based on air concentrations did not exceed health-based benchmarks. However, the estimated non-dietary ingestion of PBDEs in children ages birth to <1 year exceeded the U.S. EPA RfDs for PBDE-47 and PBDE-99 in 10.3% (4 of 39) of facilities.

3.5 Perfluorinated Compounds Results and Discussion

We analyzed dust samples collected from ECE facilities for ten perfluorinated compounds (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHS, and PFOS).

3.5.1 Perfluorinated Compounds Dust QA/QC

CERCH worked with collaborators in the National Exposure Research Laboratory (NERL) at the U.S. EPA to analyze washed silica gel (Supelco, part # 21342U) as blanks for possible PFC contamination by the HVS3, which contains gaskets and other parts made of Teflon. Before

field sampling, washed silica gel was applied to cleaned aluminum foil and vacuumed through the HVS3 vacuum into a sampling jar. This procedure was repeated twice. In addition, washed silica gel was deposited directly into a clean sample jar. Samples showed only a small peak of C11 acid in the first sample blank taken. Two other peaks, PFHpA and PFOA were near background levels. The two additional blanks showed no significant peaks. In all, U.S. EPA chemists judged dust blanks to be clean and showed the HVS3 contributed little contamination to the sample. Four dust samples were analyzed in duplicate by the U.S. EPA to validate the precision of the results. The average RSD was 11.1% (SD=11.4). See Appendix C for Dust Blank Chromatograms prepared by Dr. Mark Strynar of the U.S. EPA and additional QA information.

3.5.2 Perfluorinated Compounds Dust Results

Perfluorinated compounds (PFCs) were measured in the dust of 39 child care facilities studied (Tables 48 and 49). Perfluorooctanoic acid (PFOA) and PFDA were the PFCs most often detected in dust (>MDL (%) = 71.8 and 66.7%, respectively) with median concentrations of 8.0 and 5.8 ng/g, respectively.

Table 48. Summary of PFC Concentrations (ng/g) in Dust (n=39)

	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
PFBA	7.7	5.6	9.9	<MDL	<MDL	<MDL	<MDL	<MDL	18.0	64.0
PFPeA	5.1	4.3	2.7	<MDL	<MDL	<MDL	<MDL	<MDL	13.7	16.0
PFHxA	33.3	9.5	17.0	<MDL	<MDL	<MDL	7.2	16.6	43.0	100.0
PFHpA	15.4	6.2	9.5	<MDL	<MDL	<MDL	<MDL	10.8	28.4	57.5
PFOA	71.8	18.6	38.2	<MDL	<MDL	8.0	13.2	45.7	58.2	235.0
PFNA	48.7	28.6	56.6	<MDL	<MDL	<MDL	15.4	117.0	202.0	252.0
PFDA	66.7	13.1	32.0	<MDL	<MDL	5.8	8.7	29.0	30.9	203.0
PFBS	10.3	4.9	4.9	<MDL	<MDL	<MDL	<MDL	8.5	19.3	29.1
PFHS	15.4	7.8	13.3	<MDL	<MDL	<MDL	<MDL	19.5	51.1	69.1
PFOS	53.9	12.6	14.9	<MDL	<MDL	6.2	15.6	42.6	48.0	67.0

Table 49. Summary of PFC Loading (ng/m²) in Dust (n=39)

	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
PFBA	17.3	27.8	<MDL	<MDL	<MDL	<MDL	<MDL	8.9	168.5
PFPeA	16.8	25.2	<MDL	<MDL	<MDL	<MDL	<MDL	12.5	149.8
PFHxA	32.2	64.6	<MDL	<MDL	<MDL	13.3	47.4	124.5	388.0
PFHpA	18.6	21.0	<MDL	<MDL	<MDL	<MDL	24.1	52.5	110.2
PFOA	60.5	151.7	<MDL	<MDL	11.2	49.0	88.9	349.1	911.8
PFNA	66.5	184.7	<MDL	<MDL	<MDL	31.3	183.9	240.2	1,137.3
PFDA	45.3	124.9	<MDL	<MDL	8.2	45.0	85.5	116.9	787.6
PFBS	17.4	29.7	<MDL	<MDL	<MDL	<MDL	3.4	3.7	181.1
PFHS	35.4	83.8	<MDL	<MDL	<MDL	<MDL	110.9	182.5	476.8
PFOS	38.4	58.4	<MDL	<MDL	7.1	29.3	93.0	146.0	316.3

3.5.3 Perfluorinated Compounds Discussion

Perfluorinated chemicals (PFCs) are halogenated persistent organic pollutants that have been used widely in consumer products such as Teflon and 3M's Scotchgard since the 1950s. These chemicals are currently found at detectable levels in the blood of humans and animals across the globe[142] and exposure of the general U.S. population to PFCs is widespread.[143]

Ten PFCs were measured in dust collected from 39 ECE facilities. The most commonly detected PFCs were PFOA, PFDA, and perfluorooctane sulfonic acid (PFOS) (>MDL (%) = 72%, 67%, and 54% respectively). The other 7 PFCs were detected in 5 to 49% of samples. Median PFOA and PFOS concentrations were 8.0 and 6.2 ng/g, respectively, and the maximum concentrations were 235 and 67 ng/g, respectively.

Levels of PFCs have not been reported for California school and child care facilities previously. Currently, there are no health-based oral reference values for the PFCs we measured.

3.6 Pesticide Results and Discussion

Indoor and outdoor air and dust samples were collected from 40 ECE facilities in Alameda and Monterey Counties and analyzed for OP and pyrethroid insecticides, as well as piperonyl butoxide (a pyrethroid synergist), and chlorthal-dimethyl (dacthal) (a pre-emergent herbicide). The OP insecticides chlorpyrifos and diazinon were phased out from indoor and residential uses in the U.S. between 2001 and 2004;[144] however, residues may persist from historical indoor use or due to ingress from nearby agricultural applications. Since the phase out of chlorpyrifos and diazinon, pyrethroid pesticides have become the dominant insecticide class used in institutional environments. Of the 40 facilities, pyrethroids were stored or used in 14 (35%) of them (see Table 61, below).

Results were compared by the county where facilities were located and by the ECE facility types (home- vs. center-based). Fifteen facilities out of the 40 facilities were located in agricultural communities within the Salinas Valley of Monterey County. Air and dust pesticide concentrations were also compared between the ECE facilities located in agricultural vs. non-agricultural areas.

3.6.1 Pesticide Air and Dust Measurement QA/QC

Indoor and Outdoor Air. Four lab and two field matrix spikes were analyzed to evaluate recovery of the pesticide analytes in PUFs. The average lab matrix spike recovery for pesticide analytes in air was 74.4% (SD = 13.1). Average field matrix spike recovery was 65.4% (SD = 20.7). Two duplicate PUF measurements were collected and the average RSD was 14.2% (SD = 30.6).

Carpet Dust. For three lab matrix spikes, the average recovery was 104.1% (SD = 16.9). Duplicate pesticide analysis was performed on the two dust samples to assess precision in the analytical methods. Duplicate analyses were from dust collected at ECE#10 and 40. Duplicate dust analysis showed good precision with an average RSD of 4.3% (SD = 3.9). See Appendix C for additional pesticide QA/QC information.

3.6.2 Pesticide Air Results

Forty indoor and 14 outdoor air samples were available for pesticide analysis. Final masses of pesticides were calculated by subtracting three times the standard deviation of field matrix blanks. When duplicate samples were collected indoors (n=2), the average concentration between the two measurements was calculated and reported for that facility. The pesticide analytes most often detected in indoor air were trans-permethrin (100%) and chlorpyrifos (95%), while for outdoor measurements, trans-permethrin (92.9%) and cis-permethrin (78.6%) were the most often detected (Tables 50 and 51).

Two compounds, diazinon and piperonyl butoxide, had significantly higher concentrations in indoor versus outdoor air (Wilcoxon $p<0.05$); indoor diazinon detection frequencies were also significantly higher indoors compared to outdoors (McNemar $p<0.05$). Indoor air concentrations of dacthal were significantly higher (Mann-Whitney $p<0.05$) in Monterey County compared to Alameda County (Table 53). The probability of detecting dacthal was also significantly higher (Fischer's $p<0.05$) in Monterey County compared to Alameda County.

Indoor air concentrations were compared between ECE facilities in agricultural (n=15) versus non-agricultural (n=25) areas. Dacthal air concentrations measured in ECE facilities located in the agricultural Salinas Valley were significantly higher (Mann-Whitney p-value<0.05) than the facilities located in non-agricultural areas (Table 54).

With the exception of dacthal and, to some extent, piperonyl butoxide, the pesticide levels between counties, agricultural and non-agricultural areas, and facility type were generally similar. As noted above, dacthal is a commonly-used and relatively persistent agricultural herbicide. Piperonyl butoxide is a synergist commonly added to pyrethroid pesticide formulations.

Table 50. Summary of Indoor Air Pesticide Concentrations (ng/m^3) (n=40)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Diazinon	77.5	0.19	0.47	<MDL	0.01	0.05	0.15	0.32	0.46	3.00
Chlorpyrifos	95.0	0.31	0.23	<MDL	0.17	0.25	0.43	0.57	0.64	1.36
Dacthal	60.0	0.38	0.49	<MDL	<MDL	0.16	0.46	1.13	1.46	1.89
Imiprothrin	15.0	0.52	1.04	<MDL	<MDL	<MDL	<MDL	1.15	3.02	5.50
Piperonyl butoxide	42.5	0.19	0.86	<MDL	<MDL	<MDL	0.03	0.14	0.42	5.45
Bifenthrin	12.5	0.10	0.07	<MDL	<MDL	<MDL	<MDL	0.19	0.28	0.41
Sumithrin	5.0	0.09	0.23	<MDL	<MDL	<MDL	<MDL	<MDL	0.48	1.16
cis-Permethrin	60.0	0.11	0.14	<MDL	<MDL	0.04	0.16	0.32	0.46	0.57
trans-Permethrin	100	0.16	0.14	0.03	0.07	0.14	0.22	0.30	0.31	0.88
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Table 51. Summary of Outdoor Air Pesticide Concentrations (ng/m^3) (n=14)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	Max
Diazinon	35.7	0.13	0.09	<MDL	<MDL	<MDL	0.03	0.17	0.36
Chlorpyrifos	64.3	0.29	0.30	<MDL	<MDL	0.17	0.30	0.46	1.30
Dacthal	64.3	0.86	1.95	<MDL	<MDL	0.21	0.75	1.21	7.48
Imiprothrin	21.4	0.70	1.42	<MDL	<MDL	<MDL	<MDL	0.94	5.59
Piperonyl butoxide	14.3	0.03	0.03	<MDL	<MDL	<MDL	<MDL	0.01	0.11
Bifenthrin	21.4	0.18	0.15	<MDL	<MDL	<MDL	<MDL	0.50	0.50
Sumithrin	7.1	0.21	0.56	<MDL	<MDL	<MDL	<MDL	<MDL	2.13
cis-Permethrin	78.6	0.14	0.12	<MDL	0.02	0.11	0.24	0.34	0.39
trans-Permethrin	92.9	0.13	0.11	<MDL	0.05	0.11	0.17	0.25	0.41
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Table 52. Summary of Indoor to Outdoor Ratios for Air Pesticide Concentrations (n=14)

Analyte	Mean	SD	Min	25th %	Median	75th %	Max
Diazinon	1.8	2.4	0.2	0.4	0.6	1.7	8.9
Chlorpyrifos	1.3	0.9	0.5	0.7	1.1	1.4	3.5
Dacthal	2.8	3.4	0.1	0.6	1.0	4.7	10.8
Imiprothrin	2.1	5.2	0.1	0.5	0.7	1.0	20.2
Piperonyl butoxide	3.8	5.4	0.2	0.7	1.0	3.1	14.5
Bifenthrin	1.0	0.9	0.1	0.6	0.8	1.0	3.9
Sumithrin	0.7	0.2	0.3	0.6	0.7	1.0	1.0
cis-Permethrin	2.3	2.5	0.1	0.6	1.2	2.7	8.3
trans-Permethrin	3.3	4.7	0.1	1.0	1.3	3.8	17.2

Table 53. Indoor Air Pesticide Concentrations by County

Analyte	Alameda (n=20)					Monterey (n=20)				
	>MDL (%)	25th % (ng/m³)	Median (ng/m³)	75th % (ng/m³)	Max (ng/m³)	>MDL (%)	25th % (ng/m³)	Median (ng/m³)	75th % (ng/m³)	Max (ng/m³)
Diazinon	70.0	<MDL	0.04	0.12	3.00	85.0	0.02	0.07	0.18	0.54
Chlorpyrifos	95.0	0.14	0.21	0.31	1.36	95.0	0.19	0.26	0.50	0.63
Dacthal*	20.0	<MDL	<MDL	<MDL	1.41	100	0.20	0.39	0.98	1.89
Imiprothrin	15.0	<MDL	<MDL	<MDL	5.50	15.0	<MDL	<MDL	<MDL	2.91
Piperonyl butoxide	25.0	<MDL	<MDL	0.01	0.16	60.0	<MDL	0.01	0.08	5.45
Bifenthrin	10.0	<MDL	<MDL	<MDL	0.25	15.0	<MDL	<MDL	<MDL	0.41
Sumithrin	5.0	<MDL	<MDL	<MDL	1.16	5.0	<MDL	<MDL	<MDL	0.95
cis-Permethrin	55.0	<MDL	0.04	0.14	0.40	65.0	<MDL	0.04	0.18	0.57
trans-Permethrin	100	0.08	0.15	0.21	0.30	100	0.06	0.11	0.24	0.88
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL

* Mann-Whitney p-value <0.05.

Table 54. Indoor Air Pesticide Concentrations by Agricultural versus Non-agricultural Area

	Agricultural (n=15)					Non-Agricultural (n=25)				
Analyte	**>MDL (%)**	**25th % (ng/m³)**	**Median (ng/m³)**	**75th % (ng/m³)**	**Max (ng/m³)**	**>MDL (%)**	**25th % (ng/m³)**	**Median (ng/m³)**	**75th % (ng/m³)**	**Max (ng/m³)**
Diazinon	93.3	0.02	0.05	0.20	0.54	68.0	<MDL	0.04	0.12	3.00
Chlorpyrifos	100	0.18	0.28	0.51	0.58	92.0	0.14	0.25	0.30	1.36
Dacthal*	100	0.22	0.41	1.05	1.89	36.0	<MDL	<MDL	0.08	1.41
Imiprothrin	13.3	<MDL	<MDL	<MDL	1.39	16.0	<MDL	<MDL	<MDL	5.50
Piperonyl butoxide	53.3	<MDL	0.01	0.04	0.54	36.0	<MDL	<MDL	0.01	5.45
Bifenthrin	20.0	<MDL	<MDL	<MDL	0.41	8.0	<MDL	<MDL	<MDL	0.25
Sumithrin	6.7	<MDL	<MDL	<MDL	0.95	4.0	<MDL	<MDL	<MDL	1.16
cis-Permethrin	60.0	<MDL	0.01	0.14	0.52	60.0	<MDL	0.06	0.17	0.57
trans-Permethrin	100	0.05	0.08	0.16	0.88	100	0.08	0.17	0.23	0.31
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL

* Mann-Whitney p-value <0.05.

3.6.3 Pesticide Dust Results

Dust samples were collected from 39 ECE facilities. In facilities where laboratory duplicates were analyzed, we averaged the two measurements to obtain a single concentration.

For the information presented below, cyfluthrin and cypermethrin isomer concentrations were summed to obtain a single dust concentration for these pesticides. Because the cis- and trans- isomers of permethrin have different toxicities, they were considered separately. Cis- and trans-permethrin were detected in 100% of samples and had the highest median concentrations at 162 and 225 ng/g, respectively (Table 55). Other frequently (>90%) detected pesticides included bifenthrin, chlorpyrifos, diazinon, and dacthal, and the synergist piperonyl butoxide. Similarly, the highest median loadings were also found for cis- and trans-permethrin (511 and 752 ng/m^2, respectively) (Table 56).

Cis- and trans- permethrin and bifenthrin dust concentrations were significantly higher (Mann-Whitney p-value<0.05) in ECE facilities located in Alameda County versus Monterey County (Table 57). Conversely, dust concentrations of dacthal, an agricultural pesticide, were much higher in Monterey County compared to Alameda County ($p<0.01$). No significant differences in dust concentrations were found between home- and center-based ECE facilities.

We also compared dust concentrations among ECE facilities located in agricultural (n=14) versus non-agricultural (n=25) areas. We found significantly higher (Mann-Whitney p-value<0.05) dacthal concentrations measured in dust from ECE facilities located in the agricultural Salinas Valley compared to facilities located in non-agricultural areas (Table 58). Conversely, we found significantly higher bifenthrin, cis-permethrin and trans-permethrin concentrations measured in dust from ECE facilities located in the non-agricultural compared to agricultural areas (p-value<0.05). Piperonyl butoxide was also higher, albeit non-significantly, in non-agricultural areas.

Overall, the findings suggest that pyrethroid insecticides are more prevalent in the non-agricultural areas. Although dacthal was much higher in dust and air in the agricultural areas, levels of chlorpyrifos and diazinon were not significantly different. Agricultural pesticide use did not appear to contribute to OP pesticide levels in ECE facilities in the agricultural areas.

Table 55. Summary of Pesticide Concentrations (ng/g) in Dust (n=39)

Analyte	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Diazinon	92.3	8.6	15.1	<MDL	2.8	3.7	5.5	25.8	60.9	74.1
Chlorpyrifos	92.3	36.7	95.7	<MDL	7.1	10.6	18.8	84.1	217.4	563.4
Dacthal	92.3	14.4	17.0	<MDL	3.4	6.4	21.2	44.4	51.2	73.8
Imiprothrin	33.3	186.2	324.9	<MDL	<MDL	<MDL	222.5	644.2	759.5	1,739.8
Piperonyl butoxide	94.9	771.2	3,927.7	<MDL	40.6	76.3	145.9	390.7	1,375.7	24,629
Bifenthrin	92.3	137.7	216.1	<MDL	43.4	56.8	106.3	413.3	896.5	927.6
Sumithrin	20.5	62.7	217.7	<MDL	<MDL	<MDL	<MDL	229.2	322.6	1,299.0
cis-Permethrin	100	551.6	2,007.6	47.3	108.2	162.1	261.3	565.7	939.7	12,712
trans-Permethrin	100	884.6	3,331.4	48.0	141.7	225.3	436.5	980.1	1,500.9	21,058
Cyfluthrin	5.1	83.8	123.5	<MDL	<MDL	<MDL	<MDL	<MDL	434.4	739.2
Cypermethrin	41.0	1,207.2	5,726.3	<MDL	<MDL	<MDL	374.7	1,045.5	2,968.6	35,898

Table 56. Summary of Pesticide Loading (ng/m²) in Dust from ECE Facilities (n=39)

Analyte	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Diazinon	25.2	41.1	<MDL	1.8	8.0	30.8	66.9	131.8	208.5
Chlorpyrifos	112.7	287.2	<MDL	9.4	28.2	90.0	214.9	853.5	1,632.9
Dacthal	63.8	114.9	<MDL	3.9	13.1	66.4	150.5	478.0	531.3
Imiprothrin	955.1	1,697.8	<MDL	<MDL	<MDL	1,353.7	4,292.2	4,742.4	6,690.3
Piperonyl butoxide	8,631.5	51,668	<MDL	74.3	144.8	507.7	1,161.2	2,464.8	323,006
Bifenthrin	531.6	1,221.6	<MDL	57.2	142.0	512.6	710.8	4,585.7	6,045.7
Sumithrin	314.4	932.9	<MDL	<MDL	<MDL	<MDL	1,290.6	3,540.9	4,230.6
cis-Permethrin	903.4	1,637.8	12.6	238.0	511.1	833.1	1,764.8	5,586.7	9,082.9
trans-Permethrin	1,386.7	2,646.4	18.9	331.0	752.1	1,256.2	2,574.1	9,254.9	14,581.0
Cyfluthrin	253.0	275.0	<MDL	<MDL	<MDL	<MDL	<MDL	324.9	1,340.2
Cypermethrin	9,301.8	53,701	<MDL	<MDL	<MDL	809.3	2,812.7	4,557.8	336,004

Table 57. Summary of Pesticide Dust Concentrations by County

	Alameda (n=20)					Monterey (n=19)				
Analyte	**>MDL (%)**	**25th % (ng/g)**	**Median (ng/g)**	**75th % (ng/g)**	**Max (ng/g)**	**>MDL (%)**	**25th % (ng/g)**	**Median (ng/g)**	**75th % (ng/g)**	**Max (ng/g)**
Diazinon	95.0	2.4	3.8	9.8	74.1	89.5	3.2	3.7	5.1	27.8
Chlorpyrifos	90.0	6.8	12.9	26.9	147.6	94.7	7.1	9.8	15.1	563.4
Dacthal*	85.0	1.6	3.5	6.2	51.2	100	9.6	18.0	31.4	73.8
Imiprothrin	35.0	<MDL	<MDL	199.5	1,739.8	31.6	<MDL	<MDL	250.3	714.8
Piperonyl butoxide	95.0	30.6	101.3	178.4	613.6	94.7	46.2	69.9	106.2	24,629
Bifenthrin*	95.0	54.7	79.8	203.1	896.5	89.5	25.3	49.2	62.4	927.6
Sumithrin	15.0	<MDL	<MDL	<MDL	1,299.0	26.3	<MDL	<MDL	33.5	322.6
cis-Permethrin*	100	152.8	239.9	493.5	12,712	100	95.8	140.6	166.8	692.6
trans-Permethrin*	100	193.8	327.9	841.0	21,058	100	141.4	188.5	282.6	1,111.8
Cyfluthrin	5.0	<MDL	<MDL	<MDL	739.2	5.3	<MDL	<MDL	<MDL	434.4
Cypermethrin	25.0	<MDL	<MDL	197.4	2,968.6	57.9	<MDL	216.2	374.7	358,980

* Mann-Whitney p-value <0.05

Table 58. Pesticide Dust Concentrations by Agricultural Location

	Agricultural (n=14)					Non-Agricultural (n=25)				
Analyte	**>MDL (%)**	**25th % (ng/g)**	**Median (ng/g)**	**75th % (ng/g)**	**Maximum (ng/g)**	**>MDL (%)**	**25th % (ng/g)**	**Median (ng/g)**	**75th % (ng/g)**	**Maximum (ng/g)**
Diazinon	100	3.4	4.6	5.4	27.8	88.0	1.9	3.3	5.5	74.1
Chlorpyrifos	100	9.1	12.7	17.8	563.4	88.0	6.0	9.9	19.6	147.6
Dacthal*	100	16.8	22.7	38.8	73.8	88.0	1.7	3.6	6.0	51.2
Imiprothrin	35.7	<MDL	<MDL	250.3	644.2	32.0	<MDL	<MDL	176.5	1,739.8
Piperonyl butoxide	100	50.4	68.3	99.9	1,375.7	92.0	34.6	94.6	145.9	24,629
Bifenthrin*	85.7	24.1	46.8	58.1	927.6	96.0	53.3	75.9	198.0	896.5
Sumithrin	14.3	<MDL	<MDL	<MDL	176.1	24.0	<MDL	<MDL	<MDL	1,299.0
cis-Permethrin*	100	95.8	130.6	162.1	253.8	100	147.2	216.9	490.2	12,712
trans-Permethrin*	100	141.4	177.8	199.4	436.5	100	188.5	285.5	822.9	21,058
Cyfluthrin	7.1	<MDL	<MDL	<MDL	434.4	4.0	<MDL	<MDL	<MDL	739.2
Cypermethrin	71.4	<MDL	249.3	374.7	869.0	24.0	<MDL	<MDL	<MDL	35,898

* Mann-Whitney p-value <0.05

3.6.4 Pesticide Air and Dust Result Correlations

We computed Spearman Rank correlation coefficients to examine associations between air and dust concentrations of pesticides, and between pesticides measured in air and their dust loading (Table 59). Overall, weak to moderate correlations were observed (rho$\leq$0.5). Significant correlations between indoor air and dust concentrations were found for diazinon, chlorpyrifos, and dacthal. Significant correlations between indoor air and dust loading were found for diazinon, chlorpyrifos, dacthal, piperonyl butoxide, and cis-permethrin. These findings suggest that indoor air levels are in part derived from the reservoir of pesticides in dust, consistent with the semi-volatile properties of these pesticides.

Table 59. Spearman Rank Correlation Coefficients Testing the Relationship Between Pesticide Air Concentrations and Pesticide Concentrations and Loading in Dust

Analyte	Air to Dust Concentration (rho)	Air to Dust Loading (rho)
Diazinon	0.34*	0.31
Chlorpyrifos	0.50*	0.49*
Dacthal	0.48*	0.36*
Imiprothrin	0.22	0.28
Piperonyl butoxide	0.32	0.45*
Bifenthrin	0.01	0.08
Sumithrin	0.18	0.19
cis-Permethrin	0.19	0.38*
trans-Permethrin	0.26	0.13
Cyfluthrin	NC	NC
Cypermethrin	NC	NC

NC: Not calculated because pesticide was not detected in air.
Significant correlations ($p<0.05$) are denoted with a star (*)

3.6.5 Pesticide Concentrations and Self-Reported Pesticide Use

Pesticide use (indoor or outdoor) in the year before sampling was reported in 57.5% of the facilities examined (Table 60). Pesticide use indoors in the year before sampling was reported in 17.5% of facilities. Table 61 summarizes the active ingredients in pesticides stored or used in the ECE facilities. Pyrethroid sprays were by far the most common class of pesticides used.

We compared pesticide concentrations measured in air and dust among the ECE facilities reporting any pesticide use within the last year to facilities that reported no use. In addition, we compared air and dust concentrations between ECE facilities reporting indoor use in the past year compared to facilities reporting no indoor use.

Indoor Air. We did not observe higher airborne pesticide levels in facilities reporting any pesticide use (indoors or outdoors) within the past year (Table 62). We did observe higher detection frequency of imiprothrin in facilities that reported pesticide use inside the facility within the past year (Table 63).

Dust. We found higher dust levels of piperonyl butoxide in facilities reporting any pesticide use (indoors or outdoors) within the past year (Table 64). We also found higher imiprothrin and sumithrin dust levels in facilities that reported indoor pesticide use within the past year (Table 65). No other significant differences in dust concentrations were found.

Table 60. Summary of Reported Pesticide/Insecticide Use within the Past Year

Any pesticide use indoors or outdoors during the year before sampling	**Frequency**	**Percent**
No	16	40.0
Yes	23	57.5
Don't know	1	2.5
Any pesticide use during the year before sampling inside	**Frequency**	**Percent**
No	33	82.5
Yes	7	17.5
Don't know	0	0.0

Table 61. Active Ingredients in Pesticides Stored Inside Child Care Facilities

Pesticide Active Ingredient	Type of Pesticide	Pesticide Form	Freq.	Percent[1]
D-Allethrin	Pyrethroid	Spray	5	12.5
Pyrethrins	Pyrethroid	Spray/ Stakes	5	12.5
Cypermethrin	Pyrethroid	Spray	4	10
Piperonyl Butoxide	Synergist	Spray	4	10
Boric Acid	Pesticide	Stakes	3	7.5
Imiprothrin	Pyrethroid	Spray	3	7.5
N-Octyl Bicycloheptene Dicarboximide	Synergist	Spray/ Stakes	3	7.5
Permethrin	Pyrethroid	Spray	3	7.5
Tetramethrin	Pyrethroid	Spray	2	5
(S) Methoprene	Insecticide	Spray	1	2.5
2,4-D, Isooctyl Ester	Herbicide	Solid	1	2.5
Abamectin	Insecticide	Spray	1	2.5
Acephate	Organophosphate	Stakes	1	2.5
Arsenic Trioxide	Pesticide	Stakes	1	2.5
Bifenthrin	Pyrethroid	Spray	1	2.5
Brodifacoum	Rodenticide	Solid	1	2.5
Bromethalin	Rodenticide	Solid	1	2.5
Dicamba	Herbicide/ OC	Solid	1	2.5
Diquat Dibromide	Herbicide	Liquid	1	2.5
D-Limonene	Pesticide	Spray	1	2.5
Glyphosate, Isopropylamine Salt	Herbicide	Liquid	1	2.5
Imazapyr, Isopropylamine Salt	Herbicide	Liquid	1	2.5
Imidacloprid	Insecticide	Spray	1	2.5
Lambda- Cyhalothrin	Pyrethroid	Spray	1	2.5
Mecoprop-P	Herbicide	Solid	1	2.5
Metaldehyde	Pesticide	Solid	1	2.5
Phenothrin	Pyrethroid	Spray	1	2.5
Prallethrin	Pyrethroid	Spray	1	2.5
Resmethrin	Pyrethroid	Stakes	1	2.5
Sulfuramid	Pesticide	Liquid	1	2.5
Tralomethrin	Pyrethroid	Spray	1	2.5
Triforine	Fungicide	Stakes	1	2.5

[1]Percentages sum to >100% because multiple pesticides found in some facilities.

Table 62. Pesticide Usage Inside or Outside within the Last Year and Indoor Air Concentrations

Pesticides Used Within the Past Year?	No Reported Pesticide Use (n=16)					Yes Reported Pesticide Use (n=23)				
Analyte	**>MDL (%)**	**25th % (ng/m³)**	**Median (ng/m³)**	**75th % (ng/m³)**	**Maximum (ng/m³)**	**>MDL (%)**	**25th % (ng/m³)**	**Median (ng/m³)**	**75th % (ng/m³)**	**Maximum (ng/m³)**
Diazinon	75.0	<MDL	0.05	0.13	0.24	78.26	0.01	0.05	0.27	3.00
Chlorpyrifos	93.8	0.15	0.24	0.31	1.36	95.7	0.18	0.26	0.45	0.64
Dacthal	50.0	<MDL	0.02	0.30	1.89	65.2	<MDL	0.22	0.91	1.50
Imiprothrin	6.3	<MDL	<MDL	<MDL	5.50	17.4	<MDL	<MDL	<MDL	3.13
Piperonyl butoxide	31.3	<MDL	<MDL	0.01	0.54	52.2	<MDL	0.01	0.04	5.45
Bifenthrin	12.5	<MDL	<MDL	<MDL	0.32	13.0	<MDL	<MDL	<MDL	0.41
Sumithrin	0.0	<MDL	<MDL	<MDL	<MDL	8.7	<MDL	<MDL	<MDL	1.16
cis-Permethrin	62.5	<MDL	0.03	0.11	0.26	56.5	<MDL	0.03	0.21	0.57
trans-Permethrin	100	0.07	0.14	0.18	0.31	100	0.07	0.15	0.23	0.88
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL

Table 63. Indoor Air Pesticide Concentrations by Reported Indoor Pesticide Use (yes/no)

Pesticides Used Indoors w/in the Past Year?	No Reported Pesticide Use (n=33)					Yes Reported Pesticide Use (n=7)				
Analyte	>MDL (%)	25th % (ng/m³)	Median (ng/m³)	75th % (ng/m³)	Max (ng/m³)	>MDL (%)	25th % (ng/m³)	Median (ng/m³)	75th % (ng/m³)	Max (ng/m³)
Diazinon	78.8	0.01	0.05	0.16	3.00	71.4	<MDL	0.07	0.12	0.34
Chlorpyrifos	93.9	0.16	0.26	0.45	1.36	100	0.18	0.25	0.28	0.30
Dacthal	63.6	<MDL	0.21	0.66	1.89	42.9	<MDL	<MDL	0.08	0.22
Imiprothrin	9.1	<MDL	<MDL	<MDL	5.50	42.9	<MDL	<MDL	2.91	3.13
Piperonyl butoxide	42.4	<MDL	<MDL	0.03	0.54	42.9	<MDL	<MDL	0.04	5.45
Bifenthrin	15.2	<MDL	<MDL	<MDL	0.41	0.0	<MDL	<MDL	<MDL	<MDL
Sumithrin	3.0	<MDL	<MDL	<MDL	0.95	14.3	<MDL	<MDL	<MDL	1.16
cis-Permethrin	60.6	<MDL	0.03	0.14	0.52	57.1	<MDL	0.17	0.40	0.57
trans-Permethrin	100	0.07	0.13	0.22	0.88	100	0.08	0.17	0.23	0.31
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL

Table 64. Pesticide Usage Inside or Outside within the Last Year and Dust Concentrations

Pesticides Used Within the Past Year?	No Pesticide Use (n=16)					Yes Pesticide Use (n=22)				
Analyte	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)
Diazinon	93.8	2.2	3.1	5.7	60.9	90.9	3.3	4.5	5.5	74.1
Chlorpyrifos	93.8	6.5	9.1	15.4	217.4	90.9	7.2	12.2	19.6	563.4
Dacthal	93.8	3.4	7.2	17.6	48.5	90.9	1.7	5.6	21.9	73.8
Imiprothrin	31.3	<MDL	<MDL	168.6	644.2	36.4	<MDL	<MDL	252.9	1,739.8
Piperonyl butoxide*	87.5	24.5	54.0	110.3	613.6	100	67.2	103.0	210.9	24,629
Bifenthrin	87.5	31.7	53.6	79.8	413.3	95.5	43.6	58.3	208.2	927.6
Sumithrin	18.8	<MDL	<MDL	<MDL	267.8	22.7	<MDL	<MDL	<MDL	1,299.0
cis-Permethrin	100	122.5	160.6	310.8	939.7	100	108.9	165.9	261.3	12,712
trans-Permethrin	100	140.3	251.1	442.0	1,500.9	100	168.3	236.6	436.5	21,058
Cyfluthrin	6.3	<MDL	<MDL	<MDL	434.4	4.6	<MDL	<MDL	<MDL	739.2
Cypermethrin	43.8	<MDL	<MDL	384.1	1,506.2	36.4	<MDL	<MDL	317.5	35,898

* Mann-Whitney p-value<0.05

Table 65. Pesticide Usage Inside within the Last Year and Dust Concentrations

Pesticides Used Indoors Within the Past Year?	No Pesticide Use (n=32)					Yes Pesticide Use (n=7)				
Analyte	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)
Diazinon	93.8	2.9	3.8	5.4	74.1	85.7	2.0	3.6	13.4	25.8
Chlorpyrifos	93.8	6.5	10.2	19.2	563.4	85.7	7.2	12.9	18.4	33.0
Dacthal	93.8	3.4	10.5	22.3	73.8	85.7	1.3	3.7	4.8	21.9
Imiprothrin*	25.0	<MDL	<MDL	80.4	644.2	71.4	<MDL	250.3	759.5	1,739.8
Piperonyl butoxide	93.8	40.5	93.3	145.9	1,375.7	100	66.6	70.8	126.6	24,629
Bifenthrin	90.6	42.1	56.5	94.1	927.6	100	43.4	58.6	208.2	896.5
Sumithrin*	12.5	<MDL	<MDL	<MDL	267.8	57.1	<MDL	33.5	322.6	1299.0
cis-Permethrin	100	111.4	160.6	300.6	12,712	100	108.2	188.1	261.3	692.6
trans-Permethrin	100	140.3	221.0	469.1	21,058	100	162.2	274.4	337.5	1,111.8
Cyfluthrin	6.3	<MDL	<MDL	<MDL	739.2	0.0	<MDL	<MDL	<MDL	<MDL
Cypermethrin	43.8	<MDL	<MDL	373.8	2,968.6	28.6	<MDL	<MDL	391.6	35,898

* Mann-Whitney p-value<0.05

3.6.6 Pesticide Discussion

Pesticides were measured in air and dust collected from ECE facilities, including OP and pyrethroid insecticides, the insecticide synergist piperonyl butoxide, and the herbicide dacthal (chlorthal-dimethyl). The pesticide analytes most often detected in indoor air were trans-permethrin (100%) and chlorpyrifos (95%), while for outdoor measurements, trans-permethrin (92.9%) and cis-permethrin (78.6%) were the most often detected. Pyrethroid pesticides were detected in dust from all ECE facilities and at higher levels than other measured pesticides. Median pyrethroid levels in dust ranged from <MDL for imiprothrin and sumithrin, to 225 ng/g for trans-permethrin. Diazinon and chlorpyrifos, OP pesticides that are no longer approved for indoor use, were frequently detected in dust (>90%). Levels of these OPs were not higher in ECE facilities in agricultural compared to non-agricultural site locations. Dust and air levels of the herbicide dacthal were significantly higher in ECE facilities located in agricultural communities.

Significant correlations between indoor air and dust concentrations were found for diazinon, chlorpyrifos, and dacthal. Additionally, significant correlations between indoor air and dust loading were found for diazinon, chlorpyrifos, dacthal, piperonyl butoxide, and cis-permethrin. These findings suggest that indoor air levels are in part derived from the reservoir of pesticides in dust. Air levels are likely to increase significantly after applications, but long-term residues in dust are likely to result in low level air contamination and child exposures over time.

Pest problems were common in the ECE facilities: 90% reported at least one pest, and 58% reported using pesticides, with 45% using broadcast application methods (e.g., sprays or foggers). Pyrethroid pesticides are the most common class of pesticides used indoors since most residential and structural uses of diazinon and chlorpyrifos were phased out between 2002 and 2004. It is likely that indoor residues of diazinon and chlorpyrifos were due to historical use.

Several studies have examined OP, pyrethroid and other pesticides in indoor air and house dust in Monterey[90,103,145] and Alameda[145] Counties. Levels of dacthal in dust from Salinas Valley homes sampled in these studies were similar to the levels we observed in the ECE facilities in agricultural areas (median=16, 22, and 31 ng/g versus 23 ng/g, respectively) but much higher than levels in ECE facilities from non-agricultural facilities (3.6 ng/g).

In all the studies, cis- and trans-permethrin were the most frequently detected pesticides in house dust, and had the highest concentrations. Recent studies of homes in Alameda County and the Salinas Valley[90,145] reported cis- and trans-permethrin concentrations in house dust that were generally ~2-4 times higher than levels we observed in the ECE facilities. Similarly, concentrations of chlorpyrifos in Salinas Valley homes were ~2-7 times higher than concentrations found in the ECE facilities.

Bradman et al.[103] also measured pesticides in air from farmworker homes in the Salinas Valley. In that study, chlorpyrifos and diazinon median concentrations in indoor air were higher (1.9 and 1.8 ng/m^3, respectively) than concentrations measured in the ECE facilities (0.25 and 0.05 ng/m^3, respectively). The median concentration of dacthal in air was also higher in the Salinas Valley homes (1.8 ng/m^3) compared to the ECE facilities (0.2 ng/m^3). Conversely, the median concentrations of cis- and trans-permethrin in indoor air were higher in the ECE facilities (0.04 and 0.14 ng/m^3, respectively) compared to the Salinas Valley homes (<MDL).

Overall, where comparable, levels of many pesticides in air and dust were lower in the ECE facilities compared to homes sampled in the same regions 4-8 years ago. The higher levels of dacthal in ECE facilities located in agricultural areas suggest contamination from nearby agricultural pesticide use.

For the screening risk assessment, child pesticide exposure-dose estimates were compared to appropriate health-based benchmarks, such as U.S. EPA reference doses (RfDs). Estimated pesticide exposure levels did not exceed oral reference doses. Health-based reference concentrations were not available for any of the 11 pesticides measured in air.

Use of integrated pest management (IPM) practices rather than chemical sprays to treat pest infestation would reduce environmental pesticide contamination in ECE facilities.

3.7 Particle Measurement Results and Discussion

3.7.1 Real-Time Particle Measurement Results

We measured concentrations UFPs and fine particles ($PM_{2.5}$), using real-time instruments. Real-time instruments monitor particle concentration through time. One-minute averages are particle counts or concentrations for every minute the real-time device was sampling. Child care daily averages are the average particle counts or concentrations over the sampling period. Sampling periods varied by child care.

3.7.1.1 Ultrafine Particle Monitoring

3.7.1.1.1 Ultrafine Particle Monitoring QA/QC

The CPCs were checked by CARB in Spring 2010 prior to air sampling. To assess comparability between the two CPCs used (CPC1 and CPC2), side-by-side measurements were collected when field work began in July 2010 and after all field work was completed in May 2011 (see Appendix C Figure 22). During the first field test, CPC1 and CPC2 were highly correlated (R^2=0.99). Computed on a minute-by-minute basis, a linear regression produced the relationship: CPC1 = -19.5 + 1.04(CPC2) with a standard error of 0.002. The mean RSD was 1.72% and the standard deviation was 1.34%. After all field sampling was complete, both CPCs were run side-by-side in a UC Berkeley office building. In this case the CPC2 took longer – about 15 minutes – to warm-up and reach consistent ultrafine concentrations. The mean RSD after the CPC stabilized (~15 minutes) was 6.1% and the standard deviation was 1.7. The R-squared value was 0.98. Computed on a minute-by-minute basis, a linear regression produced the relationship: CPC1 = -176.8 + 0.93(CPC2) with a standard error of 0.007. While there was a little drift in precision between the machines during child care sampling, the relative differences were small.

In addition to the QA/QC work done by UC Berkeley, CARB also ran CPC1 and CPC2 side-by-side with an additional TSI 3781 CPC (labeled ARB3) and a TSI 3787 CPC (labeled CPC 3787). All four instruments tracked the same concentrations through time. While CPC2 again shows small periods of deviation, the pre- and post-sampling QA/QC correlation and bias of each instrument indicate that the CPCs used in this study produced precise and comparable results. For additional QA results see Appendix C.

3.7.1.1.2 Ultrafine Particle Measurement Results

Indoor UFP concentrations were measured in 39 facilities and outdoor UFP concentrations were measured at twenty-eight facilities. Table 66 summarizes the distribution of one-minute and child care full day averages for indoor and outdoor UFP concentrations. Levels varied widely, with peak one-minute average concentrations (543,000/ccm) up to 25 times higher than typical mean concentrations during a day (22,102/ccm). No significant difference between indoor and outdoor mean concentrations was observed (Wilcoxon $p>0.05$). However, above the 50^{th} percentile, the indoor distribution shows higher concentrations compared to outdoor levels. For example, Figure 8 presents a cumulative frequency distribution of the indoor and outdoor child care day average UFP concentrations. The cumulative probabilities of both indoor and outdoor mean concentrations are similar up to the ~70^{th} percentile where the mean indoor concentrations become consistently higher than outdoor concentrations.

Table 66. Summary of One-Minute and Child Care Day Averages for Indoor and Outdoor Ultrafine Concentrations (#/ccm)

	One-Minute Averages			Child Care Full Day Averages		
	Indoors	Outdoors	I/O Ratio	Indoors	Outdoors	I/O Ratio
N	18,581	12,464	10,132	39	28	27*
Mean	22,102	16,155	4.4	22,327	16,531	2.8
SD	34,358	13,590	17.2	19,672	10,896	7.1
Minimum	511	108	0.04	1,515	1,260	0.3
25^{th} %	6,680	7,030	0.5	10,452	9,891	0.7
Median	11,500	12,400	0.9	14,120	14,054	1.2
75^{th} %	20,600	20,800	2.0	29,717	19,907	2.0
90^{th} %	50,700	33,300	5.4	58,663	38,143	3.6
95^{th} %	83,500	43,100	11.7	69,439	42,096	5.7
Maximum	543,000	158,000	497.1	75,376	44,618	37.9

*At one ECE facility, UFPs were measured outdoors but not indoors due to CPC malfunction.

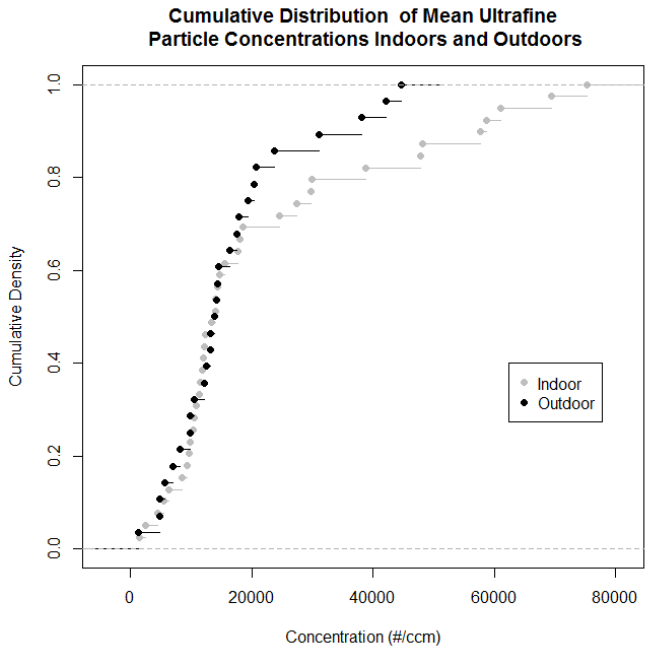

Figure 8. Cumulative probability of child care day average indoor and outdoor ultrafine particle concentrations

Table 67 presents descriptive statistics for overall mean indoor and outdoor UFP concentrations stratified by county (Alameda vs. Monterey). In general, we observed no significant differences between Alameda and Monterey County indoor or outdoor ultrafine particle concentrations (Mann-Whitney, $p>0.05$) but Monterey County did have higher indoor ultrafine particle concentrations in the higher percentiles. Table 68 presents descriptive statistics for mean indoor and outdoor UFP concentrations stratified by ECE type (home versus center). Indoor and outdoor mean UFP concentrations were higher at child care homes compared to center-licensed facilities (Mann-Whitney $p<0.01$ and 0.05, respectively). The difference in indoor UFP concentrations is most likely due to the greater frequency of combustion sources adjacent to sampling rooms in homes (100%) versus in centers (21.4%).

To test this hypothesis, we evaluated differences in UFP concentrations between child care centers with or without a combustion source or adjacent to the room where air sampling occurred. When combustion sources were in close proximity, median ultrafine concentrations were more than twice the median UFP concentrations in facilities with no nearby combustion sources (Mann-Whitney, $p<0.05$, Table 69). Figure 9 illustrates the real-time trend in ultrafine concentrations during the day in a facility without a combustion source (left figure) and in a facility with a combustion source used twice (right figure). In this instance, ECE #19 was a single family home with a gas stove that was used to prepare breakfast and lunch. Ultrafine particle concentrations increased by up to three orders of magnitude during stove use.

Overall, 18 child care facilities (45%) had a combustion source (i.e., gas cook stove, gas water heater, etc.) present or adjacent to the room where air sampling occurred. Eleven (27.5%) of the facilities had indoor gas stoves in child care areas; two home-based facilities had gas stoves with no functioning fan.

Table 67. Distribution of Child Care Full Day Average Indoor and Outdoor Ultrafine Concentrations (#/ccm) by County

	Indoors		Outdoors	
	Alameda	Monterey	Alameda	Monterey
N	20	19	12	16
Mean	19,806	24,982	18,755	14,865
SD	14,618	24,019	10,789	11,018
Minimum	2,544	1,515	4,824	1,260
25th %	10,678	9,626	13,387	8,986
Median	14,292	12,461	16,116	12,705
75th %	28,603	47,802	22,320	17,199
90th %	43,504	69,439	31,108	38,143
Maximum	57,794	75,376	44,618	42,096

Table 68. Distribution of Child Care Full Day Average Indoor and Outdoor Ultrafine Concentrations (#/ccm) by ECE Type

	Indoors		Outdoors	
	Center	Home	Center	Home
N	27	12	18	10
Mean	14,048	40,956	13,572	21,859
SD	9,891	23,638	9,250	12,062
Minimum	1,515	9,626	1,260	8,132
25th %	9,415	20,811	7,040	13,172
Median	11,997	39,071	12,711	17,938
75th %	15,596	59,915	17,628	31,108
90th %	24,579	69,439	23,843	41,381
Maximum	47,802	75,376	42,096	44,618

Table 69. Summary of Ultrafine Particle Concentration Means (#/ccm) in Child Care Facilities with and without a Combustion Source Present

	Without Combustion	With Combustion
N	21	18
Mean	12,608	33,666
SD	8,127	23,120
Minimum	1,502	9,626
25th %	8,464	12,218
Median	11,581	28,603
75th %	14,653	57,794
90th %	17,993	69,439
Maximum	38,817	75,376

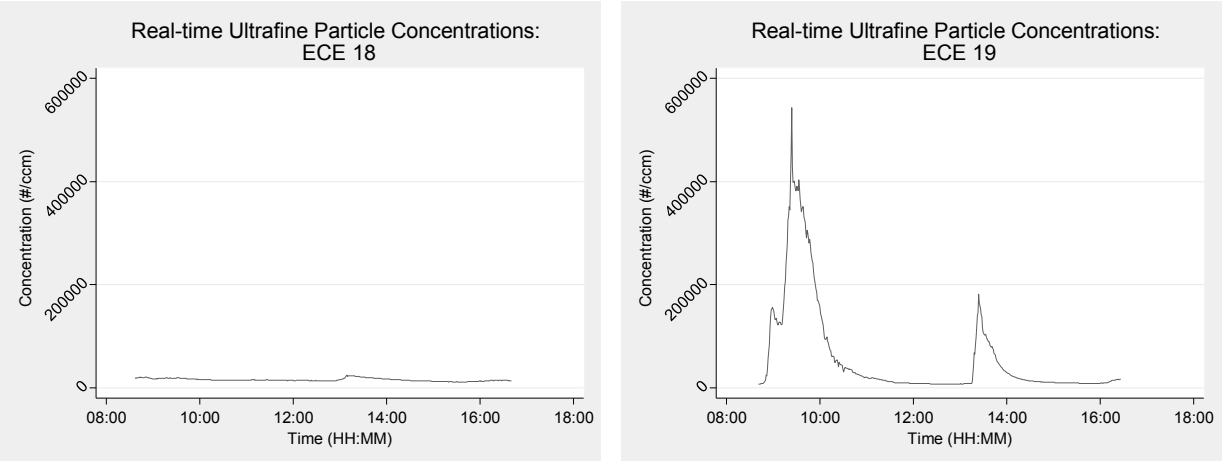

Figure 9. Comparison of full day ultrafine particle concentrations at two separate ECE facilities (ECE 18 and 19). In ECE 18, combustion sources were not present and ultrafine concentrations were low. In ECE 19, ultrafine concentrations rose twice due to use of a gas stove.

3.7.1.2 Real-Time $PM_{2.5}$ Monitoring

A DustTrak 8520 and 8530 measured real-time $PM_{2.5}$ concentrations. Indoor $PM_{2.5}$ was measured at all 40 ECE facilities and outdoor $PM_{2.5}$ was measured at 31 ECE facilities. DustTrak 8520 was designated DT1 and the DustTrak 8530 was designated DT2.

3.7.1.2.1 Real-Time $PM_{2.5}$ QA/QC

Prior to sampling, DT1 was compared to CARB's Monitoring and Laboratory Division (MLD) ambient air $PM_{2.5}$ samples collected on Teflon filters in Sacramento, California. DT1 was run for 27 hours next to the ambient monitor and hourly $PM_{2.5}$ data between the two methods was compared to assess DT1 performance. The mean relative standard deviation between the duplicate measurements was 38.9% and the standard deviation was 32.1%. Results showed a bias between measurement techniques with DT1 measuring higher concentrations of $PM_{2.5}$ than the MLD unit. A linear regression comparing the two measurements produced a line, MLD=1.9 + 0.44(DT1) with a standard error of 0.07. While the two machines follow the same concentration trend (R^2=0.62), DT1 generally measured higher $PM_{2.5}$ concentrations than results from MLD (Appendix C, Table 139).

Side-by-side comparisons between the two DustTraks were performed before and after both devices were used in a UC Berkeley office building. Side-by-side measurements between DT1 and DT2 show a strong correlation (R^2=0.80); however, there was a consistent bias between DT1 and DT2 (linear regression: DT1=-0.001 + 0.89(DT2), standard error=0.03) with an average difference in sample concentration of 7 µg/m³. Prior to sampling the mean RSD was 10.0% and the standard deviation was 1.9%. Post-sampling side-by-side DustTrak measurements also correlated well (R^2=0.95), but a bias persisted between the machines (linear regression: DT1=-0.001 + 0.84(DT2), standard error=0.01). DT1 was approximately 5 µg/m³ lower than DT2 throughout the sampling period. The post-sampling mean RSD was 17.4% and the standard deviation was 2.6%.

Overall, QA procedures for the DustTrak before and after sampling indicate strong correlations between DustTrak 1 and DustTrak 2 real-time $PM_{2.5}$ measurements, but the DustTrak 2 levels averaged 25% higher. Additionally, the DustTrak 1 values averaged 68% higher than CARB MLD measurements. Due to DustTrak 1 measuring higher $PM_{2.5}$ concentrations than the MLD but lower than the DustTrak 2, DustTrak 2 measurements were adjusted downward with a correction offset of -6 µg/m³ to be comparable to the DustTrak 1 results. See Appendix C for additional DustTrak QA/QC information.

3.7.1.2.2 Real-time $PM_{2.5}$ Results

Forty indoor real-time $PM_{2.5}$ measurements were collected and 31 outdoor real-time $PM_{2.5}$ measurements were collected. Table 70 shows the distribution of DustTrak $PM_{2.5}$ mean concentrations stratified by indoor and outdoor sampling locations. Overall, there were no significant differences in the distribution of the child care day averages between indoor and outdoor DustTrak $PM_{2.5}$ concentrations (Wilcoxon>0.05). One-minute and child care day average distributions of $PM_{2.5}$ show similar distributions until the higher percentiles when indoor levels exceed outdoor levels (Figure 10). There were no significant differences between child care day average DustTrak $PM_{2.5}$ concentrations when stratified by county or ECE type (Mann-Whitney p>0.05) (Tables 71 and 72). However, the upper range outdoor levels in Alameda County tended to be higher.

Table 70. Summary of One-Minute and Child Care Day Averages of DustTrak $PM_{2.5}$ Concentrations (µg/m³)

	One-Minute Averages			Child Care Day Averages		
	Indoor	Outdoor	I/O Ratios	Indoor	Outdoor	I/O Ratios
N	19,061	14,494	-	40	31	-
Mean	20	24	1.6	19	24	1.3
SD	26	29	3.9	16	28	1.5
Minimum	0	0	0.0	5	2	0.2
25^{th} %	9	9	0.5	11	12	0.6
Median	14	16	0.8	15	17	0.9
75^{th} %	22	26	1.4	23	25	1.1
90^{th} %	35	41	2.7	34	38	2.1
95^{th} %	46	104	4.3	55	108	5.1
Maximum	372	181	62.2	89	138	7.6

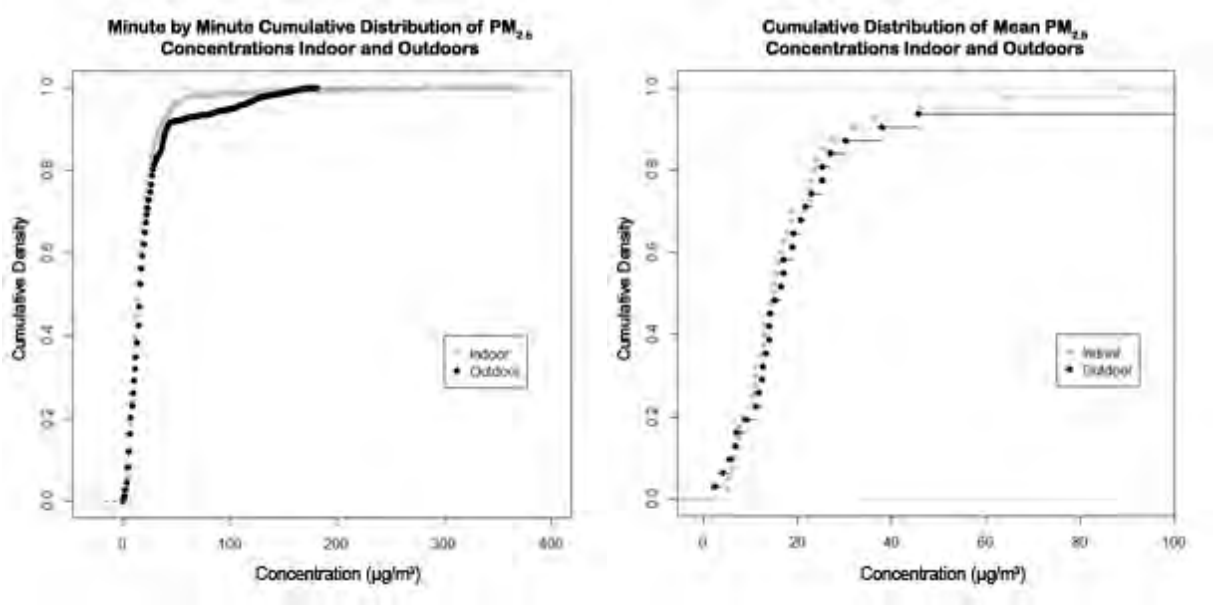

Figure 10. Cumulative distribution plots of minute-by-minute (left) and child care day averages of $PM_{2.5}$ (right) concentrations indoors and outdoors

Table 71. Comparison of Child Care Day Average DustTrak $PM_{2.5}$ Concentrations (µg/m³) by County

	Indoor		Outdoor		I/O Ratios	
	Alameda	**Monterey**	**Alameda**	**Monterey**	**Alameda**	**Monterey**
N	20	20	13	18	13	18
Mean	20	19	34	16	0.9	1.6
SD	15	17	41	10	0.8	1.8
Minimum	5	6	4	2	0.2	0.5
25th %	9	12	14	12	0.5	0.8
Median	16	14	21	14	0.6	1.0
75th %	27	21	25	19	1.0	1.5
90th %	41	24	108	30	2.1	5.1
Maximum	64	89	138	46	2.8	7.6

Table 72. Comparison of Child Care Day Average DustTrak $PM_{2.5}$ Concentrations (µg/m³) by ECE Type

	Indoor		Outdoor	
	Center	Home	Center	Home
N	28	12	21	10
Mean	16	26	28	15
SD	9	25	33	8
Minimum	5	6	4	2
25^{th} %	11	11	13	12
Median	14	17	17	15
75^{th} %	23	29	25	23
90^{th} %	28	64	46	26
Maximum	46	89	138	27

3.7.2 Gravimetric Particulate Matter Monitoring

Gravimetric $PM_{2.5}$ and PM_{10} were collected using SKC® PEMs onto 37 mm Teflon filters at flow rates of 2 and 4 lpm. Samples were collected throughout the child care day (~8 hours). A total of 35 $PM_{2.5}$ and PM_{10} samples were available for analysis.

3.7.2.1 Gravimetric PM QA/QC

Integrated PM was to be sampled only using PEMs with a flow rate of 2 lpm. However, during the pilot phase of the project (ECE #10-14), filter contamination occurred due to problems with the gaskets in some of the 2 lpm PEM (the gaskets appeared to be failing and shedding mass onto the filters during the loading and unloading process). This problem did not occur in all the filters but it was not possible, in retrospect, to determine which filters were contaminated. Upon discovering the problem, all 2 lpm PEM bodies were reconditioned and it was confirmed that the weight change of the filters during loading and unloading was within acceptable limits (i.e., less than 3 µg change between measurements). Although the 2 lpm PEMs were reconditioned, 4 lpm PEMs were purchased to increase the sample volume and accuracy of measurements. Four duplicate measurements were collected indoors for each $PM_{2.5}$ and PM_{10} for comparison. For $PM_{2.5,}$ the mean RSD was 47.5% and the standard deviation was 16.2%. For PM_{10}, the mean RSD was 6.1% and the standard deviation was 3.6%. The larger RSDs for $PM_{2.5}$ are probably due to the measurements being below/close to the MDL. The difference in PEMs between duplicate measurements may have also added to the variability.

3.7.2.2 Gravimetric PM Results

Thirty-five indoor $PM_{2.5}$ and PM_{10} samples along with 12 outdoor $PM_{2.5}$ and PM_{10} samples were available for analysis. When duplicates were taken, the average PM concentration calculated from the duplicates was used. Table 73 presents descriptive statistics for $PM_{2.5}$ and PM_{10} measurements. The median indoor $PM_{2.5}$ and PM_{10} concentrations from gravimetric measurements were 15.0 and 47.6 $\mu g/m^3$, respectively, similar to outdoor median levels (16.2 and 28.9 $\mu g/m^3$, respectively). No significant difference was found between indoor and outdoor $PM_{2.5}$ (Wilcoxon $p>0.05$). Differences between indoor and outdoor PM_{10} values were moderately significant (Wilcoxon $p=0.07$). Indoor PM_{10} concentrations tended to be higher than outdoor concentrations as presented in the I/O ratios and paired scatter plots (Table 74 and Figure 11). Additionally, no significant differences ($p>0.05$) in indoor or outdoor PM levels were found between counties or ECE type (Mann-Whitney, $p>0.05$) (Tables 75, 76, and Figure 12).

Table 73. Summary of Indoor and Outdoor $PM_{2.5}$ and PM_{10} Concentrations ($\mu g/m^3$)

	>MDL (%)	N	Mean	SD	Min	25th %	Median	75th %	90th %	Max
Indoor $PM_{2.5}$	97.1	35	17.9	11.2	<MDL	10.6	15.0	21.5	37.6	53.7
Outdoor $PM_{2.5}$	50.0	12	17.9	9.3	<MDL	<MDL	16.2	22.1	31.5	36.7
Indoor PM_{10}	100	35	54.8	32.3	13.8	31.4	47.6	75.2	93.3	172.2
Outdoor PM_{10}	83.3	12	40.3	27.2	<MDL	23.2	28.9	45.9	94.3	94.4

Table 74. Distribution of Indoor to Outdoor Gravimetric $PM_{2.5}$ and PM_{10} Concentration Ratios (n=12)

	Mean	SD	Min	25th %	Median	75th %	Max
$PM_{2.5}$	1.1	0.5	0.6	0.8	1.0	1.2	2.6
PM_{10}	2.0	1.4	0.6	1.0	1.8	2.1	4.8

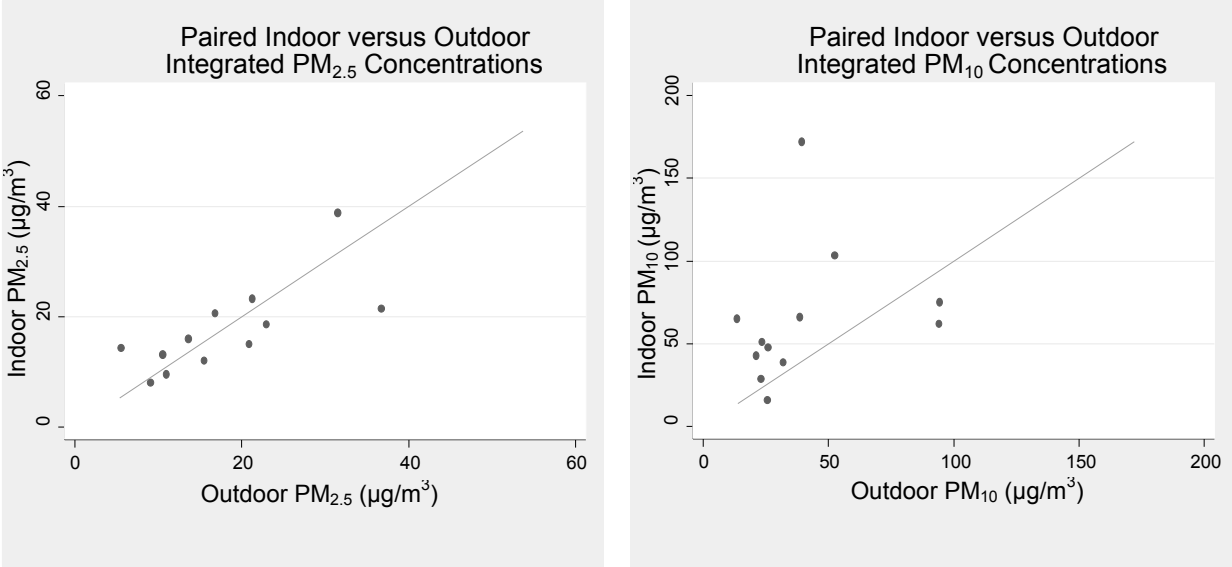

Figure 11. Scatter plot of paired indoor and outdoor $PM_{2.5}$ and PM_{10} measurements at 12 ECE facilities. A one-to-one linear line was fit to each graph.

Table 75. Summary Statistics for Indoor Gravimetric $PM_{2.5}$ and PM_{10} Concentrations (µg/m³) by County

	$PM_{2.5}$		PM_{10}	
	Alameda	**Monterey**	**Alameda**	**Monterey**
N	17	18	17	18
Mean	17.9	17.9	53.5	56.0
SD	10.0	12.5	37.0	28.3
Minimum	<MDL	<MDL	13.8	14.5
25th %	10.6	10.5	31.4	38.3
Median	16.0	13.7	47.1	49.3
75th %	22.8	20.5	65.2	81.3
90th %	37.6	44.0	84.8	100.7
Maximum	38.8	53.7	172.2	103.1

Table 76. Summary Statistics for Indoor Gravimetric $PM_{2.5}$ (µg/m³) by ECE Type

	$PM_{2.5}$		PM_{10}	
	Center	**Home**	**Center**	**Home**
N	24	11	24	11
Mean	16.4	21.1	56.3	51.5
SD	10.6	12.1	33.5	30.9
Minimum	<MDL	<MDL	17.8	13.8
25^{th} %	10.5	12.1	33.3	15.8
Median	14.2	20.2	49.3	47.1
75^{th} %	19.2	28.8	68.6	81.3
90^{th} %	23.3	37.6	93.3	84.8
Maximum	53.7	44.0	172.2	100.7

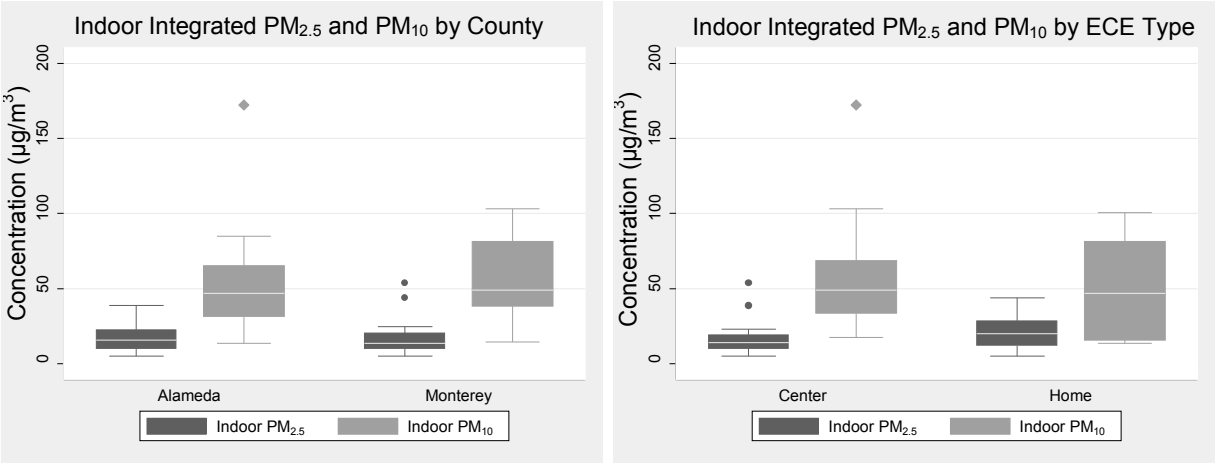

Figure 12. Indoor integrated $PM_{2.5}$ and PM_{10} concentrations by county (left figure) and by child care type (right figure)

3.7.3 Correlation of Particle Measurements

We computed Spearman rank correlations to examine the associations between the different real time and gravimetric particle measurements. Mean particle concentrations were used to characterize the real time measurements. Table 77 presents the correlation matrix. Many of the measurements were significantly positively correlated. As expected, real time and gravimetric measures of $PM_{2.5}$ and PM_{10} were strongly correlated with each other. Overall, these strong correlations validate the quality of the measurements and indicate that the real time particle instruments accurately represent cumulative daily $PM_{2.5}$ and PM_{10} levels. Indoor and outdoor $PM_{2.5}$ measurements were also strongly correlated, which suggest that outdoor sources are significant contributors to fine particulate matter levels indoors. Finally, ultrafine particle levels were generally not significantly correlated with $PM_{2.5}$ and PM_{10} levels. Indoor and outdoor ultrafine particles were weakly correlated and indoor ultrafine was significantly negatively correlated with mean outdoor DustTrak $PM_{2.5}$. These findings suggest that sources of indoor ultrafine particles are independent of outdoor sources. As noted in Section 3.7.1.1.2, indoor cooking events were a significant source of elevated ultrafine particle levels.

Table 77. Pairwise Spearman Rank Correlation (rho) between Particulate Measurements

	Mean Indoor Ultrafine	Mean Outdoor Ultrafine	PEM Indoor $PM_{2.5}$	PEM Indoor PM_{10}	PEM Outdoor $PM_{2.5}$	PEM Outdoor PM_{10}	Mean Indoor DustTrak $PM_{2.5}$
Mean Outdoor Ultrafine	0.35						
PEM Indoor $PM_{2.5}$	0.25	-0.15					
PEM Indoor PM_{10}	0.07	-0.46*	0.79*				
PEM Outdoor $PM_{2.5}$	-0.30	0.04	0.80*	0.54*			
PEM Outdoor PM_{10}	-0.12	0.38	0.44	0.57	0.61*		
Mean Indoor DustTrak $PM_{2.5}$	0.16	0.04	0.71*	0.67*	0.48	0.69*	
Mean Outdoor DustTrak $PM_{2.5}$	-0.38*	0.04	0.32	0.39*	0.49	0.76*	0.67*

* $p<0.05$

3.7.4 ECE Facility Proximity to Traffic and Association with Indoor/Outdoor Particle Pollution

Spearman correlation coefficients between particle concentrations indoors and outdoors and nearby traffic intensity (Table 78) were computed (see Section 3.2.3 for a description of traffic metrics). DustTrak mean outdoor $PM_{2.5}$ was significantly correlated with GATV. Indoor and outdoor $PM_{2.5}$ and PM_{10} levels along with outdoor ultrafine particles were weakly correlated with GATV. A larger sample size is necessary to confirm the associations reported. Additionally, because these were single-day measurements compared to annual traffic intensity estimates, the correlations may underestimate the true association with nearby traffic intensity on the monitoring day.

Table 78. Spearman Correlation Rho Between Traffic Metrics and Particle Concentrations

	Sum LATV	Sum GATV	LATV - HS
Indoor Ultrafine (n=39)[a]	-0.09	-0.19	-0.17
Outdoor Ultrafine (n=28)[a]	0.26	0.22	0.24
PEM Indoor $PM_{2.5}$ (n= 35)	-0.07	0.27	-0.13
PEM Indoor PM_{10} (n=35)	-0.19	0.16	-0.09
PEM Outdoor $PM_{2.5}$ (n=12)	0.06	0.54	-0.20
PEM Outdoor PM_{10} (n=12)	-0.01	0.29	0.16
Indoor DustTrak $PM_{2.5}$ (n=40)[a]	-0.01	0.28	-0.04
Outdoor DustTrak $PM_{2.5}$ (n=31)[a]	0.25	0.62**	0.18

[a] Child care day averages
** p-value<0.05

3.7.5 Correlation between DustTrak and PEM

As part of an additional QA analysis, mean DustTrak $PM_{2.5}$ concentration and integrated $PM_{2.5}$ concentrations were compared (Table 79). At 35 ECE facilities, a DustTrak and PEM with 2.5 µm size selectors were deployed. The average error between duplicate measurements was 18.6%. Mean and median results across the 35 facilities were consistent. The Spearman rank test also indicates a significant correlation between the results ($R=0.71$, $p<0.05$). Figure 13 shows a scatter plot of both measurements with a linear regression calculated: DT2.5=2.95+ 0.95(PEM) with a standard error of 0.21.

Table 79. Summary Comparison of Mean DustTrak $PM_{2.5}$ and PEM $PM_{2.5}$ Concentrations ($\mu g/m^3$)

	DustTrak	PEM
N	35	35
Mean	20.0	17.9
SD	17.1	11.2
Min	5.2	5.3
25th %	10.9	10.6
Median	14.8	15.0
75th %	23.8	21.5
Maximum	89.4	53.7

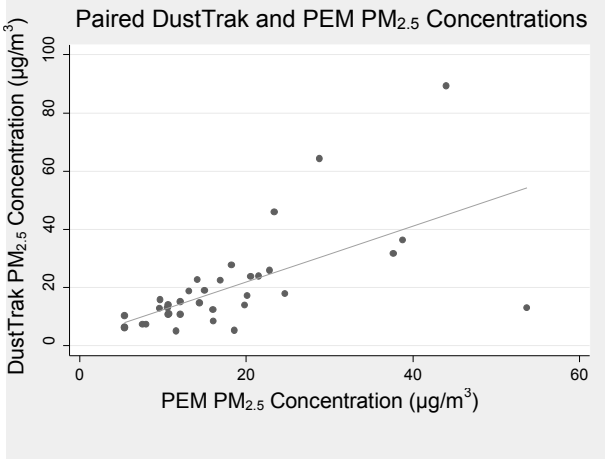

Figure 13. Scatterplot of paired DustTrak and PEM $PM_{2.5}$ indoor concentrations (n=35). DustTrak concentrations are averages over the entire child care day. Line represents linear regression between paired results.

3.7.6 Particulate Matter Discussion

Particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets. It is made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles. The size of the particles is directly linked to their potential for causing health problems. Particles that are 10 micrometers in diameter or smaller (<10 µm) can generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs and cause serious health effects. Fine particles, such as those found in smoke and haze, are 2.5 micrometers in diameter and smaller (<2.5 µm).[146] Fine and ultrafine particles (<0.1 µm) can reach the deepest regions of the lungs.[147,148] Potential effects of PM include asthma exacerbation, difficulty breathing, and bronchitis, especially in children and the elderly. Fine PM associated with diesel exhaust is listed by CARB as a Toxic Air Contaminant based on its carcinogenic potential.[149]

PM_{10} and $PM_{2.5}$ levels were measured in indoor air at 35 ECE facilities and in outdoor air at 12 facilities. Median indoor and outdoor levels of PM_{10} were 47.6 and 28.9 $\mu g/m^3$, respectively, and levels of $PM_{2.5}$ were 15.0 and 16.2 $\mu g/m^3$, respectively. Outdoor $PM_{2.5}$ levels were higher in facilities located in Alameda County, which has more traffic compared to Monterey County

(medians = 21 vs. 13 μg/m^3). In addition, outdoor $PM_{2.5}$ levels were significantly correlated with traffic intensity metrics (rho=0.62). The strong correlations found between indoor and outdoor $PM_{2.5}$ measurements (rho=0.80) also suggest that outdoor sources were significant contributors to $PM_{2.5}$ levels indoors.

The ECE facilities' indoor and outdoor $PM_{2.5}$ levels were similar to those measured in a study of ~120 Los Angeles homes (medians = 14.5 and 16.1 μg/m^3, respectively).[150] Further, outdoor PM_{10} and $PM_{2.5}$ levels were similar to or slightly higher than those measured in a study of ten San Francisco metropolitan area schools (averages = 30 and 12 μg/m^3, respectively).[148] Concentrations of PM_{10} were compared to the level of the 24-hour average California Ambient Air Quality Standard (CAAQS) and $PM_{2.5}$ concentrations were compared to the level of the National Ambient Air Quality Standard (NAAQS). Indoor PM_{10} concentrations exceeded the level of the 24-hour CAAQS in 46% of ECE facilities (16 of 35), and indoor $PM_{2.5}$ concentrations exceeded the level of the 24-hour NAAQS in 11% of ECE facilities (4 of 35; there is no 24-hour CAAQS for $PM_{2.5}$). It should be noted that the measurements in this study were obtained over an 8-10 hour period, and do not necessarily represent the levels children were exposed to for a full 24-hour period. However, the monitoring suggests many young children are experiencing a significant portion of their total PM exposures in child care facilities and that exposure mitigation may be warranted.

Ultrafine particulate matter (UFP) was measured in indoor air for ~8 hours in 39 ECE facilities, and in outdoor air at a subset of facilities (n=28). Average ultrafine particle levels were 22,327/ccm and 16,531/ccm in indoor and outdoor air, respectively. The ECE facility indoor levels were higher than those reported in a recent study of six northern California elementary schools (average = 10,800/ccm indoors and 18,100/ccm outdoors).[151] In addition, the average indoor UFP levels in the ECE facilities were somewhat higher compared to those reported in a study of seven northern California residences (17,000/ccm indoors).[152] Indoor UFP levels were generally stable during sampling periods except when cooking with gas stoves occurred; in these cases, UFP levels increased by up to three orders of magnitude. Median indoor UFP levels in center-based facilities (11,997/ccm) were much lower compared to home-based facilities (39,071/ccm), where more cooking near child activity areas occurred. Indoor and outdoor UFP levels were weakly correlated (rho=0.35) with each other, and outdoor UFP levels were weakly correlated with traffic metrics (rho=0.22-0.26). Together these findings suggest nearby traffic is a minor source of indoor UFP in ECE facilities. The average I/O ratio for daily UFP was 2.8. The average I/O for UFPs reported in the study of six California elementary schools was much lower (0.59).[151] There are currently no health-based standards for UPFs.

3.8 Metals Results and Discussion

We measured 38 dust samples for the following 8 metals: Aluminum (Al); Cadmium (Cd); elemental Chromium (Cr[0]); Copper (Cu); Iron (Fe); Manganese (Mn); Lead (Pb); and Zinc (Zn). One dust sample had insufficient mass for metals analysis.

3.8.1 Metals Dust Results

Concentrations (μg/g) and loading values were generated for all metals and are presented below (Tables 80 and 81). Except for lead (%>MDL= 94.8%), all metals had a detection frequency of 100%. The highest median metal concentrations were for aluminum and iron (8,004 and 7,682 μg/g). The median lead concentration was 35.7 μg/g.

Table 80. Distribution of Metals in Dust (µg/g) (n=38)

Metal	>MDL (%)	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Al	100	7,822	1,973	4,033	6,455	8,004.5	8,774	9,449	10,489	15,717
Cd	100	4.3	6.4	0.6	1.4	2.4	4.6	7.8	28.9	30.8
Cr	100	39.5	11.8	23.1	30.2	38.5	43.6	59.8	63.6	73.4
Cu	100	106.5	56.1	43.7	67.4	92.8	134.3	174.4	247.2	305.4
Fe	100	8,113	2,324	4,545	6,713	7,682	9,139	10,971	12,482	17,610
Mn	100	167.9	55.2	78	135	157	188	239	284	378
Pb	94.8	77.2	132.1	<MDL	25	35.7	62.2	147.6	234.3	804.9
Zn	100	667.6	419.0	236	382	556	777	1,195	2,025	2,067

Table 81. Distribution of Metal Loading (µg/m²) (n=38)

Metal	Mean	SD	Min	25th %	Median	75th %	90th %	95th %	Max
Al	32,448	34,435	724	8,237	15,076	54,516	95,944	112,776	113,199
Cd	10.8	12.3	0.5	1.9	6	15.7	28.8	33.1	57.5
Cr	149.9	149.2	4.2	42.9	93.3	211.3	378.4	449.3	561
Cu	337.1	339.9	19	98.2	201.5	459.5	935.1	1,143	1,367
Fe	33,378	36,023	699.6	8,419	15,196	47,710	88,412	121,509	131,433
Mn	717.4	842.6	19.7	172.5	330.4	864.4	1,954.1	2,652.8	3,538
Pb	229.7	392.8	<MDL	36.7	97.7	235.8	508.9	1,029.9	2,188.6
Zn	2,120	2,160	69.9	599.9	1,403.2	2,800.8	5,410.1	8,771	8,888

3.8.2 Metals Discussion

Health-based oral reference doses were available for one (Cd) of the three heavy metals (Cd, Cr and Pb) measured in dust. None of the child non-dietary Cd dose estimates exceeded its oral reference dose (i.e., HQ < 1). The International Agency for Research on Cancer (IARC) has classified inorganic lead compounds as probable human carcinogens.[153] Child lead exposure estimates exceeded age-adjusted OEHHA NSRL Safe Harbor cancer benchmarks based on carcinogenicity in 95% of facilities. (See Section 4 for more information about risk evaluation and results). Although lead has been evaluated for cancer risks, the primary concern for children is developmental toxicity. Because U.S. EPA believes there is no safe threshold for lead, there is no defined reference dose.

Because U.S. EPA believes there is no safe level of exposure to lead, there is no defined reference dose. U.S. EPA defines a threshold of 40 µg/square foot for indoor contamination.[154] However, this threshold is based on a wipe sample, and therefore is not comparable to the vacuum sampling methods used for this study. No U.S. public health agency has defined a threshold for acceptable concentrations of lead in house dust. More than 95% of the dust samples in this study were below 400 parts per million, the threshold for lead in soil that children directly play in.

Lead dust concentrations were also positively correlated (Spearman r=0.61, p<0.05) with building age (Figure 14).

Child care facilities located in older buildings could reduce lead levels in rugs by removing shoes at the door, using high quality door mats, mitigating peeling lead paint, and deep cleaning their carpets.

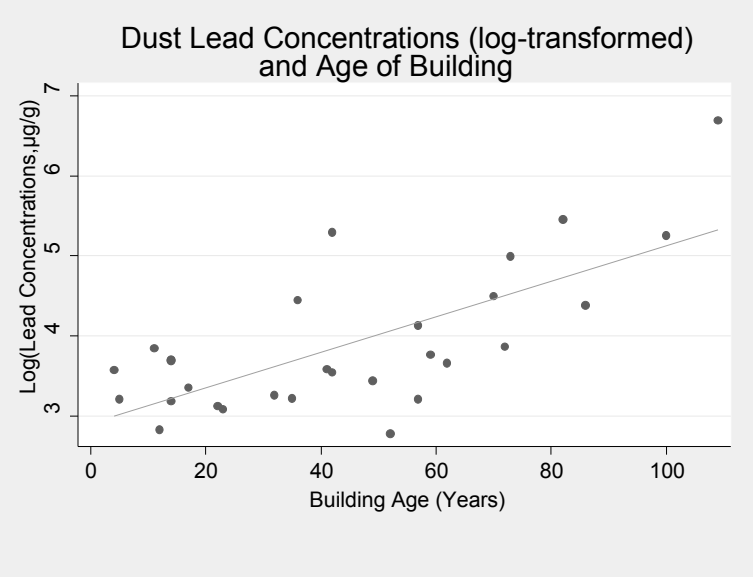

Figure 14. Lead concentrations and their association with building age. Note lead concentrations are in the log scale.

4 Health Risk Characterization

We conducted a screening risk assessment for cancer and non-cancer endpoints for chemicals measured in air and dust. The purpose of this evaluation was to provide information about the potential health risks children may experience due to exposures in California ECE facilities and help identify contaminants that may need further research or mitigation. Detailed literature reviews were not completed. Federal or state benchmarks were used for comparisons. In many cases, there were no reference exposure levels or benchmark doses available, so health risk could not be evaluated.

Our approach followed the U.S. EPA's guidance for performing a human health risk assessment on cancer and non-cancer health endpoints.[155] We compared measured concentrations of indoor air pollutants to Reference Exposure Levels (RELs), Reference Concentrations (RfCs), California Ambient Air Quality Standards (CAAQS), and National Ambient Air Quality Standards (NAAQS), when available. Child exposure-dose estimates were based on air and dust concentrations, and assumptions about inhalation, absorption, and non-dietary ingestion of house dust. These dose estimates were compared to health-based benchmarks, including U.S. EPA Reference Doses (RfDs), OEHHA No Significant Risk Levels (NSRLs), and OEHHA Maximum Allowable Dose Levels (MADLs).

Table 82 summarizes the health-based benchmarks that were used for the risk evaluation. Each are described in detail below.

Table 82. Summary of Health-based Benchmarks Used for Risk Evaluation

Benchmark	Responsible Agency	Exposure Media	Route of Exposure
aREL (acute reference exposure level)	OEHHA	Air	Inhalation
8-hr REL (8-hour reference exposure level)	OEHHA	Air	Inhalation
cREL (chronic reference exposure level)	OEHHA	Air	Inhalation
NSRL (no significant risk level [cancer])[a]	OEHHA	Air and dust	Inhalation/Ingestion
MADL (maximum adverse dose level [reproductive effects])	OEHHA	Air and dust	Inhalation/Ingestion
RfC (reference concentration)	U.S. EPA	Air	Inhalation
Oral RfD (oral reference dose)	U.S. EPA	Dust	Ingestion

[a] An NSRL is the estimated daily intake over a 70 year lifetime associated with a 10^{-5} lifetime cancer risk. This level of cancer risk is 10 times higher than the standard 10^{-6} cancer risk level used to set most health-based standards for carcinogens.

4.1 Reference Air Concentration Levels

Measured concentrations were compared to Reference Exposure Levels (RELs). RELs are developed by the California Office of Environmental Health Hazard Assessment (OEHHA) and are concentrations of air contaminants at or below levels where non-cancer health effects are not anticipated for a specified exposure duration.[156] Acute RELs (aRELs) are set for exposures averaging over 1 hour, 8-hour RELs are set for exposures averaged over 8 hours, and chronic RELs (cRELs) are set for continuous exposures over a lifetime.[156] The RELs, calculated as shown in the equation below, are the No Observed Adverse Effect Level (NOAEL) with the application of an appropriate Uncertainty Factor (UF):[157]

$$REL = \frac{NOAEL_{concentration}}{UF}$$

Measured concentrations were also compared to Reference Concentrations (RfCs) developed by the U.S. EPA. An RfCs is defined as an air concentration that is "likely to be without appreciable risk …. during a lifetime."[158]

The RELs and RfCs are based on peer-reviewed studies, most often animal experiments, but sometimes include epidemiological, clinical or experimental exposure studies on human populations.[157,158]

4.2 Inhalation and Oral Exposure Dose Calculations

We calculated child-specific dose estimates for the inhalation and oral routes of exposure based on air and dust concentrations of contaminants measured in air and dust at ECE facilities.

Air inhalation exposure dose calculations for children receiving care at ECE facilities follow the equation presented in the Agency for Toxic Substances & Disease Registry's *Public Health Assessment Guidance Manual*:[159]

$$D_{child\ care} = \frac{C \times IR \times EF \times CF}{BW}$$

Where,

D = exposure dose received in child care assuming 8 hour day (mg/kg/8 hours)
C = contaminant concentration (mg/m³)
IR = intake rate (m³/8 hours)
EF=exposure factor
CF=conversion factor
BW= body weight (kg)

Contaminant concentrations are the measured levels of concentrations found in air (mg/m³). Intake rate (inhalation rate) and body weight are specific to the child age groups (birth to <1 year, 1 to <2 years, 2 to <3 years and 3 to <6 years). The intake rate was divided by a factor of three to adjust for the amount of time a child spends at a child care facility (assuming eight hours of child care per day, or one third of a day). The full day and 8-hour day intake rates are taken from the U.S. Environmental Protection Agency's *Child-Specific Exposure Factors Handbook* (CSEFH) and are presented below (Table 83).[160]

Table 83. Inhalation Rates Based on U.S. EPA's Child-Specific Exposure Factors Handbook

	Inhalation Daily Volume	
	(m^3/day)	(m^3/8-hour)
Birth to <1 year	5.10	1.70
1 to <2 years	8.00	2.67
2 to <3 years	9.50	3.17
3 to <6 years	10.90	3.63

The exposure factor (EF) is calculated:[159]

$$EF = \frac{F \times ED}{AT}$$

Where,

F = frequency of exposure (days/year)
ED = exposure duration (years)
AT = averaging time (ED x 365 days/year)

Since children are not present in ECE facilities all hours of the day, we calculated the exposure factor (EF) based on the scenario that a child spends five days per week and 48 weeks per year (which accounts for four weeks away from day care for holidays and vacation). The averaging time will depend on how many years the child is in child care but is assumed to be one year in our calculations.[159]

$$EF = \frac{\left(5\,\frac{days}{week}\right) \times \left(48\,\frac{weeks}{year}\right) \times (1\,year)}{1\,year\,\times\,365\,\frac{days}{year}} = 0.66$$

Sample Child Inhalation Dose Calculation. Below is an example formaldehyde dose calculation based on formaldehyde concentrations measured in air. We assume a child spends 8 hours per day and 48 weeks per year in child care.

EXAMPLE of Formaldehyde
Inhalation
Birth to <1 year
40 hours/week (8 hours/day)

$$D_{child\ care\ inhalation} = \frac{C \times IR \times EF \times CF}{BW} = \frac{(17.72\,\frac{\mu g}{m^3}) \times (5.10\,\frac{m^3}{day})(\frac{1}{3}) \times (0.66) \times (10^{-3}\,\frac{mg}{\mu g})}{6.75\,kg}$$

$$D_{child\ care\ inhalation} = 0.0029\,\frac{mg}{kg - day}$$

Dust ingestion exposure dose calculations for children receiving care at ECE facilities follow the equation presented in the Agency for Toxic Substances & Disease Registry's *Public Health Assessment Guidance*:[159]

$$D_{child\ care\ ingestion} = \frac{C \times IR \times EF \times CF}{BW}$$

Where,

D = exposure dose received in child care assuming 8-hour day (mg/kg/day)
C = contaminant concentration (mg/kg)
IR = intake rate of contaminated dust (mg/day)
EF= exposure factor (unitless)
CF= conversion factor (10^{-6} kg/mg)
BW= body weight (kg)

The dust intake rate is assumed to be 100 mg per day (i.e., per 8 hours).[160]

Sample Child Oral Dose Calculation. Below is an example trans-permethrin dose calculation based on measurements of trans-permethrin in dust collected from ECE facilities. We assume a child spends 8 hours per day and 48 weeks per year in child care.

EXAMPLE trans-Permethrin
Ingestion
Birth to <1 year
40 hours/week (8 hours/day)

$$D_{child\ care} = \frac{C \times IR \times EF \times CF}{BW} = \frac{225.3\frac{ng}{g} \times 0.100\frac{g}{day} \times 0.66 \times 10^{-6}\frac{mg}{ng}}{6.75\ kg} = 2.20E-6\ \frac{mg}{kg-day}$$

4.3 Oral Reference Dose

Reference doses (RfDs) are established by the U.S. EPA and are "an estimate of the daily acute or chronic exposure … that is likely to be without risk of adverse effects."[161, 162] RfDs are estimated by dividing the no-observed-adverse-effect-level (NOAEL), lowest-observed adverse-effect-level (LOAEL) or benchmark dose by uncertainty factors to account for the limitations of the study (i.e., 10-fold factor for interspecies extrapolation).[161]

$$RfD = \frac{NOAEL,\ LOAEL,\ or\ benchmark\ dose}{UF \times MF}$$

A pesticide RfD that has been adjusted to incorporate requirements of the Food Quality Protection Act (FQPA) to protect sensitive populations is called a population-adjusted dose (PAD).[163]

$$PAD = \frac{RfD}{FQPA\ factor}$$

The FQPA safety factor is in addition to uncertainty factors already incorporated into an RfD. The FQPA safety factor takes into account data deficiencies identified for children and infants due to their increased susceptibility.[163]

4.4 No Significant Risk Levels (NSRL) for Cancer

Under California's Proposition 65, OEHHA has set 'Safe Harbor Levels" called no significant risk levels (NSRLs). The NSRL is defined as the daily intake level posing a 10^{-5} risk of cancer assuming lifetime exposure.[164] It should be noted that an age-specific NSRL, such as the $NSRL_{child\ 0-<1\ yr}$, is the estimated daily intake for that specific age range, which contributes 1/70th (assuming a 70 year lifetime) of the target lifetime cancer risk in that particular year of life (in the case of NSRLs, that "target" is a lifetime cancer risk of 10^{-5}).

The NSRL is calculated by the following equation:

$$NSRL\left(\frac{\mu g}{day}\right) = \frac{[Cancer\ Risk\ \times Body\ Weight\ (kg)]}{Cancer\ Potency\ Estimate\ (\frac{mg}{kg-day})^{-1}} * (\mathrm{CF})$$

$$NSRL_{\ adult}\left(\frac{\mu g}{day}\right) = \frac{10^{-5}\times 70kg}{Cancer\ Potency\ Estimate\left(\frac{mg}{kg-day}\right)^{-1}} * (\mathrm{CF})$$

Where, CF= Conversion factor of 1000 µg/1 mg applied to convert NSRL units from mg/day to µg/day.

A 70 kg body weight (BW) for a human adult is used as the basis for the population NSRL.[164] For a child-specific NSRL, we applied an OEHHA age sensitivity factor (ASF) of 10 for children below the age of two years, and an ASF of 3 for children between the ages of two and six years[164], and used an age-specific body weight:[160]

$$NSRL_{\ child}\left(\frac{\mu g}{day}\right) = \frac{\frac{NSRL_{adult}\left(\frac{\mu g}{day}\right)}{BW_{\ adult}(70\ kg)} \times BW_{child}\ (Varies\ by\ Age\ Group, kg)}{ASF\ (Varies\ by\ Age\ Group)}$$

Body weights (Table 84) for children are recommended values presented in the U.S. EPA's CSEFH.[160] Child inhalation rates are also from EPA's CSEFH.

Table 84. Mean Body Weights and Inhalation Rates Used for NSRL Dose Calculations

Age Group	Mean Body Weight (kg)	Mean Inhalation Rate (m^3/day)
Birth to <1	6.75 [a]	5.10
1 to <2 Years	11.4	8.00
2 to <3 Years	13.8	9.50
3 to <6 Years	18.6	10.90

[a] Value based on average of three age groups (birth to <1 month, 2 to <6 months, and 6 to <12 months) from Arcus-Arth and Blaisdell, 2007.[165]

Sample Child NSRL Ratio Calculation. Below is an example child formaldehyde NSRL ratio calculation based on formaldehyde concentrations measured in air at the ECE facilities. We assume a child spends 8 hours per day and 48 weeks per year in child care.

EXAMPLE Formaldehyde (unadjusted NSRL (adult) = 40 µg/day)
Inhalation
Birth to <1 year
40 hours/week (8 hours/day)

The NSRL is in units of µg/day, therefore, converting the inhalation dose estimate (Inhalation Example above) from mg/kg-day would result in:

$$\text{Estimated daily exposure} = 0.00294 \frac{mg}{kg-day} \times 6.75\ kg \times \frac{1000\ \mu g}{1\ mg} = 19.88\ \frac{\mu g}{day}$$

The NSRL is calculated using values for an adult, therefore we must adjust accordingly:

$$NSRL\ adjusted\ \left(\frac{\mu g}{day}\right) = NSRL\left(\frac{\mu g}{day}\right) \times \frac{\left[\frac{BW\ Child\ (6.75\ kg)}{BW\ Adult\ (70\ kg)}\right]}{ASF\ (10)}$$

Where the ASF is the age-sensitivity factor:
Birth to <2 years: ASF=10
2 years to <16 years: ASF=3

$$NSRL\ adjusted\ \left(\frac{\mu g}{day}\right) = 40\frac{\mu g}{day} \times \frac{\frac{6.75\ kg}{70 kg}}{10} = 0.39\frac{\mu g}{day}$$

Ratio of Estimate to $NSRL_{child\ (0\ to\ <1\ yr)}$:

$$\frac{19.88\frac{\mu g}{day}}{0.39\frac{\mu g}{day}} = \mathbf{51.0}$$

4.5 Definition of Hazard Quotient

Hazard Quotients (HQ) are the ratio of an estimated dose to the reference dose (RfD) for a given chemical. If the HQ is greater than 1, the exposure dose estimate exceeded health-based exposure limits. For many compounds, no RfD or population adjusted dose (PAD) was available.

4.6 Maximum Allowable Dose Levels (MADL) for Reproductive Effects

Under California's Proposition 65, OEHHA has set 'Safe Harbor Levels" called Maximum Allowable Dose Levels (MADL) for reproductive toxicants. The MADL is defined as "the highest level at which the chemical would have no observable reproductive effect assuming exposure at 1,000 times that level."[164] We calculated adjusted dose estimates for adult women and compared them to the MADL values, when available. For these calculations, we assumed an adult woman weighs 70.9 kgs and breathes at a rate of 13.5 m^3/day based on the average weight of women between the ages of 16 to 41 from U.S. EPA's *Exposure Factors Handbook*.[166] The same methods are used to calculate the adjusted dose estimate (µg/day) for comparison with the MADL as described above for the NSRL assessment.

4.7 Health Risk Characterization Results

Below we present results of our comparisons of child dose estimates based on contaminant concentrations of VOCs, pesticides, phthalates, and flame retardants in air and dust to health-based cancer and non-cancer reference values, when available. For all assessments, we grouped children into four age groups (birth to 1 year; 1 year to <2 years; 2 years to <3 years and 3 years to <6 years), and assumed they spent 8 hours per day, 40 hours per week in ECE facilities. For each class of compound, we provided an assessment for up to two potential routes of exposure: inhalation and non-dietary ingestion.

4.7.1 VOC Health Risk Characterization Results

4.7.1.1 Non-Cancer VOC Hazard Assessment: Ratio of Analyte Concentrations in Air to RELs and RfCs

Table 85 presents the air concentrations of VOCs measured in the ECE facilities compared to the aREL, cREL and RfC values, when available. Two carbonyl compounds, aldehyde and formaldehyde, had ratios exceeding 1. The 95th percentile air concentration of acetaldehyde (19 µg/m^3) exceeded the U.S. EPA RfC (9 µg/m^3) (ratio=2.1). The 50th and 95th percentile formaldehyde air concentrations (17.7 and 37.0 µg/m^3, respectively) exceeded the 8-hour REL and cREL (9 µg/m^3). The ratios of the formaldehyde 50th and 95th percentile concentrations to the 8-hour REL and cREL were 2.0 and 4.1, respectively. Currently, no final U.S. EPA RfC exists for formaldehyde. Out of forty ECE facilities, thirty-five (87.5%) had formaldehyde concentrations above the 8-hour REL and cREL, with the highest concentration 5.4 times the RELs. Out of forty ECE facilities, twelve (30%) had acetaldehyde concentrations above the RfC, with the highest concentration 2.6 times the RfC.

The OEHHA 8-hour REL and cREL for formaldehyde is based on health effects including nasal obstruction and discomfort, lower airway discomfort, and eye irritation.[167] The U.S. EPA's reference concentration for chronic acetaldehyde inhalation is based on degeneration of olfactory epithelium in two short-term rat inhalation studies.[45]

There were no other VOCs with 50th or 95th percentile air concentrations exceeding health-based reference concentrations.

Table 85. Ratios of VOC Air Concentrations to the Acute Reference Exposure Level (aREL), the 8-hour REL, the Chronic REL (cREL) and the Reference Concentration (RfC)

Chemical	Measurements (µg/m³)		aREL (µg/m³)	Ratio (aREL)		8-hour REL (µg/m³)	Ratio (8-hour REL)		cREL (µg/m³)	Ratio (cREL)[a]		Inh. RfC (mg/m³)	Ratio (Inh. RfC)[a]	
	50th %	95th %		50th %	95th %		50th %	95th %		50th %	95th %		50th %	95th %
VOC														
2-Butoxyethanol (ethylene glycol monobutyl ether)	2.95	63.98	14,000	0.0002	0.005	-	NC	NC	-	NC	NC	1.6	0.002	0.04
Benzaldehyde	2.39	6.30	-	NC	NC	-	NC	NC	-	NC	NC	-	NC	NC
Benzene	0.85	2.02	1,300	0.0007	0.001	-	NC	NC	60	0.01	0.03	0.03	0.03	0.07
Carbon tetrachloride	ND	ND	1,900	NC	NC	-	NC	NC	40	NC	NC	0.1	NC	NC
Chloroform	ND	7.73	150	NC	0.05	-	NC	NC	300	NC	0.03	-	NC	NC
Dibutyl phthalate	ND	1.65	-	NC	NC	-	NC	NC	-	NC	NC	-	NC	NC
Dichloromethane (methylene chloride)	ND	ND	14,000	NC	NC	-	NC	NC	400	NC	NC	-	NC	NC
Diethyl phthalate	0.47	1.15	-	NC	NC	-	NC	NC	-	NC	NC	-	NC	NC
Ethylbenzene	0.60	1.96	-	NC	NC	-	NC	NC	2,000	0.0003	1E-03	1	0.0006	0.002
Hexane	0.56	2.85	-	NC	NC	-	NC	NC	7,000	8E-05	4E-04	0.7	0.0008	0.004
Methyl tert-butyl ether (as hexane)	ND	ND	-	NC	NC	-	NC	NC	8,000	NC	NC	3	NC	NC
o-Xylene	0.83	2.71	22,000	3.8E-05	0.0001	-	NC	NC	700	0.001	0.004	0.1	0.008	0.03
p-Xylene	1.62	6.75	22,000	7.3E-05	0.0003	-	NC	NC	700	0.002	0.01	0.1	0.02	0.07
Tetrachloroethylene	0.08	0.97	20,000	4.0E-06	4.9E-05	-	NC	NC	35	0.002	0.03	-	NC	NC
Toluene	3.05	11.19	37,000	8.2E-05	0.0003	-	NC	NC	300	0.01	0.04	5	0.0006	0.002
Carbonyls														
Acetaldehyde	7.54	19.11	470	0.02	0.04	300	0.03	0.06	140	0.05	0.1	0.009	0.8	2.1
Acetone	19.82	148.19	-	NC	NC	-	NC	NC	-	NC	NC	-	NC	NC
Formaldehyde	17.72	36.97	55	0.3	0.7	9	2.0	4.1	9	2.0	4.1	-	NC	NC

ND: Analyte not detected in air (<MDL); NC: ratio not calculated

[a]A conversion factor of 1 mg/1,000 µg was applied to the ratios of the Inh. RfC to account for the different units in the concentrations.

4.7.1.2 VOC Inhalation Exposure Dose Estimates Compared to Maximum Allowable Dose Levels (MADLs)

We calculated the ratios of the 50th and 95th percentile VOC dose estimates for adult women and compared them to available health-based MADL values. Two measured VOCs (benzene and toluene) had MADL values; neither compound's dose estimate exceeded the MADL (benzene MADL: 49 µg/day [inhalation] and toluene MADL: 13,000 µg/day [inhalation]).

4.7.1.3 Cancer Risk Assessment: Child VOC Inhalation Dose Estimates Compared to NSRLs

The 50th and 95th percentile inhalation exposure dose estimates compared to the $NSRL_{child}$ values are presented by age group in Tables 86 to 89. There were five VOCs with NSRL ratios exceeding 1: benzene; chloroform; ethylbenzene; acetaldehyde; and formaldehyde.

Benzene: The 50th and 95th percentile exposure estimates for benzene exceeded the age-specific NSRL in all four age groups assessed. The benzene 50th and 95th percentile NSRL ratios for the four age groups were 7.6 and 18.1; 7.1 and 16.8; 2.1 and 4.9; and 1.8 and 4.2, respectively. Child benzene exposure estimates exceeded age-adjusted NSRL benchmarks based on carcinogenicity in 70.6% of facilities.

Chloroform: The 95th percentile exposure estimates for chloroform exceeded the age-specific NSRL in all four age groups assessed. The chloroform 95th percentile NSRL ratios for the four age groups were 22.5, 20.9, 6.2 and 5.2, respectively. Child chloroform exposure estimates exceeded age-adjusted NSRL benchmarks based on carcinogenicity in 38.2% of facilities.

Ethylbenzene: The 50th and 95th percentile exposure estimates for ethylbenzene exceeded the age-specific NSRL in three of the age groups assessed (birth to <1 year; 1 to <2 years; and 2 to <3 years). The ethylbenzene 50th and 95th percentile NSRL ratios for the three age groups were 1.3 and 4.2; 1.2 and 3.9; and 0.35 and 1.2, respectively. Child ethylbenzene exposure estimates exceeded age-adjusted NSRL benchmarks based on carcinogenicity in 61.8% of facilities.

Acetaldehyde: The 50th and 95th percentile exposure estimates for acetaldehyde exceeded the age-specific NSRL in all four age groups assessed. The acetaldehyde 50th and 95th percentile NSRL ratios for the four age groups were 9.8 and 24.7; 9.1 and 23.0; 2.7 and 6.8; and 2.3 and 5.8, respectively. Child formaldehyde exposure estimates exceeded age-adjusted NSRL benchmarks based on carcinogenicity in 97.5% of facilities.

Formaldehyde: The 50th and 95th percentile exposure estimates for formaldehyde exceeded the age-specific NSRL in all four age groups assessed. The formaldehyde 50th and 95th percentile NSRL ratios for the four age groups were 51.6 and 107.6; 47.9 and 99.9; 14.1 and 29.4; and 12.0 and 25.0, respectively. Child formaldehyde exposure estimates exceeded age-adjusted NSRL benchmarks based on carcinogenicity in 100% of facilities.

There were no other VOC compounds with that have OEHHA NSRLS with air exposure estimates exceeding this benchmark.

Table 86. Inhalation VOC Exposure Estimates Compared to $NSRL_{child\ (0\ to\ <1\ yr)}$ in the Age Group of Birth to <1 Year

Target Analyte	Birth to <1 year				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
VOC					
Benzene	0.96	2.3	0.13	7.6	18.1
Carbon tetrachloride	NC	NC	0.05	NC	NC
Chloroform	NC	8.7	0.39	NC	22.5
Dichloromethane (methylene chloride)	NC	NC	1.93	NC	NC
Ethylbenzene	0.67	2.2	0.52	1.3	4.2
Carbonyls					
Acetaldehyde (ethanal)	8.5	21.4	0.87	9.75	24.7
Formaldehyde	19.9	41.5	0.39	51.6	107.6

NC: not calculated because analyte was not detected in air (<MDL)

Table 87. Inhalation VOC Exposure Estimates Compared to $NSRL_{child\ (1\ to\ <2\ yrs)}$ in the Age Group of 1 to <2 Years

Target Analyte	1 to <2 years				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
VOC					
Benzene	1.5	3.6	0.21	7.1	16.8
Carbon tetrachloride	NC	NC	0.08	NC	NC
Chloroform	NC	13.6	0.65	NC	20.9
Dichloromethane (methylene chloride)	NC	NC	3.3	NC	NC
Ethylbenzene	1.1	3.5	0.88	1.2	3.2
Carbonyls					
Acetaldehyde (ethanal)	13.3	33.6	1.45	9.1	22.9
Formaldehyde	31.2	65.1	0.65	47.9	99.9

NC: not calculated because analyte was not detected in air (<MDL)

Table 88. Inhalation VOC Exposure Estimates Compared to $NSRL_{child\ (2\ to\ <3\ yrs)}$ in the Age Group of 2 to <3 Years

Target Analyte	2 to <3 years				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
VOC					
Benzene	1.8	4.2	0.85	2.1	4.9
Carbon tetrachloride	NC	NC	0.3	NC	NC
Chloroform	NC	16.2	2.6	NC	6.2
Dichloromethane (methylene chloride)	NC	NC	13.1	NC	NC
Ethylbenzene	1.3	4.1	3.6	0.35	1.2
Carbonyls					
Acetaldehyde (ethanal)	15.8	39.9	5.9	2.7	6.8
Formaldehyde	37.0	77.3	2.6	14.1	29.4

NC: not calculated because analyte was not detected in air (<MDL)

Table 89. Inhalation VOC Exposure Estimates Compared to $NSRL_{child\ (3\ to\ <6\ yrs)}$ in the Age Group of 3 to <6 Years

Target Analyte	3 to <6 years				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
VOC					
Benzene	2.1	4.8	1.2	1.8	4.2
Carbon tetrachloride	NC	NC	0.44	NC	NC
Chloroform	NC	18.5	3.5	NC	5.2
Dichloromethane (methylene chloride)	NC	NC	17.7	NC	NC
Ethylbenzene	1.4	4.7	4.8	0.3	1.0
Carbonyls					
Acetaldehyde (ethanal)	18.1	45.8	8.0	2.2	5.8
Formaldehyde	42.5	88.7	3.5	12.0	25.0

NC: not calculated because analyte was not detected in air (<MDL)

4.7.2 Phthalates Health Risk Characterization Results

4.7.2.1 Non-Cancer Phthalate Hazard Assessment: Ratio of Analyte Concentrations in Air to RELs and RfCs

Currently, no REL or RfC values exist for the five phthalate compounds we measured in indoor air.

4.7.2.2 Phthalate Inhalation Exposure Dose Estimates Compared to Maximum Allowable Dose Levels (MADLs)

We calculated the ratio of the 50th and 95th percentile dose estimates of dibutyl phthalate for adult women to its health-based MADL value (dibutyl phthalate is the only phthalate measured with an MADL for inhalation). Dibutyl phthalate's dose estimates did not exceed its MADL (8.7 µg/day [inhalation]). See Appendix A, Table 110, for a table comparing dibutyl phthalate's inhalation exposure dose estimate to its MADL value.

4.7.2.3 Phthalate Oral Exposure Dose Estimates Compared to Oral RfDs: Hazard Quotients

Health-based oral reference doses were available for four phthalates measured in dust from ECE facilities. Tables 90 and 91 summarize the age-specific phthalate dose estimates in comparison with oral RfDs. None of these four phthalate compounds had 50th or 95th percentile dose estimates exceeding oral reference doses for any of the age groups.

Table 90. Hazard Quotients for Phthalate Non-dietary Ingestion Dose Estimates Compared to Oral Reference Doses (RfDs) by Age Group: Birth to <1 Year and 1 to <2 Years

Chemical	Age Group									
	Birth to <1 year					1 to <2 years				
	Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
Phthalates										
Butyl benzyl phthalate	0.00046	0.012	0.2	0.002	0.06	0.00027	0.0069	0.2	0.001	0.04
Dibutyl phthalate	0.00013	0.0012	0.1	0.001	0.01	7.94E-05	0.00069	0.1	0.0008	0.007
Diethyl phthalate	0.000014	4.45E-05	0.8	0.00002	5.6E-05	8.34E-06	2.63E-05	0.8	1.04E-05	3.3E-05
Di(2-ethylhexyl) phthalate	0.0017	0.0053	0.02	0.08	0.3	0.0010	0.0032	0.02	0.05	0.2

Table 91. Hazard Quotients for Phthalate Non-dietary Ingestion Dose Estimates Compared to Oral Reference Doses (RfDs) by Age Group: 2 to <3 Years and 3 to <6 Years

Chemical	Age Group									
	2 to <3 years					3 to <6 years				
	Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
Phthalates										
Butyl benzyl phthalate	0.00022	0.0057	0.2	0.001	0.03	0.00017	0.0042	0.2	0.0008	0.02
Dibutyl phthalate	6.56E-05	0.00057	0.1	0.0007	0.006	4.87E-05	0.00043	0.1	0.0005	0.004
Diethyl phthalate	6.89E-06	2.18E-05	0.8	8.6E-06	2.7E-05	5.10E-06	1.61E-05	0.8	6.4E-06	2.0E-05
Di(2-ethylhexyl) phthalate	0.00082	0.0026	0.02	0.04	0.13	0.00061	0.0019	0.02	0.03	0.1

4.7.2.4 Cancer Risk Assessment: Child Phthalate Inhalation Dose Estimates Compared to NSRLs

Only one phthalate compound (DEHP) measured in air from ECE facilities had an OEHHA NSRL. Neither the 50th nor 95th percentile exposure estimates exceeded any age-specific NSRL values (Tables 92-95).

Table 92. Inhalation Exposure Estimates Compared to $NSRL_{child\ (0\ to\ <1\ yr)}$ in the Age Group of Birth to <1 Year

Target Analyte	Birth to <1 year				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
Phthalate					
Di(2-ethylhexyl) phthalate	0.011	0.67	2.99	0.004	0.22

Table 93. Inhalation Exposure Estimates Compared to $NSRL_{child\ (1\ to\ <2\ yrs)}$ in the Age Group of 1 to <2 Years

Target Analyte	1 to <2 years				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
Phthalate					
Di(2-ethylhexyl) phthalate	0.018	0.67	5.05	0.003	0.13

Table 94. Inhalation Exposure Estimates Compared to $NSRL_{child\ (2\ to\ <3\ yrs)}$ in the Age Group of 2 to <3 Years

Target Analyte	2 to <3 years				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
Phthalate					
Di(2-ethylhexyl) phthalate	0.021	0.79	20.37	0.001	0.04

Table 95. Inhalation Exposure Estimates Compared to $NSRL_{child\ (3\ to\ <6\ yrs)}$ in the Age Group of 3 to <6 Years

Target Analyte	3 to <6 years				
	Exposure Estimates (µg/day) 50th %	Exposure Estimates (µg/day) 95th %	$NSRL_{child}$ (µg/day)	Ratio 50th %	Ratio 95th %
Phthalate					
Di(2-ethylhexyl) phthalate	0.024	0.91	27.46	0.0009	0.03

4.7.3 Flame Retardants Health Risk Characterization Results

4.7.3.1 Non Cancer Flame Retardant Hazard Assessment: Ratios of Analyte Concentrations in Air to RELs and RfCs

Currently, no REL or RfC values exist for the 11 flame retardants we measured in indoor air.

4.7.3.2 Oral PBDE Exposure Dose Estimates and Hazard Quotients

The hazard quotients (HQs) for the age-specific PBDE ingestion dose estimates are presented in Tables 96 and 97. Two PBDE congeners (BDE-47 and -99) had 95th percentile child dose estimates (age group birth to <1 year) that exceeded the oral reference doses (0.0001 mg/kg-day) for the two congeners. Ten percent of facilities had children with dose estimates that exceeded the oral benchmark. For the birth to <1 year old age group, the BDE-47 and BDE-99 95th percentile HQ values were 1.14 and 1.29, respectively. No other PBDE congeners had HQs greater than 1.

Brominated flame retardants are known endocrine disruptors and neurotoxicants. The RfDs for these PBDE congeners were established based on adverse neurobehavioral effects in animals.[168-170]

Table 96. Hazard Quotients for PBDE Non-dietary Ingestion Dose Estimates Compared to Oral Reference Doses (RfDs) by Age Group: Birth to <1 Year and 1 to <2 Years

Chemical	Age Group									
	Birth to <1 year					1 to <2 years				
	Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
BDEs										
BDE-47	7.52E-06	0.00011	0.0001	0.07	1.1	4.15E-06	6.73E-05	0.0001	0.04	0.7
BDE-99	1.0082E-05	0.00013	0.0001	0.1	1.3	5.97E-06	7.66E-05	0.0001	0.06	0.8
BDE-153	1.22E-06	1.26E-05	0.0002	0.006	0.06	7.24E-07	7.44E-06	0.0002	0.004	0.04
BDE-209	1.41E-05	0.00011	0.007	0.002	0.02	8.35E-06	6.58E-05	0.007	0.001	0.009

Table 97. Hazard Quotients for PBDE Non-dietary Ingestion Dose Estimates Compared to Oral Reference Doses (RfDs) by Age Group: 2 to <3 Years and 3 to <6 Years

Chemical	Age Group									
	2 to <3 years					3 to <6 years				
	Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose Estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
BDEs										
BDE-47	3.68E-06	5.60E-05	0.0001	0.04	0. 6	2.73E-06	4.15E-05	0.0001	0.03	0.4
BDE-99	4.938E-06	6.33E-05	0.0001	0.05	0.6	3.66E-06	4.69E-05	0.0001	0.04	0.5
BDE-153	5.988E-07	6.15E-06	0.0002	0.003	0.03	4.46E-07	4.56E-06	0.0002	0.002	0.02
BDE-209	6.90E-06	5.44E-05	0.007	0.001	0.008	5.12E-06	4.034E-05	0.007	0.0007	0.006

4.7.3.3 Cancer Risk Assessment: Child Flame Retardant Inhalation Dose Estimates Compared to NSRLs

Currently, no OEHHA NSRL values exist for the flame retardant compounds measured in air.

Recently, OEHHA has proposed an NSRL for TDCPP of 5.4 µg/day. This proposed NSRL for TDCPP is not yet final.[171]

4.7.4 Pesticides Risk Evaluation Results

4.7.4.1 Non-Cancer Pesticide Hazard Assessment: Ratio of Analyte Concentrations in Air to RELs and RfCs

Currently, no REL or RfC values exist for the 11 pesticides we measured in indoor air.

4.7.4.2 Oral Pesticide Exposure Dose Estimates and Hazard Quotients

We computed age-specific child dose estimates based on dust pesticide levels and compared them to oral RfD and PAD values, when available. Tables 98 and 99 summarize pesticide non-dietary ingestion exposure estimates and hazard quotients. Health-based oral reference doses were available for eight pesticides and one synergist (piperonyl butoxide) measured in dust from ECE facilities. We found no pesticide compounds with 50^{th} or 95^{th} percentile dose estimates exceeding oral reference doses for any of the four age groups assessed.

Table 98. Hazard Quotients for Non-dietary Pesticide Ingestion compared to Oral Reference Doses (RfDs)[a] by Age Group: Birth to <1 year and 1 to <2 years

Chemical	Age Group									
	Birth to <1 year					1 to <2 years				
	Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
Pesticides										
Bifenthrin (biphenthrin)	5.56E-07	8.77E-06	0.015	3.7E-05	0.2	3.29E-07	5.19E-06	0.015	2.2E-05	0.2
Chlorpyrifos	1.04E-07	2.126E-06	0.0003 (cPAD)	0.0003	0.007	6.16E-08	1.25E-06	0.0003 (cPAD)	0.0002	0.004
cis-Permethrin	1.58E-06	9.19E-06	0.25 (cPAD)	6.3E-06	3.7E-05	9.39E-07	5.44E-06	0.25 (cPAD)	3.7E-06	2.2E-05
Cypermethrin	ND	2.90E-05	0.06 (cPAD)	NC	0.0005	ND	1.72E-05	0.06 (cPAD)	NC	0.00029
Dacthal	6.29E-08	5.0033E-07	0.01 (cPAD)	6.3E-06	5.0E-05	3.72E-08	2.96E-07	0.01 (cPAD)	3.7E-06	3.0E-05
Diazinon	3.60E-08	5.95E-07	0.0002 (cPAD)	0.0002	0.003	2.13E-08	3.52E-07	0.0002 (cPAD)	0.0001	0.002
trans-Permethrin	2.20E-06	1.47E-05	0.25 (cPAD)	8.8E-06	5.9E-05	1.30E-06	8.69E-06	0.25 (cPAD)	5.2E-06	3.5E-05
Piperonyl butoxide	7.46E-07	1.34E-05	0.16 (cPAD)	4.7E-06	8.4E-05	4.42E-07	7.96E-06	0.16 (cPAD)	2.8E-06	5.0E-05
Sumithrin	ND	3.15E-06	0.007 (cPAD)	NC	0.0005	ND	1.87E-06	0.007 (cPAD)	NC	0.0003

[a] cPADs, rather that RfDs, are listed when available.
ND: compound not detected in dust (<MDL); NC: ratio not calculated.

Table 99. Hazard Quotients for Non-dietary Pesticide Ingestion compared to Oral Reference Doses (RfDs)[a] by Age Group: 2 to <3 Years and 3 to <6 Years

Chemical	Age Group									
	2 to <3 years					3 to <6 years				
	Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
Pesticides										
Bifenthrin	2.72E-07	4.29E-06	0.015	1.8 E-05	0.2	2.016E-07	3.18E-06	0.015	1.3E-05	0.2
Chlorpyrifos	5.09E-08	1.04E-06	0.0003 (cPAD)	0.0002	0.005	3.77E-08	7.71E-07	0.0003 (cPAD)	0.0001	0.003
cis-Permethrin	7.75E-07	4.49E-06	0.25 (cPAD)	3.1 E-06	1.8E-05	5.75E-07	3.33E-06	0.25 (cPAD)	2.3E-06	1.3E-05
Cypermethrin	ND	1.42E-05	0.06 (cPAD)	NC	0.0002	ND	1.05E-05	0.06 (cPAD)	NC	0.0002
Dacthal	3.07E-08	2.45E-07	0.01 (cPAD)	3.07E-06	2.4E-05	2.28E-08	1.82E-07	0.01 (cPAD)	2.3E-06	1.8E-05
Diazinon	1.76E-08	2.91E-07	0.0002 (cPAD)	0.00009	0.0014	1.31E-08	2.16E-07	0.0002 (cPAD)	6.5E-05	0.001
trans-Permethrin	1.078E-06	7.18E-06	0.25 (cPAD)	4.3 E-06	2.9E-05	7.99E-07	5.33E-06	0.25 (cPAD)	3.2E-06	2.1E-05
Piperonyl butoxide	3.65E-07	6.58E-06	0.16 (cPAD)	2.3 E-06	4.1E-05	2.71E-07	4.88E-06	0.16 (cPAD)	1.7E-06	3.051E-05
Sumithrin	ND	1.54E-06	0.007 (cPAD)	NC	0.0002	ND	1.14E-06	0.007 (cPAD)	NC	0.0002

[a] cPADs, rather that RfDs, are listed when available.
ND: compound not detected in air (<MDL); NC: ratio not calculated.

4.7.4.3 Cancer Risk Assessment: Child Pesticide Dose Estimates Compared to NSRLs

Currently, no OEHHA NSRL values exist for the pesticide compounds we measured in air or dust.

4.7.5 Perfluorinated Compounds Risk Results

We measured four PFCs in dust collected from ECE facilities. PFOA, a common environmental contaminant, has been associated with increased incidence of liver, Leydig cell and pancreatic tumors in rodent bioassays, and is currently under review by the National Toxicology Program (NTP)[172] and the OEHHA Carcinogen Identification Committee.[173] Currently, however, no RfD, MADL or NSRL values exist for the PFCs we measured.

4.7.6 Particulate Matter Risk Results

CARB established the CAAQS which are designed to protect sensitive populations including infants and children, the elderly, and individuals with heart or lung disease. In children, health effects associated with increased exposure to PM include reduced lung function and increased respiratory symptoms and illnesses.[174] For $PM_{2.5}$ and PM_{10}, the "24-hour" standards are PM concentrations that should not be exceeded over a 24-hour averaging period. As of April 2012, the 24-hour standard for PM_{10} is 50 µg/m³. Although CARB has not established a 24-hour standard for $PM_{2.5}$, the U.S. EPA has recommended a 24-hour average standard of 35 µg/m³.[174]

We compared our indoor $PM_{2.5}$ and PM_{10} results from the gravimetric sampling to current air quality PM standards. In 4 of 35 (11%) ECE facilities, indoor $PM_{2.5}$ concentrations were higher than the level of the U.S. EPA 24-hour standard of 35 µg/m³. In 16 out of 35 (46%) ECE facilities, indoor PM_{10} concentrations exceeded the level of the 24-hour CAAQS standard of 50 µg/m³.

4.7.7 Heavy Metal Health Risk Characterization Results

Of the three heavy metals measured in dust (Cd, Cr, Pb), health-based oral RfDs were available for Cd only. The Cd child dose estimates did not exceed the RfD (i.e., HQ<1). The HQs for age-specific heavy metal non-dietary ingestion dose estimates are presented in Tables 100 and 101.

Table 100. Hazard Quotients for Heavy Metal Non-dietary Ingestion Dose Estimates compared to Oral Reference Doses (RfDs) by Age Group: Birth to <1 Year and 1 to <2 Years

Chemical	Age Group									
	Birth to <1 year					1 to <2 years				
	Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
Heavy Metals										
Cadmium	2.35E-05	2.83E-04	0.001	0.02	0.3	0.000014	0.00017	0.001	0.01	0.2

Table 101. Hazard Quotients for Heavy Metal Non-dietary Ingestion Dose Estimates compared to Oral Reference Doses (RfDs) by Age Group: 2 to <3 Years and 3 to <6 Years

Chemical	Age Group									
	2 to <3 years					3 to <6 years				
	Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)		Dose estimates (mg/kg/day)		Oral RfD (mg/kg-day)	Hazard Quotient (RfD)	
	50th %	95th %		50th %	95th %	50th %	95th %		50th %	95th %
Heavy Metals										
Cadmium	1.15E-05	1.38E-04	0.001	0.01	0.1	8.52E-06	0.00010	0.001	0.008	0.1

4.7.7.1 Cancer Risk Assessment: Child Oral Lead Exposure Dose Estimates Compared to NSRLs

The 50th and 95th percentile exposure estimates for lead exceeded the age-specific NSRL in all four age groups assessed (birth to <1 year; 1 to <2 years; 2 to <3 years and 3 to <6 years). The 50th and 95th percentile lead NSRL ratios for the four age groups were 16.3 and 106.9; 9.6 and 63.3; 2.4 and 15.7; and 1.8 and 11.6, respectively (Table 102). Child lead exposure estimates exceeded age-adjusted NSRL benchmarks based on carcinogenicity in 95% of facilities.

Table 102. Oral Lead Exposure Dose Estimates Compared to Age-Adjusted NSRL[a] by Age Group

Age Group	$NSRL_{child}$ (µg/day)	Ratio 50^{th} %	Ratio 95^{th} %
Birth to <1 year	0.14	16.3	106.9
1 to <2 years	0.24	9.6	63.3
2 to <3 years	0.99	2.4	15.7
3 to <6 years	1.33	1.8	11.6

[a] Unadjusted NSRL (adult)=15 µg/day (oral)

4.7.7.2 Health Risk Characterization Summary

The majority of compounds we measured did not have state or federal health-based reference values and thus it was not possible to evaluate the potential health risks due to exposures to these compounds. Among the compounds with health-based benchmarks, the estimated exposures for most compounds were well below levels of concern. Two VOC compounds, acetaldehyde and formaldehyde, were present in the indoor air of ECE facilities at levels that exceeded health-based reference concentrations. In addition, child dose estimates for five VOCs (benzene, chloroform, ethylbenzene, acetaldehyde, and formaldehyde) in indoor air exceeded the age-specific NSRL values for carcinogenic compounds computed by the report authors. Further, we identified two brominated flame retardants (BDE-47 and -99) with 95th percentile child dose estimates (age group birth to <1 year) that exceeded the non-cancer oral reference doses. Finally, lead was frequently detected in the dust collected from ECE facilities, and the 50th and 95th percentile child lead exposure estimates exceeded age-adjusted NSRL values for each of the four age groups examined.

Because most health-based reference values include safety factors, exposures exceeding these levels are not necessarily likely to result in adverse health effects. However, these chemicals warrant further study and common-sense steps are warranted to reduce exposures. The California Air Resources Board has published suggestions to reduce formaldehyde levels in schools and homes and these guidelines are likely to apply to ECE settings. ECE managers should also avoid building materials and cleaning and other products known to contain chemicals that may affect children's health. For example, some of the cleaning materials described in Appendix E, Table 153 contain petroleum distillates, potential sources of benzene and ethylbenzene. Cooking with natural gas without proper ventilation can also increase benzene levels, and, as described in Section 3.7.1.1.2, indoor cooking dramatically increases ultrafine particle levels. Although there are no regulatory standards for ultrafine particles, emerging evidence suggests they may be associated with respiratory illnesses.

Several recent studies have suggested that dust is a primary pathway of flame retardant exposure in children and that simple hand washing can reduce exposures. Managers of ECE facilities should encourage children to wash their hands frequently and implement frequent cleaning and vacuuming to minimize contaminated dust loading on floors. Finally, proper ventilation is important to maintain indoor air quality.

This screening health risk characterization has several limitations. As noted above, most of the compounds did not have reference health values that can be used to examine potential risk. In many cases, only oral reference dose benchmarks were available. The exposure estimates were also based on a single day of monitoring, which may not be representative of daily or annual contaminant levels.

5 Summary and Conclusions

Approximately 1.1 million California children ages 0-5 and 146,000 staff spend 40 or more hours per week in child care centers or preschools. There is virtually no information available on environmental exposures to volatile organic compounds (VOCs) or semi-volatile organic compounds such as brominated flame retardants or phthalates in California child care environments. These chemicals can exacerbate asthma and other respiratory illnesses or impair neurocognitive functioning in children. For this study, environmental inspections were conducted and air and dust samples were collected from 40 licensed early childhood education (ECE) facilities located in two California counties (Monterey and Alameda). In air, VOCs, aldehydes and acetone, phthalate esters, flame retardants, pesticides, and fine and ultrafine particles were measured. In dust, flame retardants, phthalates, perfluorinated compounds, pesticides, and metals including lead were measured. Limited outdoor air measurements were obtained as well. These measurements were used to characterize contaminant levels in the ECE facilities and estimate potential exposure and health risks. Because the VOC measurement techniques indicated a large number of unknown chemicals were also present, mass spectra libraries from the National Institute of Science and Technology (NIST) were used to identify these chemicals which were then semi-quantitatively estimated by comparing the instrument response to a toluene-based calibration curve.

Environmental Inspections

Average indoor temperature and relative humidity were within ASHRAE standards. Air exchange rates were also acceptable in most facilities (median=1.4 air changes per hour); however, 7.5% had rates below the California Building Code assumed minimum ventilation level of 0.35 air changes per hour. Carbon monoxide levels (median=2.2 ppm, max=4.0 ppm) were well within health-based guidelines. Pest problems were common (90% reported at least one pest), and 58% reported using pesticides, with 45% using broadcast application methods (e.g., sprays). Mold, rotting wood, or water damage was present in 23% of facilities, but no serious problems were observed. Overall, although pest problems (mainly ants) were common, the ECE child care environments were in good physical condition and well-maintained.

VOC air sampling results

Overall, levels of VOCs were comparable to those found in other CARB studies examining elementary school or residential environments. The VOCs measured in the highest concentrations in indoor air tended to be from cleaning agents or personal care products such

as soaps. For example, d-limonene (a solvent in cleaning products) and decamethylcyclopentasiloxane (a lubricant in soaps or lotions) were the VOCs detected at the highest concentration (median [range] = 33 [0.8-82] and 51 [2.6-88] $\mu g/m^3$, respectively). Levels of d-limonene were higher in the ECE facilities than levels measured in recent studies in homes. D-limonene, a terpene, may be a respiratory irritant, and can, along with other VOCs, react with ozone to form secondary air contaminants.

Levels of several VOCs may result in exposures that exceed health-based benchmarks. For example, indoor air concentrations of formaldehyde exceeded the 8-hour Reference Exposure Level (REL) and/or chronic REL in 87.5% of facilities (35 of 40). Acetaldehyde concentrations were lower than the California RELs, but exceeded the U.S. EPA Reference Concentration in 30% of facilities.

Additionally, indoor air concentrations of five potentially carcinogenic VOC compounds (benzene, chloroform, ethylbenzene, acetaldehyde, and formaldehyde) exceeded the age-adjusted No Significant Risk Level defined as a Safe Harbor Level (one in 100,000 excess cancer risk) by the California Office of Environmental Health Hazard Assessment for one or more of the age groups examined. For formaldehyde, the ratio of age-adjusted child dose estimates to the age-specific NSRL benchmarks ranged from 12.0 to 107.5 for the four age groups assessed (i.e., birth to <1 year; 1 to <2 years; 2 to <3 years; and 3 to <6 years). Overall, VOCs were detected more frequently and at significantly higher levels indoors compared to outdoors. The indoor VOC levels were also inversely related to ventilation rates (for example, the correlation between air exchange rates and formaldehyde concentrations was -0.59), confirming that indoor sources were important determinants of the VOC levels.

Finally, based on comparison of the unknown chemical mass spectra to the NIST libraries, it is likely that approximately 130 additional airborne chemicals were present in the ECE facilities and warrant further study.

Measurements of semi-volatile chemicals (SVOCs) in air and dust

Phthalates: Five phthalate compounds measured in carpet dust (diethyl phthalate, diisobutyl phthalate, dibutyl phthalate, butyl benzyl phthalate [BBP], and di(2-ethylhexyl phthalate [DEHP]) were detected in 100% of the samples. Three of these compounds (diethyl phthalate, diisobutyl phthalate, dibutyl phthalate) were frequently detected in air (>85% of facilities). Estimated exposures to two phthalates that have been evaluated by OEHHA for cancer (DEHP) or reproductive risk (dibutyl phthalate) were below levels of concern. Additionally, exposures to four of the phthalates (butyl benzyl phthalate, dibutyl phthalate, diethyl phthalate, DEHP) with U.S. EPA oral reference doses were also below levels of concern.

Flame Retardants: Flame retardants were detected in 100% of dust samples, including the now banned penta-PBDEs and replacement chemicals, including Firemaster 550 components and tris phosphate compounds. The median levels of two tris phosphate compounds, TDCPP (2,265 ng/g) and TCEP (319 ng/g), were similar to or higher than any of the individual PBDE congener levels. Overall, the median levels of brominated flame retardants in dust were lower than those found in other studies focusing on residential environments in California, possibly due to the frequent cleaning that occurs in ECE facilities, but maximum levels were similar to the upper-bound levels measured in other California studies.

Flame retardants have relatively low vapor pressures. Detection frequencies in air ranged from 0-95%. Exposure estimates based on air concentrations did not exceed health-based

benchmarks. Currently, of the flame retardants measured, only four (BDE-47, -99, -153, and -209) have an oral reference dose. Estimated non-dietary ingestion of these PBDEs in children ages birth to <1 year exceeded the U.S. EPA RfDs for BDE-47 and BDE-99 in 10.3% (4 of 39) of facilities. Brominated flame retardants are known endocrine disruptors and neurotoxicants. The RfDs for these PBDE congeners were established based on adverse neurobehavioral effects in animals.[168-170]

Pesticides: Pyrethroid pesticides were the most common class of insecticides stored or used in the ECE facilities, and they were detected in all ECE facilities. Consistent with reported use, pyrethroid concentrations in dust were higher than concentrations of other measured pesticides; for example, median levels of trans-permethrin were ~20 times higher than median levels of chlorpyrifos. In contrast, pyrethroids have relatively low vapor pressures, and air concentrations were lower than concentrations of the OP pesticides. Because residues of pesticides can persist indoors for long periods due to low sunlight, moisture, and biological activity, it is likely that residues of diazinon and chlorpyrifos, which are no longer approved for indoor use, were due to historical use. Pesticide exposure estimates did not exceed health-based benchmarks.

Perfluorinated compounds (PFCs): PFCs have low vapor pressures, and measurements of PFCs in air were not successful. Ten PFC compounds were measured in dust collected from the ECE facilities. The most common PFC breakdown compounds, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), were detected in 72% and 54% of facilities, respectively. PFOA exposure has been associated with increased incidence of liver, Leydig cell and pancreatic tumors in rodent bioassays. The compound is currently being tested by the National Toxicology Program (NTP)[172] and is under review for possible listing by the OEHHA Carcinogen Identification Committee.[173] Currently, there are no health-based benchmarks to evaluate the risk of PFC exposures.

Lead in Dust

Lead, a ubiquitous metal, was frequently detected in dust (95% of samples), with a median of 35 µg/g and maximum of 805 µg/g. Because U.S. EPA believes there is no safe level of exposure to lead, there is no defined reference dose. U.S. EPA defines a threshold of 40 µg/square foot for indoor contamination.[154] However, this threshold is based on a wipe sample, and therefore is not comparable to the vacuum sampling methods used for this study. No U.S. public health agency has defined a threshold for acceptable concentrations of lead in house dust. More than 95% of the dust samples in this study were below 400 parts per million, the threshold for lead in soil that children directly play in.

Child lead exposure estimates exceeded child-specific cancer NSRL benchmarks computed for this report in 95% of the facilities. Although lead has been evaluated for cancer risks, the primary concern for children is developmental toxicity. Because U.S. EPA believes there is no safe level of exposure to lead, there is no defined reference dose.

Particle Monitoring in Air

Several measurements of particles in air were completed in each child care facility, including continuous measurements of very small ultrafine particles (UFP)(down to 6 nanometers), coarse particulate matter less than 10 micrometers (PM_{10}), and fine particulate matter less than 2.5 micrometers ($PM_{2.5}$).

Ultrafine particles: The average indoor UFP levels (22,327/ccm) were higher than those reported in a recent study of California elementary schools (average=10,800/ccm indoors). Ultrafine particle levels were higher indoors and uncorrelated with outdoor sources. Median indoor UFP levels in center-based facilities (11,997/ccm) were lower compared to home-based facilities (39,071/ccm), where more cooking occurred. UFP levels increased dramatically, up to three orders of magnitude, for short periods during gas stove use. Currently, there are no health-based standards defining acceptable UFP levels; however, these particles may increase lung inflammation and exacerbate asthma. Additional research is needed on the health effects and mitigation of ultrafine particles in air.

Coarse and Fine Particulate Matter (PM): Median indoor and outdoor air levels of PM_{10} were 47.6 and 28.9 μg/m^3, respectively, and, for $PM_{2.5}$, were 15.0 and 16.2 μg/m^3, respectively. Indoor and outdoor $PM_{2.5}$ levels were strongly correlated, suggesting that indoor $PM_{2.5}$ levels were largely derived from outdoor air. Indoor PM_{10} concentrations exceeded the 24-hour California Ambient Air Quality Standard (CAAQS) in 46% of ECE facilities, while the indoor $PM_{2.5}$ concentrations exceeded the 24-hour National Ambient Air Quality Standard (NAAQS) in 13% of ECE facilities (there is no 24-hour CAAQS for $PM_{2.5}$). It should be noted that the measurements in this study were conducted over an 8-10 hour period, and do not necessarily represent the levels children were exposed to for a full 24-hour period the duration of the exposure period defined in the air quality standards. However, the monitoring suggests many young children are experiencing a significant portion of total PM_{10} exposures in child care facilities and that exposure mitigation may be warranted.

Potential Sources of Indoor Chemical Contaminants

Sources of many of the measured chemicals in air include building materials, furnishings, and consumer products. For example, the primary sources of formaldehyde are believed to be composite wood products such as medium density fiberboard, particle board, and plywood. Other sources include certain types of foam insulation, textiles, paints and sealants, and indoor combustion sources such as unvented gas stoves. Several VOCs with relatively high levels, such as d-limonene and decamethyl-cyclopentasiloxane, are often used in cleaners or personal care products. Sources of benzene, ethylbenzene and several related VOCs are likely due to nearby traffic and vehicle fuel evaporation, as well as indoor combustion sources, paints, and cleaners containing petroleum distillates. Sources of chloroform include vaporization from chlorinated tap water and consumer products containing bleach for sanitization purposes.

Many of these sources were present in the ECE facilities tested. For example, 88% (35 of 40) of the facilities contained pressed wood or plywood; 28% of the facilities had indoor gas stoves located in child care areas; and two home-based facilities had gas stoves with no functioning fan. Bleach (sodium hypochlorite) was a component of cleaners or sanitizers in 26 (65%) of the facilities. Other sources of measured VOCs include consumer products used or stored in the facilities. For example, 135 chemical ingredients were identified in a variety of consumer products, including personal care products (hand soaps), cleaners, sanitizers, air fresheners, paints, pesticides, etc.

Indoor sources are also important for the less volatile chemicals measured in air, including phthalates, flame retardants, and pesticides, all of which were commonly detected in indoor air or dust. Phthalates have historically been used in plastics, toys, certain building products, and personal care products. Flame retardants are heavily used in furnishings and electronics to comply with the California Bureau of Electronic and Appliance Repair, Home Furnishings, and Thermal Insulation flammability standards defined in Technical Bulletin 117. Pyrethroid

pesticides are the most common class of pesticides used indoors since most residential and structural uses of diazinon and chlorpyrifos were phased out between 2002 and 2004. It is likely that indoor residues of diazinon and chlorpyrifos were due to historical use. Finally, the higher levels of dacthal in ECE facilities located in agricultural areas suggest contamination from nearby agricultural pesticide use.

Conclusions

For this study, extensive environmental monitoring of 40 Early Childhood Education (ECE) facilities in northern California was performed and dozens of toxicants were measured in the air and dust. Overall, levels of contaminants were similar to levels in other indoor environments and most exposures were below health-based benchmarks when they were available. For most chemicals, however, no health screening information was available.

The risk evaluation identified five VOCs (benzene, chloroform, ethylbenzene, acetaldehyde, and formaldehyde) and one metal in dust (lead) that exceeded age-specific OEHHA Safe Harbor guidelines for cancer computed by the report authors. Formaldehyde levels also exceeded OEHHA 8-hour and chronic reference exposure levels (RELs). In addition, levels of acetaldehyde, while lower than the California RELs, exceeded the U.S. EPA reference concentration. Finally, estimated exposures to two brominated flame retardants (BDE-47 and BDE-99) exceeded the U.S. EPA non-cancer reference dose (RfD).

While regulatory steps have been taken to reduce indoor sources of formaldehyde (Section 93120-93120.12, Title 17, California Code of Regulations), more action may be needed. Mitigation measures are also warranted to reduce exposure to other compounds that exceeded health-based benchmarks. Additionally, UFP levels were shown to increase dramatically when gas stoves were used for cooking, especially when no functioning fan was present. If these high levels are shown to cause respiratory or other health problems in young children, CARB may want to consider recommending steps to mitigate these exposures.

In summary, given the overriding interest in providing safe and healthy environments for young children, additional research is needed to identify strategies to reduce indoor sources of chemicals and particulate matter that may pose hazards. This information will be important for targeted education and outreach efforts to successfully improve the public health of young children receiving child care in California's ECE facilities.

6 Strengths and Limitations

This study is the first and largest in California and nationally to examine particulate matter and a broad spectrum of chemical contaminants, including emerging pollutants such as flame retardants, phthalates, and perfluorinated compounds, in ECE facilities. The purpose of the study was to obtain a "snapshot" of the environmental quality in ECE facilities in California. Due to costs, the sample size was limited to 40 ECE facilities in two counties, which limits the power to draw inferences. Another important limitation of the study is that only one day of data was collected at each site. Thus, results may not reflect contaminant levels on other days, long-term averages, or seasonal variation.

Challenges in recruitment were another limitation. Participation rates among child care centers was less than 5% of those contacted, and the participation rate of home-based child care facilities was even lower. Low recruitment rates may have resulted in selection bias in the

study. In general, directors of the enrolled ECE facilities were interested in environmental risks to children's health and may have previously implemented policies to minimize the use of contaminant sources. Despite these limitations, the participating centers represent a broad cross-section of institutions providing child care in California, including Head Start facilities, public school district facilities, private centers, and child care homes; the children were also typical of California populations, representing low-income, immigrant, and middle class families. Increasing the number of participating ECE facilities and expanding the geographic distribution would improve generalizability of the findings to the state as a whole.

7 Recommendations

The research team recommends the following, based on the study results:

1. Additional research on levels of contaminants in indoor air in ECE facilities is warranted, including sampling over longer periods to assess long-term averages and trends, seasonal impacts, and to identify indoor sources.

    a. If, based on more comprehensive monitoring, cumulative exposures to formaldehyde in child care exceed California RELs and/or Proposition 65 No Significant Risk (NSRL) Safe Harbor Levels for carcinogenicity, mitigation measures beyond current rules (Section 93120-93120.12, Title 17, California Code of Regulations) should be considered.

    b. Other VOCs that exceeded the child-specific NSRL should be a priority for future research (benzene, chloroform, ethylbenzene, acetaldehyde).

    c. Levels of d-limonene were higher in the ECE facilities compared to levels measured in recent studies of homes. D-limonene, a terpene, may be a respiratory irritant, and can, along with other VOCs, react with ozone to form secondary air contaminants. Additional research is warranted to evaluate the contribution of d-limonene to secondary contaminants and potential health risks.

    d. In addition to the *a priori* target list of VOC analytes in air, hundreds of other VOCs were identified as likely present in the ECE facilities. A priority for future research should be to measure the levels and potential health risks of these contaminants.

2. Ultrafine particle levels were higher in the ECE facilities compared to elementary schools, primarily due to increased levels in home-based facilities with gas stoves. Research is needed to assess the health impacts of these exposures. As a precautionary step, and given that simple methods are available to reduce these levels (e.g., fan use), outreach to increase ventilation when cooking in home-based child care facilities should be considered.

3. Estimated exposures to two brominated flame retardants (BDE-47 and BDE-99) exceeded the U.S. EPA non-cancer reference dose (RfD) for some children. These congeners of the penta-BDE flame retardant mixture are no longer approved for use in California. However, replacement flame retardant chemicals were present in all facilities sampled. The potential health risks to children of individual and mixed exposures to the brominated and organophosphate flame retardants should be formally assessed.

4. Most of the chemicals measured have not been evaluated for potential health impacts and no health-based exposure benchmarks were available to assess risks. A screening health review of the chemicals present in the ECE facilities should be completed to target compounds for further toxicological review.

5. Given the overriding interest in providing safe and healthy environments for young children, outreach to child care providers and professional groups focusing on strategies to improve indoor air quality should be increased.

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Glossary of Terms, Abbreviations, and Symbols

Acronym	Description
^{o}C	Degree Celsius
[C]	Concentration (units vary)
∑GATV	Sum of Gauss-Adjusted Traffic Volume
∑LATV	Sum of Length-Adjusted Traffic Volume
CAAQS	California Ambient Air Quality Standard
AER	Air Exchange Rate
Al	Aluminum
aREL	Acute Reference Exposure Level
ASHRAE	American Society of Heating, Refrigerating and Air-conditioning Engineers
ASF	Age Sensitivity Factor
ASTM	American Society for Testing Materials
BBP	Butyl Benzyl Phthalate
BDE	Brominated Diphenyl Ether
BEHTBP	Bis(2-Ethylhexyl)tetrabromophthalate
BFR	Brominated Flame Retardant
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
BW	Body Weight
CARB	California Air Resource Board
CCLD	Community Care Licensing Division
ccm	Cubic Centimeter
Cd	Cadmium
CDPH	California Department of Public Health
CDSS	California Department of Social Services
CEHTP	California's Environmental Health Tracking Program
CERCH	Center for Environmental Research and Children's Health
cRfD	Chronic Reference Dose
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CPC	Condensation Particle Counter
CPIC	Cancer Prevention Institute of California
CPSC	Consumer Products Safety commission
Cr	Chromium
Cu	Copper
cREL	Chronic Reference Exposure Level
CSEFH	US EPA *Child-Specific Exposure Factors Handbook Final Report (2008)*
DBP	Dibutyl Phthalate
DEP	Diethyl Phthalate
DEHP	Di(2-Ethylhexyl) Phthalate

Acronym	Description
DIBP	Diisobutyl Phthalate
DT	DustTrak
ECE	Early Childhood Education
EHTBB	2-Ethylhexyl Tetrabromobenzoate
EIC	Extracted Ion Chromatogram
ESI	Electrospray Ionisation
Fe	Iron
FQPA	Food Quality Protection Act
g	Gram
GC	Gas Chromatography
H_2O_2	Hydrogen Peroxide
HNO_3	Nitric Acid
HPLC	High Performance Liquid Chromatography
Hr	Hour
HVAC	Heating, Ventilation, and Air Conditioning
HVS3	High Volume Small Surface Sampler
IARC	International Agency for Research on Cancer
ICP	Inductive Coupled Plasma
IED	Indoor Environment Department
Inh	Inhalation
km	kilometer
LATV_HS	Length-Adjusted Traffic Volume of Highest Segment
LBNL	Lawrence Berkeley National Laboratory
LFCCH	Large Family Child Care Homes
LOQ	Limit of Quantification
lpm	Liters Per Minute
m	Meter
MADL	Maximum Allowable Dose Level
Max	Maximum
MDL	Method Detection Limit
mg	Milligram
MID	Modified Isotope Dilution
ml	Milliliter
MLD	Monitoring and Laboratory Division
mM	Millimolar
Mn	Manganese
MPa	Megapascal (1 MPa ≡ 1,000,000 Pa)
MS	Mass Spectroscopy
MSE	Mean Squared Error
NAAQS	National Ambient Air Quality Standard

Acronym	Description
NERL	National Exposure Research Laboratory
ng	Nanogram
NHANES	National Health and Nutrition Examination Survey
NIST	National Institute of Standards and Technology
nm	Nanometer
NSRL	No Significant Risk Level
OEHHA	Office of Environmental Health Hazard Assessment
OES	Optical Emission Spectrometry
OP	Organophosphates
PAD	Population Adjusted Dose
Pb	Lead
PBDE	Polybrominated Diphenyl Ether
PEM	Personal Environmental Monitor
PFBA	Perfluorobutyric Acid
PFBS	Perfluorobutane Sulfonate
PFC	Perfluorinated Compound
PFDA	Perfluorodecanoic Acid
PFHpA	Perfluoroheptanoic Acid
PFHxA	Perfluorohexanoic Acid
PFHS	Perfluorohexane Sulfonate
PFNA	Perfluorononanoic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonic Acid
PFPeA	Perfluoropentanoic Acid
PM	Particulate Matter
PM_{10}	Particulate matter with an aerodynamic diameter of less than or equal to 10 micrometer
$PM_{2.5}$	Particulate matter with an aerodynamic diameter of less than or equal to 2.5 micrometer
ppb	Parts per billion
ppm	Parts per million
PUF	Polyurethane Foam
QA	Quality Assurance
QA/QC	Quality Assurance and Quality Control
REL	Reference Exposure Level
RfC	Reference Concentrations
RfD	Reference Dose
RH	Relative Humidity
RSD	Relative Standard Deviation
SD	Standard Deviation
SFCCH	Small Family Child Care Homes

Acronym	Description
SIM	Selective Ion Monitoring
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
SRS	Surrogate Recovery Standards
SVOC	Semi- Volatile Organic Compounds
TD	Thermally Desorbed
TAC	Toxic Air Contaminant
TCEP	Tris (2-Chloroethyl) Phosphate
TDCPP	Tris (1,3-Dichloro-2-Propyl) Phosphate
TIC	Total Ion Chromatogram
TSI	Texas Science Instruments
TVOC	Total Volatile Organic Compounds
U.S. EPA	United States Environmental Protection Agency
U.S. HUD	United States Department of Housing and Urban Development
µg	Microgram
µm	Micrometer
UPLC	Ultra Performance Liquid Chromatography
VOC	Volatile Organic Compound
Y	Yttrium
Zn	Zinc

APPENDIX A- Supplemental Tables and Figures

Sampling Information Supplemental

Table 103. Visit Dates for Child Care Centers and Homes

ECE	1st Site Visit Date	2nd Site Visit Date	Additional Sample Date	ECE	1st Site Visit Date	2nd Site Visit Date	Additional Sample Date
10	5/21/2010	6/1/2010	6/16/2010[1]	30	1/11/2011	1/13/2011	
11	6/18/2010	6/22/2010		31	1/12/2011	1/14/2011	
12	7/7/2010	7/8/2010		32	1/18/2011	1/21/2011	
13	7/7/2010	7/14/2010		33	1/21/2011	2/4/2011	
14	7/16/2010	7/21/2010		34	2/8/2011	1/29/2011	
15	7/20/2010	8/3/2010	9/14/2010[2]	35	2/28/2011	1/31/2011	
16	8/2/2010	8/4/2010		36	2/1/2011	2/9/2011	
17	8/12/2010	3/4/2011		37	2/11/2011	2/11/2011	
18	8/24/2010	11/2/2010		38	2/23/2011	3/2/2011	
19	9/16/2010	11/4/2010		39	2/28/2011	3/9/2011	
20	11/9/2010	2/16/2011		40	3/25/2011	3/25/2011	4/8/2011[3]
21	11/11/2010	11/18/2010		41	3/24/2011	3/30/2011	
22	11/23/2010	12/15/2010		42	3/16/2011	3/21/2011	
23	11/23/2010	12/7/2010		43	3/16/2011	3/18/2011	
24	11/29/2010	11/30/2010		44	3/29/2011	4/1/2011	
25	11/29/2010	12/1/2010		45	4/6/2011	4/27/2011	
26	12/8/2010	12/17/2010		46	4/21/2011	4/22/2011	
27	12/13/2010	12/28/2010		47	4/21/2011	5/6/2011	
28	12/14/2010	12/29/2010		48	5/3/2011	5/13/2011	
29	1/5/2011	1/7/2011		49	5/4/2011	5/12/2011	

[1]ECE 10 was visited a third time to re-sample VOCs using the original SOP for VOC collection onto multibed sorbent tubes with a primary bed of Tenax-TA® sorbent backed with a section of Carbosieve™.
[2]ECE 15 was revisited to re-sample using the new VOC SOP of collecting onto separate Tenax-TA® and CarboTrap™ tubes.
[3]ECE 40 was revisited to sample for pesticides in air which was not completed at the previous visit. Four PUFs were sampled indoors for pesticides and PBDEs (which allowed for QA duplication) along with two outdoor samples for the same analytes.

Table 104. List of Real-time Devices Deployed by ECE (Dark Box Indicates Device Deployed and Valid Data)

	CPC			DustTrak		QTrak		
ECE	Indoor	Outdoor	Indoor Duplicate	Indoor	Outdoor	Indoor	Outdoor	Indoor Duplicate
10	■			■		■		
11	■			■		■		■
12	■		■	■		■		■
13	■			■		■		■
14	■			■		■		
15	■			■		■		
16	■			■		■		
17	■	■		■	■	■	■	
18	■			■		■	■	
19	■			■		■	■	
20	■	■		■	■	■	■	
21	■	■		■	■	■		
22	■			■	■	■	■	
23	■	■		■	■	■	■	
24	■			■	■	■	■	
25	■	■		■	■	■	■	
26	■	■		■	■	■	■	
27	■			■	■	■	■	
28	■	■		■	■	■	■	
29	■	■		■	■	■	■	
30	■	■		■	■	■	■	
31	■	■		■	■	■	■	
32	■	■		■	■	■	■	
33	■	■		■	■	■	■	
34	■	■		■	■	■	■	
35	■	■		■	■	■	■	
36	■	■		■	■	■	■	
37	■	■		■	■	■	■	
38	■	■		■	■	■	■	
39	■	■		■	■	■	■	
40	■	■		■	■	■		
41	■	■		■	■	■	■	
42	■	■		■	■	■	■	
43	■	■		■	■	■	■	
44	■	■		■	■	■	■	
45	■	■		■	■	■	■	
46	■	■		■	■	■	■	
47	■	■		■	■	■	■	
48	■	■		■	■	■	■	
49	■	■		■	■	■	■	
TOTAL	39	28	1	40	31	40	30	3

VOC Supplemental

Table 105. Results of Wilcoxon Signed Rank Test Comparing Indoor and Outdoor VOC Concentrations

	Indoor Concentration Greater than Outdoor Concentration?	
Analyte	**Wilcoxon p-value**	**Significant?**
Hexane	0.015	Yes
Methylene chloride	.	No
Carbon tetrachloride	.	No
Chloroform	0.0051	Yes
Benzene	0.48	No
Butanal	0.0001	Yes
Heptane	0.0001	Yes
Octane	0.0001	Yes
Toluene	0.0001	Yes
Hexamethylcyclotrisiloxane	0.42	No
Tetrachloroethylene	0.0703	No
Hexanal	0.0001	Yes
Ethylbenzene	0.0001	Yes
m/p-Xylene	0.0006	Yes
a-Pinene	0.0001	Yes
o-Xylene	0.0002	Yes
Octamethylcyclotetrasiloxane	0.0002	Yes
Heptanal	0.0001	Yes
Decane	0.0001	Yes
2-Butoxyethanol	0.0001	Yes
3-Carene	0.0002	Yes
Trimethylbenzene (1,2,4)	0.0006	Yes
d-Limonene	0.0001	Yes
Trimethylbenzene (1,2,3)	0.03	Yes
g-Terpinene	0.0019	Yes
Benzaldehyde	0.14	No
Octanal	0.0001	Yes
Undecane	0.0002	Yes
Butylbenzene	0.32	No
Decamethylcyclopentasiloxane	0.0001	Yes
2-Ethyl-1-hexanol	0.0001	Yes
Nonanal	0.0001	Yes
Dodecane	0.0001	Yes

Table 105 Continued. Results of Wilcoxon Signed Rank Test Comparing Indoor and Outdoor VOC Concentrations

Decanal	0.0001	Yes
a-Terpineol	0.0002	Yes
Tetradecane	0.0001	Yes
Texanol	0.0001	Yes
Hexadecane	0.0001	Yes
TXIB	0.0001	Yes

Flame Retardant Supplemental

Table 106. Mann-Whitney Signed Rank Test Comparing Flame Retardant Indoor Air Concentrations by Facilities with Upholstered Furniture and Napping Equipment made out of Foam in the Child Care Room

Question:	**Upholstered Furniture Present?**	**Napping Equipment Made Out of Foam?**
Analyte	**p-value**	**p-value**
BDE-47	0.97	0.10
BDE-99	0.41	0.08
BDE-100	0.28	0.16
BDE-153	0.48	0.38
BDE-154	0.91	0.91
TCEP	0.69	0.21
TDCPP	0.25	0.05
EHTBB	0.78	0.05
BEHTBP	0.91	0.56

Table 107. Mann-Whitney Signed Rank Test Comparing Flame Retardant Dust Concentrations by Facilities with Upholstered Furniture and Napping Equipment made out of Foam in the Child Care Room

Question:	Upholstered Furniture Present?	Napping Equipment Made Out of Foam?
Analyte	**p-value**	**p-value**
BDE-47	0.38	0.14
BDE-99	0.36	0.18
BDE-100	0.27	0.25
BDE-118	0.59	0.33
BDE-153	0.27	0.28
BDE-154	0.17	0.21
BDE-183	0.61	0.17
BDE-190	0.38	0.33
BDE-197	0.84	0.04*
BDE-203	0.06	0.37
BDE-206	0.03	0.74
BDE-207	0.02*	0.79
BDE-209	0.007*	0.69
∑ BDE	0.05	0.32
TCEP	0.76	0.04*
TDCPP	0.86	0.03*
EHTBB	0.98	0.95
BEHTBP	1.00	0.60

* p-value<0.05

Pesticide Supplemental

Table 108. Comparison of Indoor Air Pesticide Concentrations by ECE Type

	Home (n=12)					Center (n=28)				
	>MDL (%)	25th % (ng/m³)	Median (ng/m³)	75th % (ng/m³)	Max (ng/m³)	>MDL (%)	25th % (ng/m³)	Median (ng/m³)	75th % (ng/m³)	Max (ng/m³)
Diazinon	66.7	<MDL	0.05	0.11	0.30	82.1	0.01	0.05	0.18	3.00
Chlorpyrifos	100	0.15	0.27	0.38	0.58	92.9	0.17	0.24	0.47	1.36
Dacthal	58.3	<MDL	0.10	0.39	1.19	60.7	<MDL	0.20	0.61	1.89
Imiprothrin	8.3	<MDL	<MDL	<MDL	2.91	17.9	<MDL	<MDL	<MDL	5.50
Piperonyl butoxide	58.3	<MDL	0.01	0.14	5.45	35.7	<MDL	<MDL	0.01	0.30
Bifenthrin	25.0	<MDL	<MDL	0.09	0.41	7.1	<MDL	<MDL	<MDL	0.25
Sumithrin	16.7	<MDL	<MDL	<MDL	1.16	0.0	<MDL	<MDL	<MDL	<MDL
cis-Permethrin	50.0	<MDL	0.05	0.24	0.57	64.3	<MDL	0.04	0.14	0.40
trans-Permethrin	100	0.08	0.13	0.22	0.88	100	0.07	0.14	0.22	0.31
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL
Cypermethrin	0.0	<MDL	<MDL	<MDL	<MDL	0.0	<MDL	<MDL	<MDL	<MDL

Table 109. Summary of Pesticide Concentrations in Dust by ECE Type

	Home (n=11)					Center (n=28)				
	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)	>MDL (%)	25th % (ng/g)	Median (ng/g)	75th % (ng/g)	Max (ng/g)
Diazinon	90.9	2.8	5.0	6.3	27.8	92.9	2.7	3.4	5.3	74.1
Chlorpyrifos	90.9	6.0	9.9	19.6	217.4	92.9	7.1	11.1	18.6	563.4
Dacthal	72.7	<MDL	3.4	16.8	51.2	100.0	3.7	9.0	22.7	73.8
Imiprothrin	54.6	<MDL	144.3	222.5	459.5	25.0	<MDL	<MDL	125.2	1,739.8
Piperonyl butoxide	100.0	57.5	145.9	613.6	24,629	92.9	37.6	73.6	115.9	390.7
Bifenthrin	100.0	44.6	54.6	79.3	106.3	89.3	39.8	60.2	203.1	927.6
Sumithrin	27.3	<MDL	<MDL	41.9	322.6	17.9	<MDL	<MDL	<MDL	1,299.0
cis-Permethrin	100.0	104.4	164.9	498.4	939.7	100.0	113.6	160.6	257.5	12,712
trans-Permethrin	100.0	141.4	247.9	859.2	1,500.9	100.0	155.0	221.0	391.6	21,058
Cyfluthrin	0.0	<MDL	<MDL	<MDL	<MDL	7.1	<MDL	<MDL	<MDL	739.2
Cypermethrin	36.4	<MDL	<MDL	317.5	421.0	42.9	<MDL	<MDL	383.1	35,898

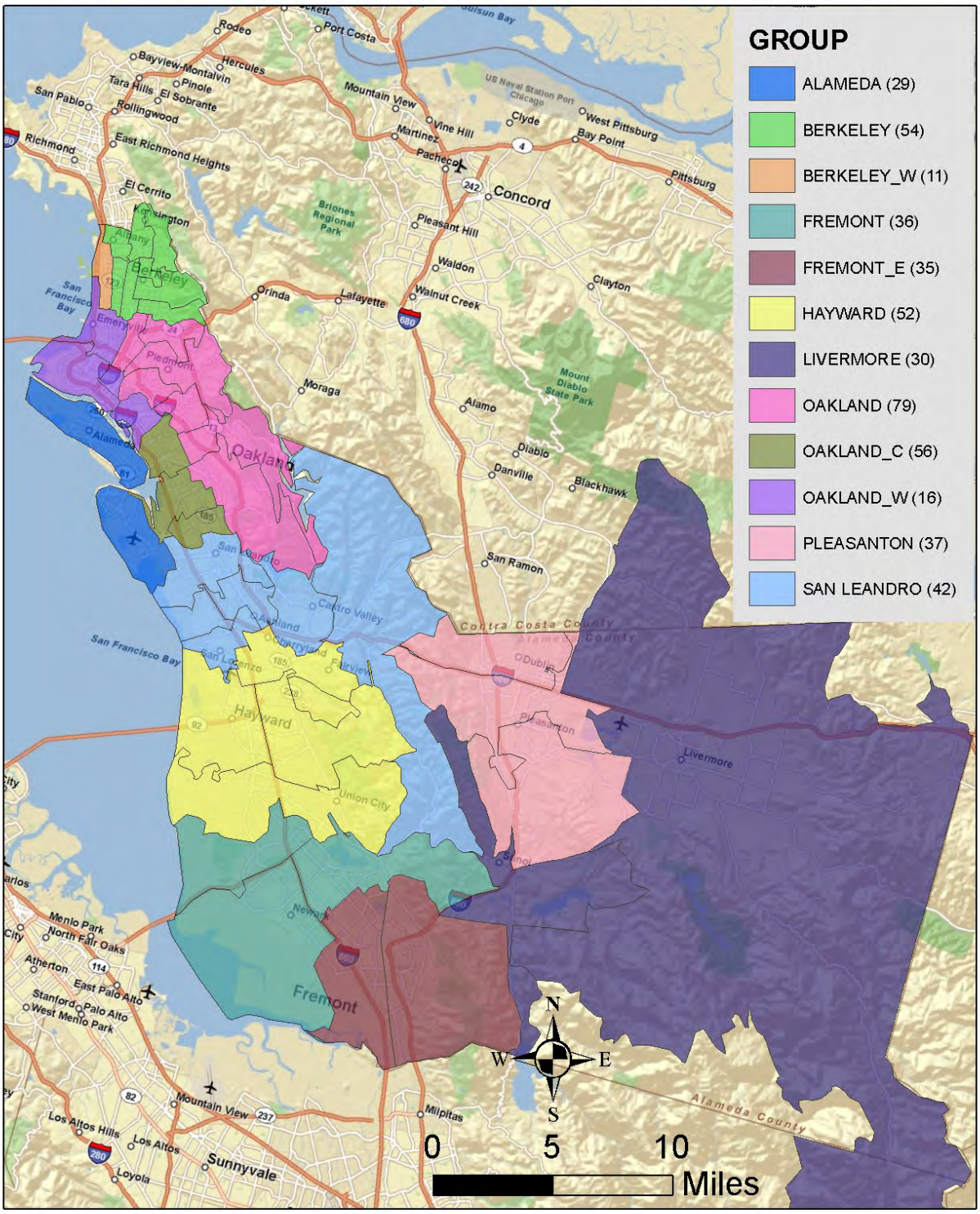
Health Risk Characterization Supplementary Tables

Table 110. Calculated Ratios of 50th and 95th Percentile VOC Dose Estimates for Adult Women Compared to MADLs, When Available

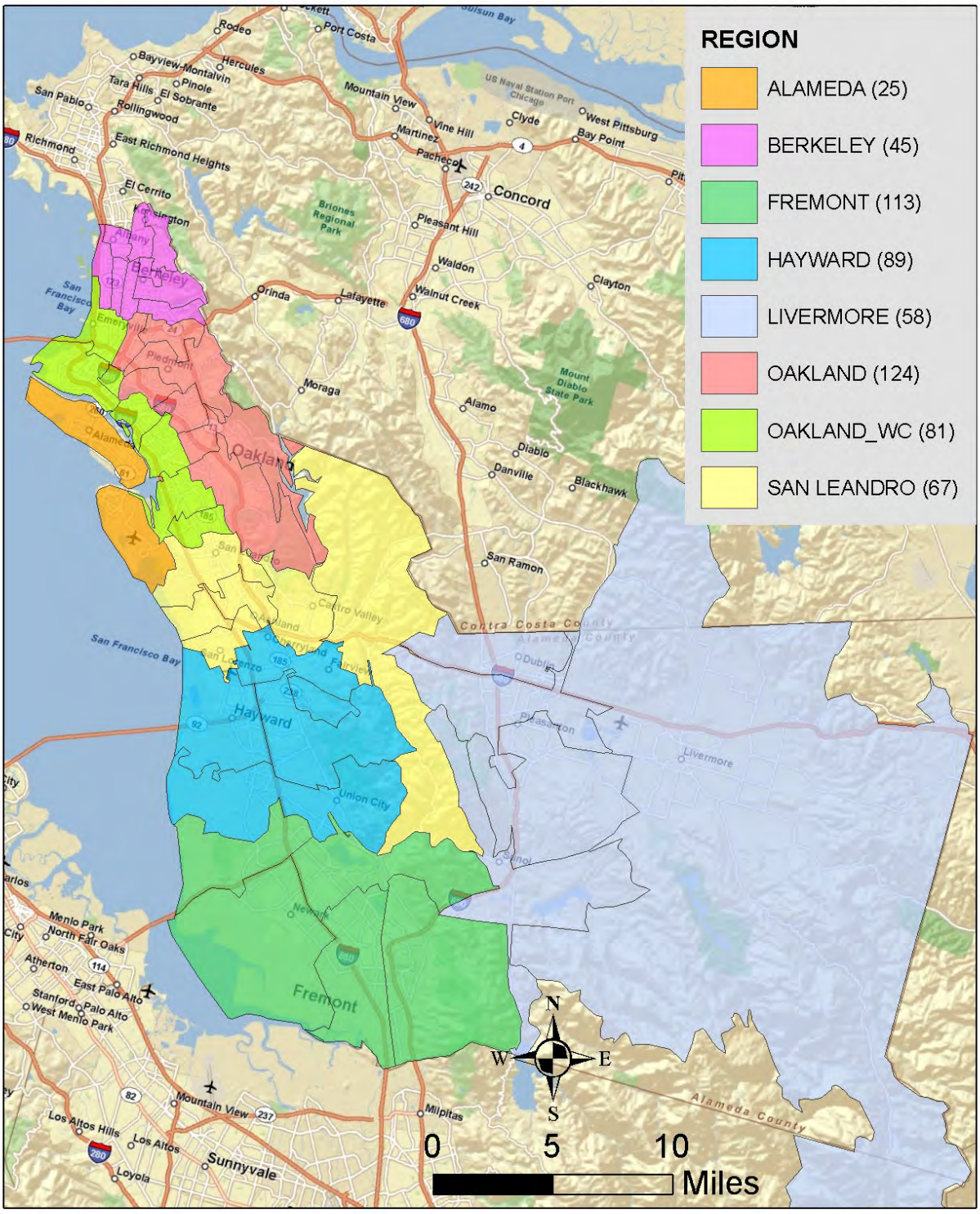
	Women of Ages 16-41						
	Dose estimates (mg/kg/day)		Adjusted estimates (µg/day)		MADL (µg/day)	Ratio 50th %	Ratio 95th %
	50th %	95th %	50th %	95th %			
VOC							
Benzene	3.58E-06	8.45E-05	2.53	5.99	24 (oral)	0.11	0.25
					49 (inhalation)	0.05	0.12
Toluene	0.00013	0.0005	9.07	33.22	6,525 (absorbed)	0.001	0.005
					13,000 (inh)	0.0007	0.0026
Phthalates							
Dibutyl phthalate	2.17E-05	0.0001	1.54	7.14	8.7 (oral & inhalation)	0.18	0.82
Di(2-ethylhexyl) phthalate	4.19E-07	1.59E-05	0.030	1.13	4,200 (IV)	7.07E-06	0.0003
					410 (oral)	7.24E-05	0.0027

APPENDIX B- Group Maps

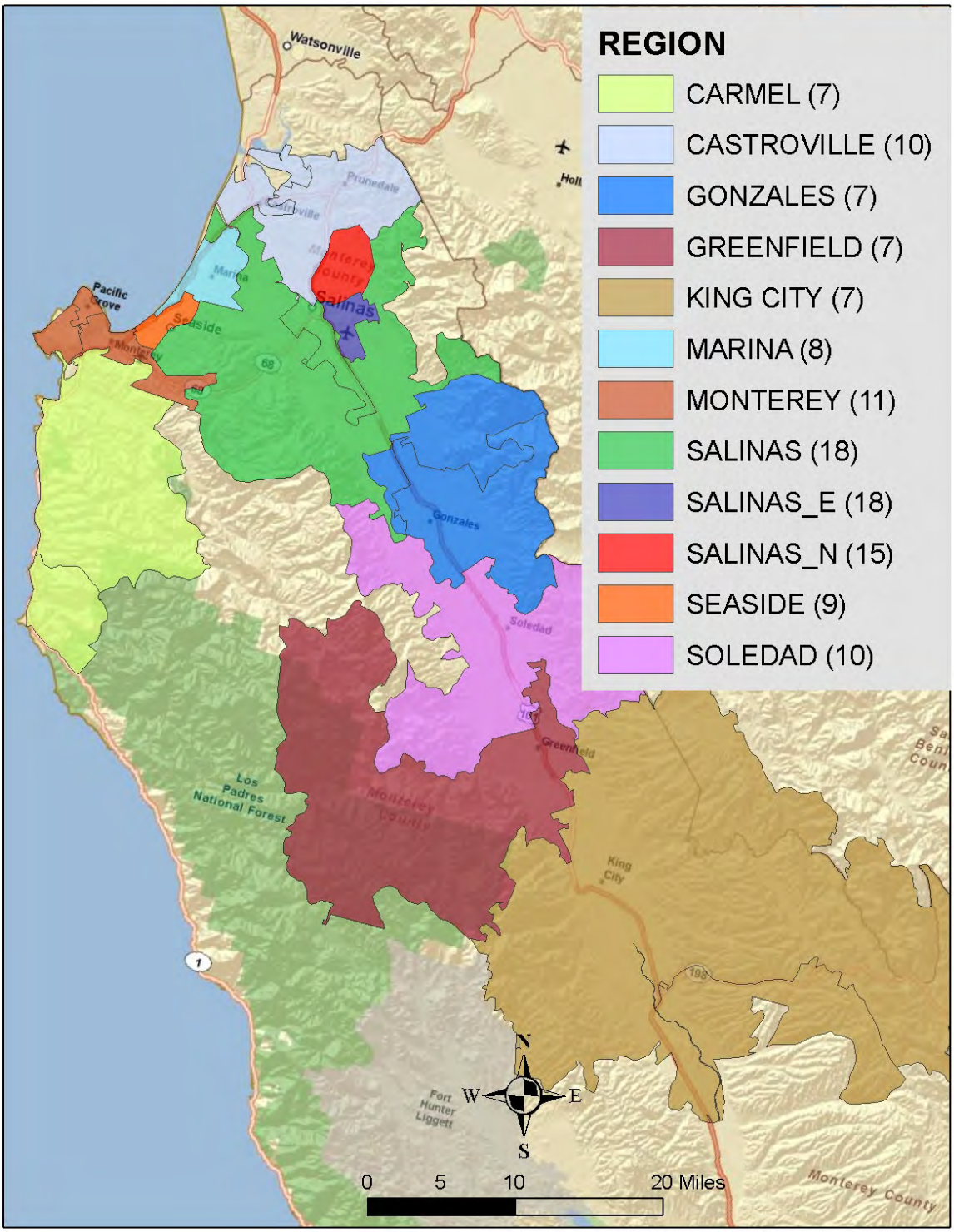
ALAMEDA COUNTY CHILD CARE CENTERS



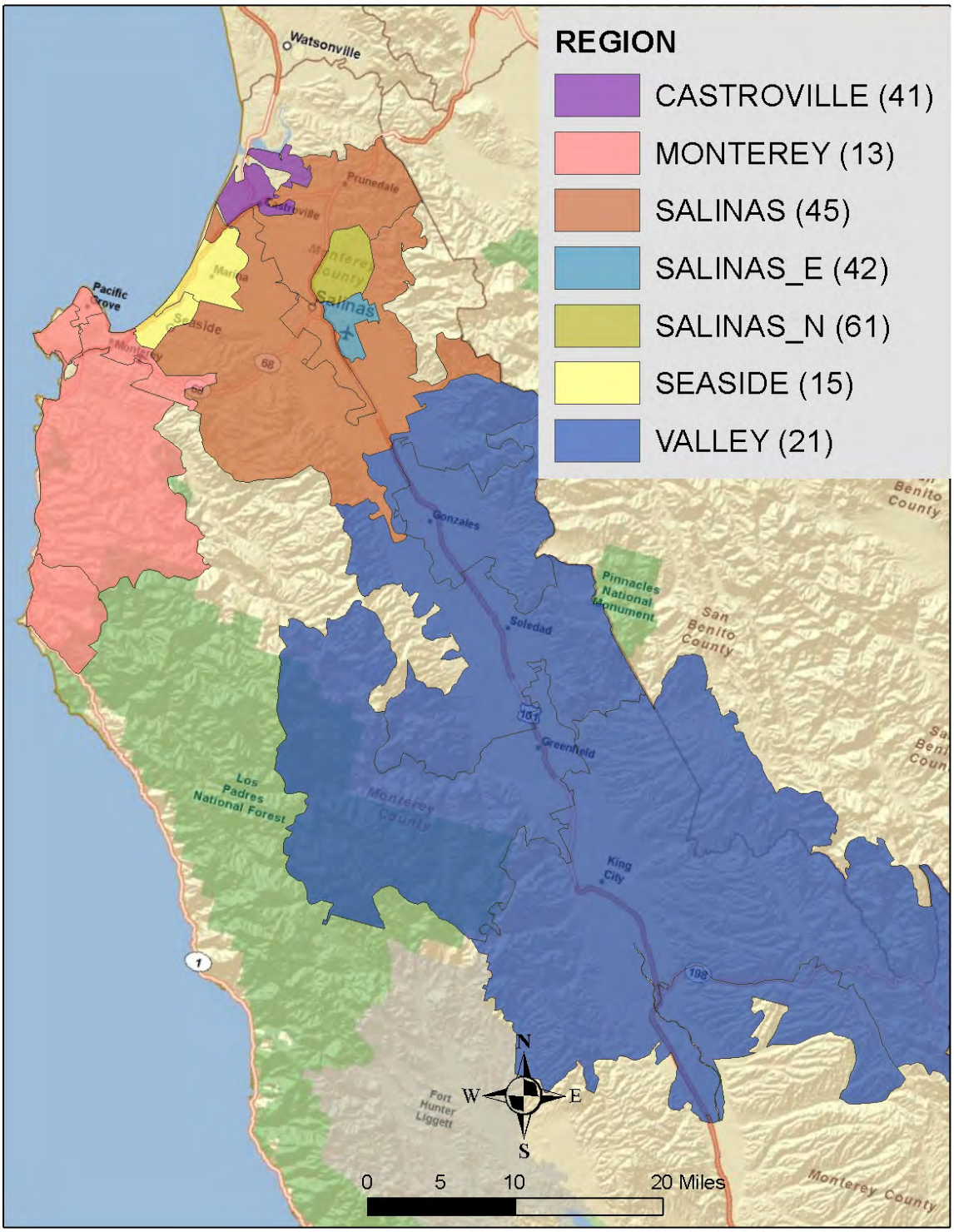
ALAMEDA COUNTY FAMILY CHILD CARE HOMES



MONTEREY COUNTY CHILD CARE CENTERS



MONTEREY COUNTY FAMILY CHILD CARE HOMES



APPENDIX C- Additional QA/QC Information

VOC QA/QC

The VOC MDLs are presented in Table 111 with the calibration range of each VOC analyte. Calibration ranges are the low and high masses from laboratory prepared standards. MDL and low/high calibration masses are converted to µg/m³ by dividing the mass by the average sample volume collected in this study for indoor VOC measurements (~7 liters). VOC MDLs ranged from 0.03 µg/m³ to 1.80 µg/m³. For four compounds (D4 and D5 siloxanes, d-limonene, and 2-butoxyethanol) in 29 cases, the VOC levels were above the calibration high mass. In those cases, the mass above the range was substituted with the high calibration mass. Three Tenax travel spikes were prepared with a Level 4 calibration standard (~100ng) in 1 µL of methanol then purged with 2L of He. Travel spikes were prepared, brought into the field, and returned to the laboratory to quantify recovery.

Table 111. MDL and Calibration Ranges for VOC Analytes

Analyte	MDL (µg/m³)[1]	Low Mass Calibration (µg/m³)	High Mass Calibration (µg/m³)
Hexane*	0.44	0.9	57
Methylene Chloride*	0.36	1.0	57
Carbon tetrachloride*	0.72	1.1	69
Chloroform*	0.46	1.1	64
Benzene	0.58	0.9	56
Butanal	0.06	0.5	74
Heptane	0.07	0.5	71
Octane	0.04	0.5	74
Toluene	0.05	0.5	74
Hexamethylcyclotrisiloxane	1.80	0.6	92
Tetrachloroethylene	0.07	0.5	80
Hexanal	0.07	0.5	74
Ethylbenzene	0.04	0.5	73
m/p-Xylene	0.08	0.5	73
a-Pinene	0.05	0.5	73
o-Xylene	0.07	0.5	73
Octamethylcyclotetrasiloxane	0.18	0.5	73
Heptanal	0.06	0.5	72
Decane	0.13	0.5	71
2-Butoxyethanol	0.07	0.5	76
3-Carene	0.03	0.5	71
Trimethylbenzene (1,2,4)	0.05	0.5	75
d-Limonene	0.03	0.5	71
Trimethylbenzene (1,2,3)	0.04	0.5	75
g-Terpinene	0.03	0.5	70
Benzaldehyde	0.27	0.5	74
Octanal	0.09	0.5	75

Analyte	MDL (µg/m³)[1]	Low Mass Calibration (µg/m³)	High Mass Calibration (µg/m³)
Undecane	0.22	0.5	73
Butylbenzene	0.04	0.5	73
Decamethylcyclopentasiloxane	0.06	0.5	73
2-Ethyl-1-hexanol	0.06	0.5	71
Nonanal	0.09	0.5	73
Dodecane	0.21	0.5	73
Decanal	0.09	0.5	76
a-Terpineol	0.05	0.5	72
Tetradecane	0.06	0.5	70
Texanol	0.05	0.5	74
Hexadecane	0.07	0.5	71
TXIB	0.07	0.5	70

[1] Assuming typical sample volume of 7 liters

For the first six ECE facilities, VOCs were collected onto multibed sorbent tubes with a primary bed of Tenax-TA® sorbent backed with a section of Carbosieve™. At each of the first six facilities except ECE#11, VOC results had a large contaminant peak early in the chromatogram that invalidated the run. We returned a second time to ECE#10 and collected duplicate VOC samples using peristaltic pumps (original samples were collected with the rotary vane pump manifold described in methods). These duplicate samples also had problems with low recovery of the internal standard and shifting retention times indicating the presence of large contamination in the sample that was eluting during the solvent delay period but that was adversely impacting the results. Identification of these unknown contaminant peaks with a NIST mass spectral library search was inconclusive but suggested a low molecular weight alcohol such as ethyl alcohol or isopropyl alcohol. To address the contamination issue, we ran experiments to identify the source of these alcohols and options for sampling in child care facilities that may have elevated levels of volatile alcohols.

Given the episodic nature of the contaminant peak and the tentative identification of the peak as ethyl alcohol, we suspected that the use of hand sanitizer in the facilities might be causing elevated levels of volatile alcohols. To test this idea, we purchased several different brands of hand sanitizers with different active ingredients and simulated a field sampling event in an office space (~45 m^3). While collecting VOC samples on several different sorbent media (Tenax-TA, Tenax-TA/Carboseive and Carbotrap 300), we applied a volume of each hand sanitizer to a foil sheet in an amount that represented approximately one hand cleaning event for each product. The use of sampling tubes containing Tenax-TA without the Carboseive provides a sorbent bed that allows high volatility polar contaminants to pass through while capturing the other VOCs. A second tube installed in series provided a backup bed of Carbotrap material to verify the breakthrough of the alcohols. A third tube containing Tenax-TA backed with carboseive was collected in parallel to replicate previous sampling events. The results comparing the Tenax-TA/Carboseive to the Tenax-TA and Carbotrap are illustrated in Figure 15. As the figure shows, the original method of sampling onto Tenax-TA backed by Carbosieve was adversely affected by the presence of volatile alcohols while the Tenax-TA in series with the Carbotrap effectively separates the alcohol from the other VOCs.

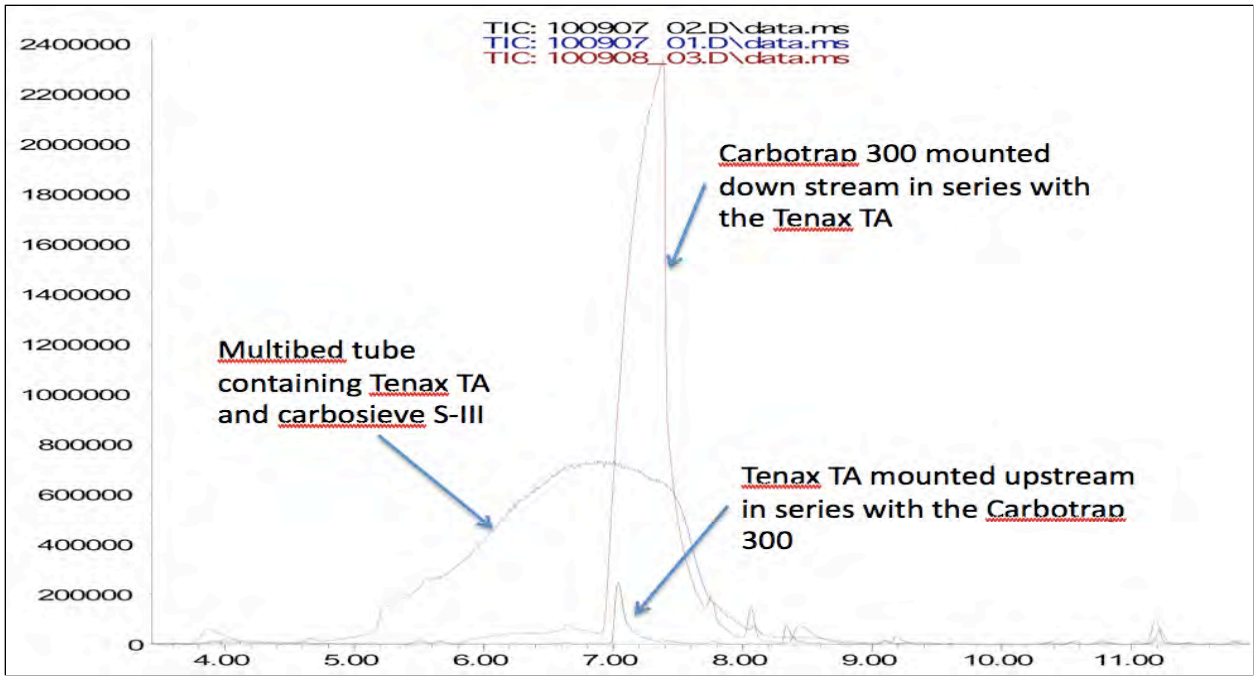


Figure 15. Comparison of the three sorbent materials. Graph shows that the original method of sampling onto Tenax-TA backed by Carbosieve is adversely affected by the presence of volatile alcohols while the Tenax-TA in series with the CarboTrap 300 effectively separates the alcohol from the other VOCs

In Figure 16, we compare the original method of sampling onto Tenax-TA backed by Carbosieve with the sample collected on Tenax-TA only, illustrating that the Tenax-TA cartridge efficiently collects all the VOCs without becoming saturated with the volatile alcohol. The large peak eluting early in the inverted chromatogram was identified as ethyl alcohol using a small volume (0.5 liter) sample collected directly on a CarboTrap sampling tube. The results confirmed the problem with volatile alcohols using the Carbosieve backed Tenax-TA and the ability of the Tenax-TA tube to collect VOCs in the presence of these high volatility polar contaminants.

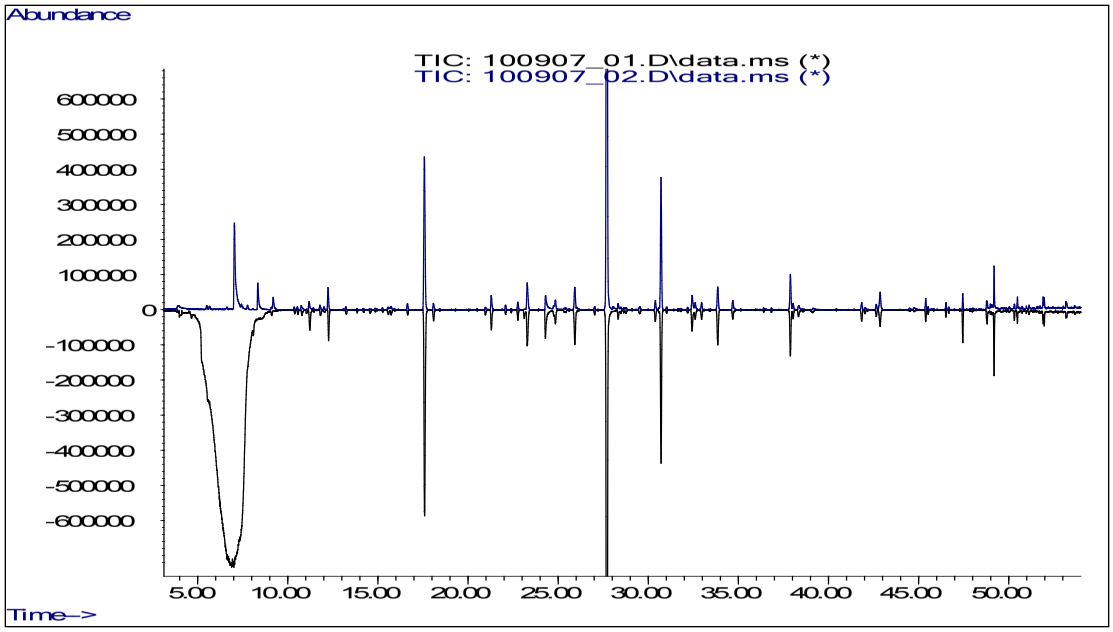


Figure 16. Inverted overlay of chromatograms from VOC sample collected in office room using Tenax-TA only (top chromatogram) and Tenax-TA/Carbosieve (inverted chromatogram) in the presence of hand sanitizers

We returned to a previously tested facility (ECE#15) that had problems with the VOC analysis and the early eluting contaminant peak to collect additional samples to verify improvements in the sampling method. In this instance, we did not have problems with a contaminant peak. However, the samples were collected over one hour to minimize disturbance to the child care program versus ~9 hours for the original samples. We sampled CarboTrap only, Tenax-TA only, and Tenax-TA backed by Carbosieve sorbent tubes. For the CarboTrap only tubes, we sampled 0.5 Liters/ 30 minutes or 16.67 cc/min. For the Tenax-TA only and Tenax-TA backed by Carbosieve, we sampled 3L/60mins or 50 cc/min. While children and staff were present and hand soaps were used during the sampling, it did not appear that alcohol-based sanitizers were used during this period. As a result, we did not see elevated alcohol contamination on any of the samples. The results, however, showed that the measurements on the Tenax-TA/Carbosieve tubes were similar to measurements on Tenax-TA only tubes. Because the alcohol levels were low, we could not confirm that the CarboTrap only tube could be used to quantify high levels of alcohol. Nevertheless, confirming that this strategy should successfully sample the VOC levels in the ECE facilities was useful. Based on the results from the experimental sampling described above, we adopted a standard operating procedure to sample VOCs using separate Tenax-TA only and CarboTrap only tubes where the volume of air sampled on the CarboTrap will be approximately 10% of that normally collected for VOCs to address the extremely elevated but episodic nature of the alcohol contamination. We also added several low molecular weight alcohols commonly used in hand sanitizers to the calibration mix for the ECE facilities to allow for identification and quantification of these contaminants.

CO_2 Cylinder Test for VOCs

Medical grade CO_2 (Praxair, Part Number CD M-10, United States Pharmacopeia grade) was released as a tracer gas in ECE facilities to help define air exchange rates (See Section

2.5.3, above). Before implementing the CO_2 tracer protocol, we performed a quality assurance test to ensure use of the gas did not contribute to contamination in the child care facility. To accomplish this, flexible tubing from a CO_2 tank gas regulator was fed directly into a Tenax sampler for thirty minutes at an average flow rate of 192 cc/min. Analysis results are presented in Table 112. When taking into consideration the total room volume and the relatively small amount of CO_2 released, cylinder test results indicate that the introduction of medical grade CO_2 into ECE facilities contributed minimal contamination. For example, the highest contaminant in the medical grade CO_2, hexamethylcyclotrisiloxane, would haved added less than 5% error to the total analyte measured.

Table 112. Mass and Concentration from Direct Sampling of Medical Grade CO_2

Analyte	Mass (ng)	Concentration (ng/m^3)
Hexane	3.2	552.7
Methylene chloride	<MDL	<MDL
Carbon tetrachloride	<MDL	<MDL
Chloroform	<MDL	<MDL
Benzene	<MDL	<MDL
Butanal	<MDL	<MDL
Heptane	11.6	2,013.2
Octane	2.6	450.5
Toluene	1.1	183.7
Hexamethylcyclotrisiloxane	276.4	47,893
Tetrachloroethylene	<MDL	<MDL
Hexanal	9.3	1618.2
Ethylbenzene	<MDL	<MDL
m/p-Xylene	<MDL	<MDL
a-Pinene	<MDL	<MDL
o-Xylene	<MDL	<MDL
Octamethylcyclotetrasiloxane	8.4	1,458.8
Heptanal	2.0	353.4
Decane	<MDL	<MDL
2-Butoxyethanol	1.3	220.0
3-Carene	<MDL	<MDL
1,2,4-Trimethylbenzene	<MDL	<MDL
d-Limonene	1.5	265.1
1,2,3-Trimethylbenzene	<MDL	<MDL
g-Terpinene	<MDL	<MDL
Benzaldehyde	2.1	356.9
Octanal	3.1	538.8
Undecane	<MDL	<MDL
Butylbenzene	<MDL	<MDL
Decamethylcyclopentasiloxane	4.7	816.0

Analyte	Mass (ng)	Concentration (ng/m^3)
2-Ethyl-1-hexanol	2.0	343.0
Nonanal	10.8	1,878.0
Dodecane	<MDL	<MDL
Decanal	3.5	613.3
a-Terpineol	<MDL	<MDL
Tetradecane	<MDL	<MDL
Texanol	<MDL	<MDL
Hexadecane	<MDL	<MDL
Dimethyl phthalate	<MDL	<MDL
TXIB	<MDL	<MDL
Diethyl phthalate	<MDL	<MDL
Dibutyl phthalate	<MDL	<MDL

VOC Duplicate, Blank, Spike, and Breakthrough Results

Three duplicate VOC samples were collected. In one facility, duplicate samples utilized sample tubes with Tenax backed by CarboTrap; at the other two, duplicate samples utilized Tenax-only sample tubes. For all VOC analytes, the mean relative standard deviation was 11.8% (SD= 8.3), showing a relatively small error between measurements (Table 113). Seventeen travel blanks were analyzed to quantify possible contamination (Table 114). Travel blanks are brought to the field but are not opened then brought back to the laboratory for analysis. Results show little contamination during travel and analysis. Of the 39 analytes measured, only two had median blank masses above the method detection limit (Hexamethylcyclotrisiloxane- 4.1 ng and benzaldehyde-1.5 ng). Three Tenax travel spikes were prepared with a Level 4 calibration standard (~100 ng) in 1 µL of methanol then purged with 2L of He. Travel spikes were prepared and brought into the field and returned to the laboratory to quantify recovery. For all 39 analytes, average recovery for the travel spikes was 96.2% (SD= 7.9) (Table 115).

Table 113. Summary of RSDs (%) between Field and Duplicate Samples Collected at Three Facilities

Analyte	Mean RSD (%)	Standard Deviation of RSD (%)
Hexane	12.0	19.8
Methylene chloride	13.5	16.1
Carbon tetrachloride	8.9	8.7
Chloroform	2.6	2.6
Benzene	6.6	8.8
Butanal	10.0	9.7
Heptane	11.6	9.4

Analyte	Mean RSD (%)	Standard Deviation of RSD (%)
Octane	13.1	11.0
Toluene	12.3	11.2
Hexamethylcyclotrisiloxane	58.4	71.9
Tetrachloroethylene*	13.0	14.1
Hexanal	11.5	10.5
Ethylbenzene	10.2	11.5
m/p-Xylene	9.7	11.9
a-Pinene	9.8	9.8
o-Xylene	11.5	9.9
Octamethylcyclotetrasiloxane*	11.4	12.3
Heptanal	10.0	11.5
Decane*	14.6	15.3
2-Butoxyethanol	16.7	13.6
3-Carene	7.8	10.9
Trimethylbenzene (1,2,4)	8.6	12.6
d-Limonene	4.9	4.6
Trimethylbenzene (1,2,3)	7.7	13.1
g-Terpinene	6.5	8.0
Benzaldehyde	7.5	11.1
Octanal	10.6	9.5
Undecane	13.4	12.1
Butylbenzene	19.7	15.1
Decamethylcyclopentasiloxane	8.5	14.4
2-Ethyl-1-hexanol	13.7	6.2
Nonanal	6.8	7.4
Dodecane	13.8	11.0
Decanal	11.9	10.4
a-Terpineol	10.4	10.9
Tetradecane	9.6	12.7
Texanol	9.0	7.6
Hexadecane	8.3	12.3
TXIB	13.1	17.3

*Analytes not measured at ECE#11

Table 114. Results of VOC Sorbent Tube Travel Blanks

Analyte	N	Median (ng)	Maximum (ng)
Hexane	17	<MDL	1.1
Methylene chloride	17	<MDL	3.2
Carbon tetrachloride	17	<MDL	0.2
Chloroform	17	<MDL	0.2
Benzene	17	<MDL	1.9
Butanal	17	<MDL	<MDL
Heptane	17	<MDL	1.4
Octane	17	<MDL	1.0
Toluene	17	<MDL	2.4
Hexamethylcyclotrisiloxane	17	4.1	46.6
Tetrachloroethylene	17	<MDL	<MDL
Hexanal	17	<MDL	3.4
Ethylbenzene	17	<MDL	0.2
m/p-Xylene	17	<MDL	1.7
a-Pinene	17	<MDL	5.8
o-Xylene	17	<MDL	0.3
Octamethylcyclotetrasiloxane	17	<MDL	2.3
Heptanal	17	<MDL	0.2
Decane	17	<MDL	1.6
2-Butoxyethanol	17	<MDL	5.1
3-Carene	17	<MDL	<MDL
Trimethylbenzene (1,2,4)	17	<MDL	0.2
d-Limonene	17	<MDL	6.8
Trimethylbenzene (1,2,3)	17	<MDL	0.5
g-Terpinene	17	<MDL	<MDL
Benzaldehyde	17	1.5	4.0
Octanal	17	<MDL	1.5
Undecane	17	<MDL	0.3
Butylbenzene	17	<MDL	<MDL
Decamethylcyclopentasiloxane	17	<MDL	1.5
2-Ethyl-1-hexanol	17	<MDL	0.5
Nonanal	17	<MDL	3.9
Dodecane	17	<MDL	0.4
Decanal	17	<MDL	2.7
a-Terpineol	17	<MDL	0.1
Tetradecane	17	<MDL	0.2
Texanol	17	<MDL	0.1
Hexadecane	17	<MDL	0.2

Analyte	N	Median (ng)	Maximum (ng)
TXIB	17	<MDL	1.1

Table 115. VOC Travel Spike Recovery Results

Analyte	Spike 01 Recovery (%)	Spike 02 Recovery (%)	Spike 03 Recovery (%)	Average Spike Recovery (%)
Benzene	108.9	88.4	98.1	98.5
Butanal	105.3	101.6	103.2	103.3
Heptane	106.5	87.5	96.4	96.8
Octane	106.5	95.1	101.3	101.0
Toluene	109.1	95.7	104.4	103.1
Hexamethylcyclotrisiloxane	106.0	127.8	107.8	113.9
Tetrachloroethylene	107.9	99.2	104.5	103.9
Hexanal	98.3	97.1	95.6	97.0
Ethylbenzene	103.6	96.8	102.9	101.1
m/p-Xylene	102.4	97.2	102.3	100.6
a-Pinene	102.8	98.7	102.3	101.3
o-Xylene	103.7	100.0	104.4	102.7
Octamethylcyclotetrasiloxane	107.4	111.8	112.4	110.5
Heptanal	100.6	101.4	100.6	100.9
Decane	98.1	97.3	98.9	98.1
2-Butoxyethanol	101.5	101.8	105.2	102.8
3-Carene	97.2	95.4	98.1	96.9
1,2,4-Trimethylbenzene	95.2	93.9	97.2	95.4
d-Limonene	96.0	95.3	97.5	96.3
1,2,3-Trimethylbenzene	93.0	92.4	95.1	93.5
g-Terpinene	94.3	94.4	94.3	94.3
Benzaldehyde	96.8	94.4	99.8	97.0
Octanal	94.4	93.0	94.6	94.0
Undecane	92.2	93.4	95.0	93.5
Butylbenzene	89.9	90.2	92.1	90.8
Decamethylcyclopentasiloxane	88.1	90.7	90.6	89.8
2-Ethyl-1-hexanol	92.7	94.3	94.2	93.8
Nonanal	90.9	92.2	91.0	91.4
Dodecane	88.8	90.8	91.4	90.4
Decanal	90.9	92.7	93.0	92.2
a-Terpineol	90.4	91.6	91.1	91.0
Tetradecane	84.6	85.7	85.8	85.3

Analyte	Spike 01 Recovery (%)	Spike 02 Recovery (%)	Spike 03 Recovery (%)	Average Spike Recovery (%)
Texanol	90.8	93.1	92.3	92.1
Hexadecane	82.5	83.0	83.3	82.9
TXIB	72.0	67.9	67.8	69.2

Table 116. Breakthrough Concentrations (ng/m³) from Five ECE Facilities

Analyte	ECE 28	ECE 40	ECE 41	ECE 45	ECE 47
Hexane	<MDL	<MDL	<MDL	<MDL	<MDL
Methylene chloride	<MDL	<MDL	<MDL	<MDL	<MDL
Carbon tetrachloride	<MDL	<MDL	<MDL	<MDL	<MDL
Chloroform	<MDL	<MDL	<MDL	0.8	<MDL
Benzene	<MDL	<MDL	<MDL	<MDL	<MDL
Butanal	<MDL	<MDL	0.2	<MDL	0.4
Heptane	<MDL	<MDL	<MDL	<MDL	<MDL
Octane	0.2	<MDL	<MDL	<MDL	<MDL
Toluene	0.5	<MDL	<MDL	<MDL	<MDL
Hexamethylcyclotrisiloxane	89.1	<MDL	<MDL	<MDL	<MDL
Tetrachloroethylene	<MDL	<MDL	<MDL	<MDL	<MDL
Hexanal	3.6	<MDL	<MDL	<MDL	<MDL
Ethylbenzene	0.2	<MDL	<MDL	<MDL	<MDL
m/p-Xylene	0.8	<MDL	<MDL	<MDL	<MDL
a-Pinene	5.6	<MDL	<MDL	<MDL	<MDL
o-Xylene	0.6	<MDL	<MDL	<MDL	<MDL
Octamethylcyclotetrasiloxane	4.6	<MDL	<MDL	<MDL	<MDL
Heptanal	<MDL	<MDL	<MDL	<MDL	<MDL
Decane	0.3	<MDL	<MDL	<MDL	<MDL
2-Butoxyethanol	13.0	<MDL	<MDL	<MDL	<MDL
3-Carene	0.2	<MDL	<MDL	<MDL	<MDL
Trimethylbenzene (1,2,4)	1.1	<MDL	<MDL	<MDL	<MDL
d-Limonene	13.2	<MDL	<MDL	<MDL	<MDL
Trimethylbenzene (1,2,3)	0.3	<MDL	<MDL	<MDL	<MDL
g-Terpinene	0.2	<MDL	<MDL	<MDL	<MDL
Benzaldehyde	1.4	0.3	<MDL	0.4	0.3
Octanal	2.2	<MDL	<MDL	0.2	0.2
Undecane	2.0	<MDL	<MDL	<MDL	<MDL
Butylbenzene	<MDL	<MDL	<MDL	<MDL	<MDL
Decamethylcyclopentasiloxane	18.8	<MDL	<MDL	0.2	<MDL
2-Ethyl-1-hexanol	2.5	<MDL	<MDL	<MDL	<MDL
Nonanal	8.0	0.4	0.4	0.8	0.5

Analyte	ECE 28	ECE 40	ECE 41	ECE 45	ECE 47
Dodecane	3.7	<MDL	<MDL	<MDL	<MDL
Decanal	12.4	<MDL	0.1	0.3	<MDL
a-Terpineol	0.7	<MDL	<MDL	<MDL	<MDL
Tetradecane	1.4	<MDL	<MDL	<MDL	<MDL
Texanol	1.5	<MDL	<MDL	<MDL	<MDL
Hexadecane	0.2	<MDL	<MDL	<MDL	<MDL
TXIB	3.6	<MDL	<MDL	<MDL	<MDL

Table 117. Comparison of Field vs. Breakthrough Concentrations at ECE 28

	Field Sample (ng/m^3)	Breakthrough Sample (ng/m^3)	Field to Breakthrough Ratio
Hexane	<MDL	<MDL	.
Methylene chloride	<MDL	<MDL	.
Carbon tetrachloride	<MDL	<MDL	.
Chloroform	<MDL	<MDL	.
Benzene	0.9	<MDL	.
Butanal	0.6	<MDL	.
Heptane	0.8	<MDL	.
Octane	1.3	0.2	5.6
Toluene	1.6	0.5	3.5
Hexamethylcyclotrisiloxane	4.8	89.1	0.1
Tetrachloroethylene	<MDL	<MDL	.
Hexanal	3.8	3.6	1.0
Ethylbenzene	0.1	0.2	0.6
m/p-Xylene	0.3	0.8	0.4
a-Pinene	1.9	5.6	0.3
o-Xylene	0.2	0.6	0.3
Octamethylcyclotetrasiloxane	2.9	4.6	0.6
Heptanal	0.6	<MDL	.
Decane	<MDL	0.3	.
2-Butoxyethanol	3.1	13.0	0.2
3-Carene	<MDL	0.2	.
Trimethylbenzene (1,2,4)	<MDL	1.1	.
d-Limonene	14.8	13.2	1.1
Trimethylbenzene (1,2,3)	<MDL	0.3	.
g-Terpinene	<MDL	0.2	.
Benzaldehyde	2.4	1.4	1.8
Octanal	1.3	2.2	0.6

	Field Sample (ng/m^3)	Breakthrough Sample (ng/m^3)	Field to Breakthrough Ratio
Undecane	0.4	2.0	0.2
Butylbenzene	<MDL	<MDL	.
Decamethylcyclopentasiloxane	39.9	18.8	2.1
2-Ethyl-1-hexanol	1.4	2.5	0.5
Nonanal	8.4	8.0	1.0
Dodecane	2.0	3.7	0.5
Decanal	<MDL	12.4	.
a-Terpineol	0.9	0.7	1.3
Tetradecane	3.8	1.4	2.7
Texanol	4.6	1.5	3.1
Hexadecane	0.7	0.2	3.7
TXIB	4.4	3.6	1.2

Carbonyl QA/QC

Nine field blanks were collected from the 40 ECE facilities (~23%). Field blanks consisted of Xposure samplers brought to the ECE facilities but not mounted on the air sampling lines. Median formaldehyde, acetaldehyde, and acetone field blank masses were 40.6, 36.6, and 108.6 ng, respectively. Table 118 summarizes carbonyl levels measured in the blanks. Overall, levels are very low compared to the measured concentrations, suggesting minimal background contamination.

Table 118. Carbonyl Field Blank Summary Statistics

	Formaldehyde (ng)	Acetaldehyde (ng)	Acetone (ng)
Mean	48.8	51.9	106.7
Median	40.6	36.6	108.6
Std.Deviation	18.8	28.6	40.6
Minimum	30.7	28.8	54.4
Maximum	89.7	114.6	183.5

A total of twelve duplicate indoor carbonyl samples were collected for QA/QC purposes. The duplicate measurements were taken side-by-side and assessed for precision. Duplicate precision was assessed by calculating the relative standard deviation (RSD) between the field and duplicate carbonyl samples. The mean RSDS were 4.6% (SD=4.3), 4.0% (SD=3.2), and 4.3% (SD=4.3) for formaldehyde, acetaldehyde, and acetone duplicate samples, respectively (Table 119).These values indicate good precision for field duplicate. Tables 120, 121, and 122 show individual field and duplicate results.

Table 119. Summary Statistics of the RSD (%) for Duplicate Indoor Samples (n=12)

	Formaldehyde	Acetaldehyde	Acetone
Mean RSD	4.6	4.0	4.3
SD of RSD	4.3	3.2	4.3

Table 120. Duplicate Formaldehyde Indoor Measurements

ECE#	Field Sample (µg/m³)	Duplicate Sample (µg/m³)	SD (µg/m³)	RSD (%)
11	9.73	8.58	0.82	8.92
12	8.19	6.95	0.87	11.55
13	27.29	29.52	1.58	5.55
14	9.03	9.20	0.12	1.31
15	8.33	8.43	0.07	0.82
16	10.33	10.27	0.04	0.36
18	19.00	17.36	1.16	6.39
19	33.93	39.89	4.21	11.41
21	10.60	10.57	0.02	0.22
23	49.11	48.43	0.48	0.98
24	13.85	14.19	0.24	1.69
25	17.82	16.51	0.92	5.38

Table 121. Duplicate Acetaldehyde Indoor Measurements

ECE#	Field Sample (µg/m³)	Duplicate Sample (µg/m³)	SD (µg/m³)	RSD (%)
11	3.18	2.94	0.17	5.57
12	3.02	2.60	0.30	10.61
13	9.90	9.40	0.35	3.62
14	4.82	4.71	0.08	1.65
15	2.60	2.68	0.06	2.28
16	4.11	3.86	0.18	4.42
18	5.60	5.38	0.16	2.88
19	11.54	13.22	1.18	9.57
21	7.46	7.55	0.06	0.78
23	17.21	16.86	0.25	1.47
24	7.12	7.24	0.09	1.19
25	12.63	11.92	0.50	4.10

Table 122. Duplicate Acetone Indoor Measurements

ECE#	Field Sample (µg/m³)	Duplicate Sample (µg/m³)	SD (µg/m³)	RSD (%)
11	7.74	7.79	0.03	0.40
12	6.42	5.29	0.80	13.68
13	28.86	27.44	1.00	3.55
14	10.66	10.73	0.05	0.48
15	9.06	9.55	0.35	3.74
16	12.74	11.64	0.78	6.41
18	19.67	18.31	0.96	5.06
19	31.97	37.12	3.64	10.54
21	15.64	15.93	0.20	1.26
23	62.43	61.86	0.41	0.65
24	52.13	52.50	0.26	0.49
25	58.40	54.31	2.89	5.13

Phthalate QA/QC

Four lab matrix spikes and one field matrix spike were analyzed for recovery of phthalate analytes. The percent recoveries were calculated after subtracting out the field matrix blank values. Lab matrix spike recoveries average was 112.9% (SD=14.1). Field matrix spike recoveries average was 106.2% (SD= 28.5) (Table 123). MDLs for all phthalate analytes were approximately 1 ng, which includes a field matrix blank correction of three times the standard deviation. Using the average indoor air volume for SVOCs (1.9 m³), the MDL as a concentration for phthalates was 0.5 ng/m³. Two duplicate indoor air phthalate measurements were collected at ECE#16 and #40 and analyzed for precision between measurements. The average RSD was 42.2% (SD=34.7) (Table 124).

Table 123. Lab and Field Matrix Spike Recovery Results for Phthalates in PUFs

Analyte	Mean Lab Matrix Spike Recovery (%)	Mean Field Matrix Spike Recovery (%)	MDL (ng)	MDL (ng/m³)[1]
Diethyl Phthalate	100.4	79.8	1	0.5
Diisobutyl Phthalate	102.8	94.9	1	0.5
Dibutyl Phthalate	139.5	73.0	1	0.5
Butyl Benzyl Phthalate	108.3	113.0	1	0.5
Di(2-Ethylhexyl) Phthalate	114.8	141.5	1	0.5
BBP-d4[2]	111.3	135.0	.	

[1] MDL in ng/m³ calculated with average total sample volume SVOCs (1.9 m³).

[2] Phthalate surrogate recovery standard.

Table 124. Summary of RSDs for Two Duplicate Phthalate Indoor Air Measurements

Analyte	Mean RSD (%)	Standard Deviation of RSD (%)
Diethyl Phthalate	26.2	6.8
Diisobutyl Phthalate	16.7	23.7
Dibutyl Phthalate	10.4	5.1
Butyl Benzyl Phthalate	88.9	68.6
Di(2-Ethylhexyl) Phthalate	68.7	97.2

Three phthalate dust samples were analyzed in duplicate. Table 125 presents the recovery and MDL for phthalate dust analysis with the average lab matrix recovery 98.6% (SD=5.4). The average RSD was 5.7% (SD=1.4), showing strong precision in phthalate dust analysis (Table 126).

Table 125. Phthalate Recoveries and MDLs in Dust

Analyte	Mean Lab Matrix Recovery (%)	MDL (ng/g)
Diethyl Phthalate	91.3	20
Diisobutyl Phthalate	99.4	20
Dibutyl Phthalate	104.0	20
Butyl Benzyl Phthalate	103.3	20
Di(2-ethylhexyl) Phthalate	NC[1]	20
BBP-d4[2]	95.0	.

[1] Not calculated due to spike too low relative to matrix levels
[2] Phthalate surrogate Recovery Standard

Table 126. Summary of the RSDs for Three Duplicate Phthalate Dust Analysis

Analyte	Mean RSD (%)	Standard Deviation of RSD (%)
Diethyl Phthalate	7.5	7.1
Diisobutyl Phthalate	5.2	2.7
Dibutyl Phthalate	3.8	4.0
Butyl Benzyl Phthalate	5.6	3.5
Di(2-Ethylhexyl) Phthalate	6.6	5.6

Flame Retardant QA/QC

Two lab and field matrix spikes were analyzed for flame retardants in PUFs by Battelle Laboratories. The average recovery for lab matrix spikes was 82.0% (SD=9.2). Average field matrix spike recovery was 86.2% (SD=16.9) (Table 127). BDE 209 was an original target analyte for air analysis. However, after the first set of PUF analysis, the calibration curves and/or its C13-labelled analogue did not meet laboratory QA/QC standards. Therefore, only BDE 209 values for the first set of analysis are presented in this report. For the non-BDE flame retardants in air, MDLs ranged from 0.2 to 0.5 ng for the non-BDE flame retardants (Table 127). Using the average indoor air volume for SVOCs (1.9 m^3), the MDL as a concentration for non-BDE flame retardants had a range of 0.1 to 0.3 ng/m^3. BEHTBP was not detected in the spike analysis due to sensitivity problems in the EI GC/MS mode.

Two indoor duplicates air samples were collected at ECE#15 and 40 for BDEs and Firemaster 550 constituents and ECE#16 and 40 for tris phosphate flame retardants. Summary of the RSDs are presented in Tables 128. The average RSD was 42.1% (SD=41.7).

BDE dust method detection limits and analytical spike recoveries are presented in Table 129. Non-BDE flame retardant dust method detection limits and analytical spike recoveries are presented in Table 130. For flame retardants in dust, three lab spikes were analyzed for recovery. The average lab spike recovery was 85.5% (SD=12.6). One dust sample was analyzed in duplicate for BDE flame retardants using measured concentrations of 0.25 g/ml and 1 g/ml (Table 131).Two dust samples were analyzed in duplicate for Firemaster 550 and tris phosphate flame (Table 132). The average RSD for flame retardants analyzed in duplicate was 25.6% (SD=31.4).

Table 127. Lab and Field Matrix Spike Recovery and Method Detection Limits for BDE Analytes in PUFs

Analyte	Mean Lab Matrix Spike Recovery (%)	Mean Field Matrix Spike Recovery (%)	MDL (ng)	MDL (ng/m^3)[1]
BDE 47	90.4	98.6	0.02	0.01
BDE 99	87.8	108.6	0.02	0.01
BDE 100	86.7	96.1	0.02	0.01
BDE 153	88.2	90.0	0.02	0.01
BDE 154	83.5	93.5	0.02	0.01
BDE 126[2]	87.5	92.4	.	.
TCEP	79.0	59.8	0.5	0.3
TDCPP	73.2	76.0	0.2	0.1
EHTBB	62.0	61.0	0.2	0.1
BEHTBP[3]	.	.	0.2	0.1

[1] MDL in ng/m^3 calculated with average total sample volume SVOCs (1.9 m^3)
[2] Surrogate recovery standard
[3] Not detected in spike analysis

Table 128. Summary of RSDs for Two Duplicate Indoor Air Flame Retardant Measurements

Analyte	Mean RSD (%)	Standard Deviation of RSD (%)
BDE 47	48.5	49.5
BDE 99	49.5	70.0
BDE 100	22.0	3.7
BDE 153	0.0	0.0
BDE 154	59.2	83.8
EHTBB	137.8	2.0
BEHTBP	44.2	62.5
TCEP	8.8	10.3
TDCPP	9.4	3.9

Table 129. BDE Recoveries and MDLs in Dust

	Mean Lab Matrix Spike Recovery (%)	MDL (ng/ml)	MDL (ng/g)[1]
BDE-47	80.8	4	6.9
BDE-99	83.9	4	6.9
BDE-100	82.9	5	8.6
BDE-118	83.7	4	6.9
BDE-153	84.8	5	8.6
BDE-154	82.7	6	10.3
BDE-183	77.3	6	10.3
BDE-190	79.9	8	13.8
BDE-197	68.7	8	13.8
BDE-203	70.3	8	13.8
BDE-205	67.7	9	15.5
BDE-206	83.1	18	31.0
BDE-207	77.3	4	6.9
BDE-209	116.9	17	29.3
MCDE-86L*	80.7	.	.
BDE-181*	78.4	.	.
BDE-209L*	94.6	.	.

*Surrogate Recovery Standards
[1]MDL in ng/g calculated using the average mass of dust used in BDE analyses per volume of extract solvent (0.58 g/mL)

Table 130. Non-BDE Flame Retardant Recoveries and MDLs in Dust

Analyte	Mean Lab Matrix Spike Recovery (%)	MDL (ng/g)
TCEP	97.9	1
TDCPP	107.3	1
EHTBB	101.1	1
BEHTBP	95.4	1

Table 131. Summary of Analytical Duplicate Sample Results for BDE Flame Retardants in Dust

	ECE# 38			
	Field Sample (ng/g)	Duplicate Sample (ng/g)	SD (ng/g)	RSD (%)
BDE-47	1109.2	1241.3	93.4	7.9
BDE-99	1584.7	1678.0	66.0	4.0
BDE-100	412.0	320.4	64.8	17.7
BDE-118	10.1	2.8	5.1	79.6
BDE-153	313.9	227.9	60.8	22.4
BDE-154	226.4	171.6	38.7	19.4
BDE-183	2.6	0.9	1.2	67.2
BDE-190	5.7	5.7	0.0	0.0
BDE-197	7.2	26.1	13.4	80.6
BDE-203	5.4	27.2	15.4	94.3
BDE-205	6.4	6.4	0.0	0.0
BDE-206	68.7	77.0	5.9	8.1
BDE-207	44.7	66.8	15.6	27.9
BDE-209	1665.2	1721.3	39.6	2.3
∑ BDE	5462.1	5573.4	78.67	1.4

Table 132. Summary of the RSDs for Two Duplicate Non-BDE Flame Retardant Dust Analysis

	Mean RSD (%)	Standard Deviation of RSD (%)
TCEP	8.7	6.6
TDCPP	4.8	6.2
EHTBB	7.6	2.7
BEHTBP	8.7	2.6

Perfluorinated Compound QA/QC

CERCH worked with collaborators in the National Exposure Research Laboratory (NERL) at the US EPA to analyze washed silica gel (Supelco, part # 21342U) as dust blanks for possible contamination by the HVS3 Vacuum sampler, which contains some Teflon gaskets. Before field sampling, washed silica gel was applied to cleaned aluminum foil and vacuumed through the HVS3 vacuum into ICHEM sample container. This procedure was repeated twice. In addition, washed silica gel was deposited directly into a clean sample jar. Samples showed only a small peak of C11 acid in the first sample blank taken. Two other peaks, PFHpA and PFOA were near background levels. The two additional blanks showed no significant peaks. Dust Blank Chromatograms prepared by Dr. Mark Strynar are presented in Figures 17-21. In all, US EPA chemists judged dust blanks to be clean and showed the HVS3 contributed little contamination to the sample. Four dust samples were analyzed in duplicate by the U.S. EPA to validate the precision of the results. The average RSD was 11.1% (SD=11.4) (Table 133).

Table 133. Summary of Four Duplicate PFC Analysis in Dust

Analyte	Mean RSD (%)	Standard Deviation of RSD (%)
PFBA	0.0	0.0
PFPeA	21.9	43.9
PFHxA	27.7	28.0
PFHpA	28.9	37.2
PFOA	4.0	2.7
PFNA	5.3	6.5
PFDA	12.2	11.9
PFBS	0.0	0.0
PFHS	0.0	0.0
PFOS	11.3	14.4

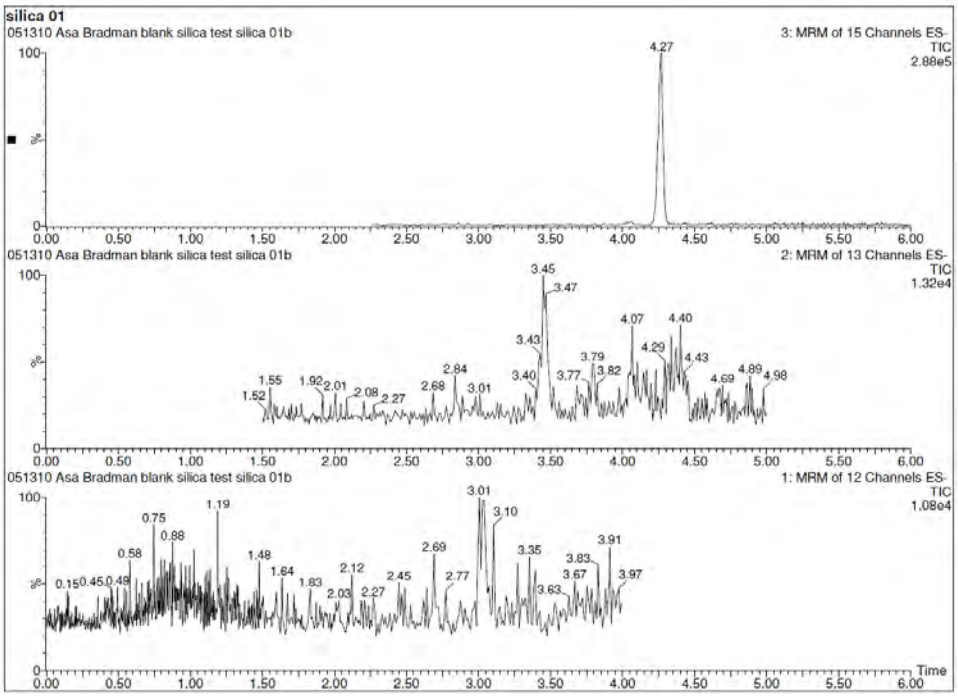


Figure 17. First round of washed silica gel run through HVS3- labeled silica 01

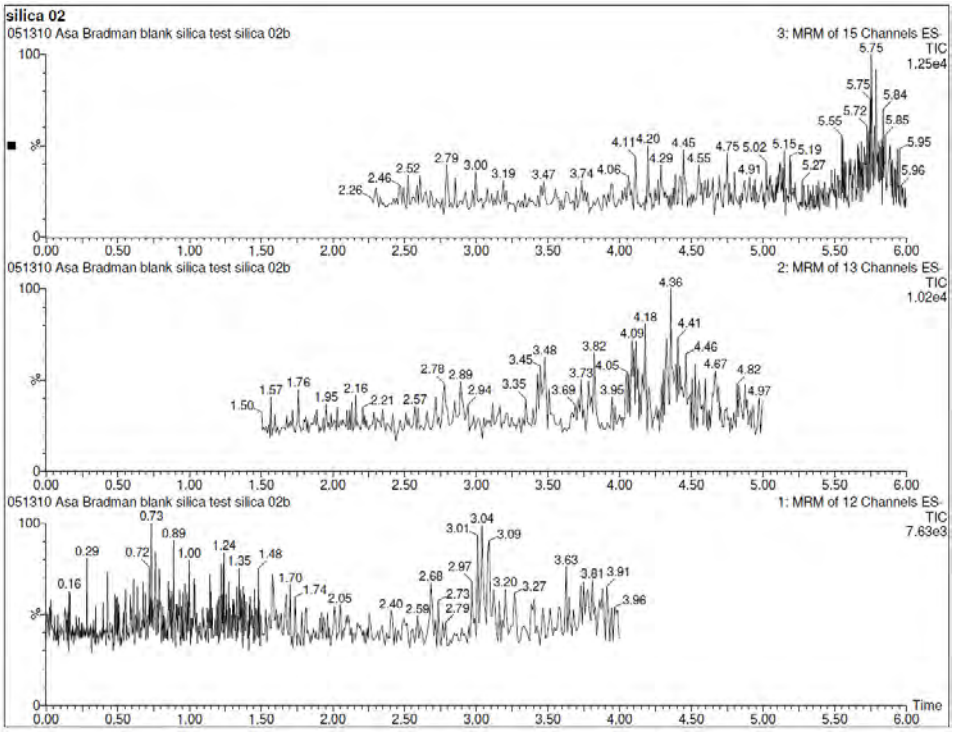


Figure 18. Second round of washed silica gel run through HVS3- labeled silica 02

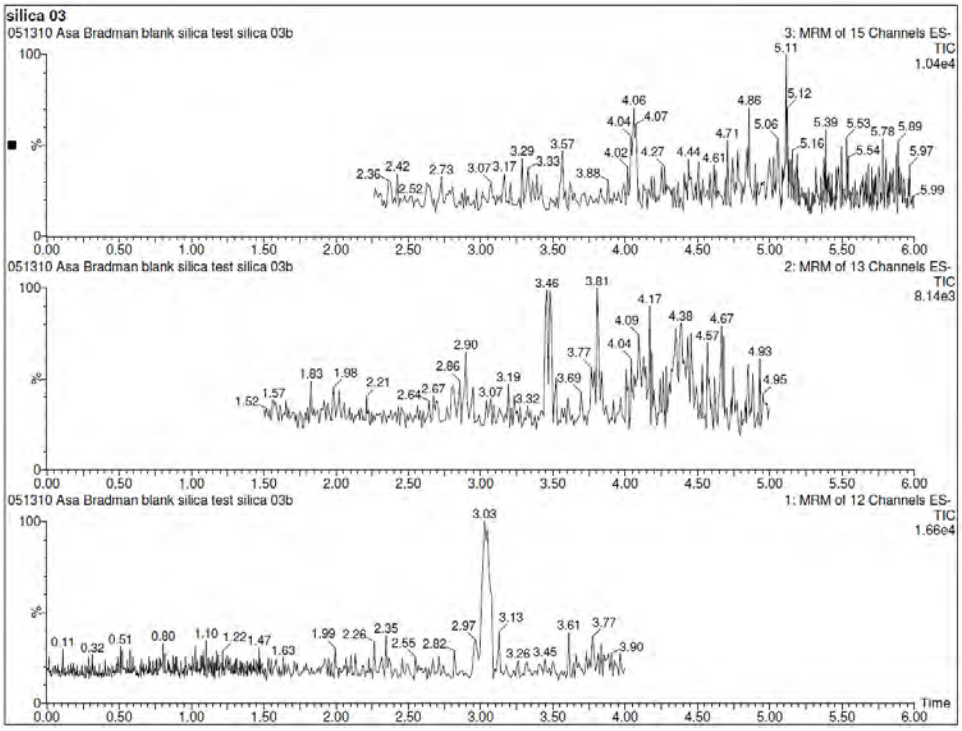


Figure 19. Washed silica deposited directly into sample container and not run through HVS3- labeled silica 03.

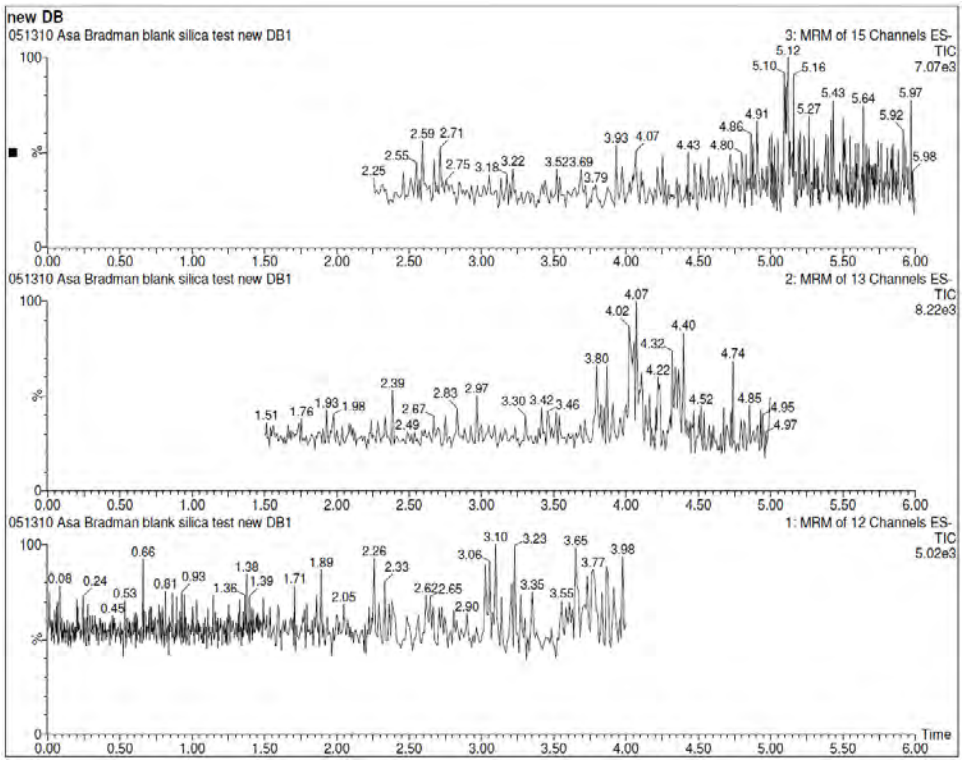


Figure 20. Lab prepared dust blank- labeled DB

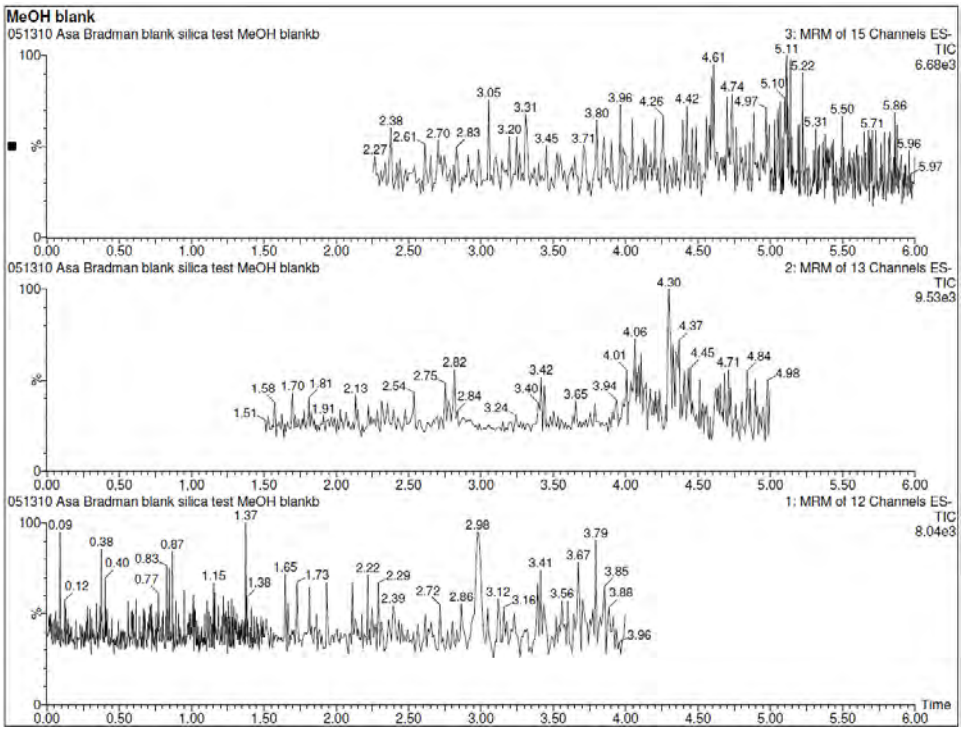


Figure 21. Lab prepared methanol blank- labeled MeOH blank

Pesticide QA/QC

Four lab and two field matrix spikes were analyzed to evaluate recovery of the pesticide analytes in PUFs (Table 134). The average lab matrix spike recovery for pesticide analytes in air was 74.4% (SD=13.1) Average field matrix spike recovery was 65.4% (SD= 20.7). For air measurements, pesticide MDLs were calculated by subtracting the three times the standard deviation of field matrix blanks and ranged from 0.05-0.4 ng. Using the average indoor air volume for SVOCs (1.9 m³), the MDL as a concentration for pesticides ranged from 0.03 to 0.26 ng/m³. Two duplicate PUF measurements were taken at ECE#16 and 40. Side-by-side measurements were collected and analyzed for precision between measured pesticide concentrations (Table 135). The average RSD was 14.2 % (SD= 30.6).

Table 134. Lab and Field Matrix Spike Recovery Results for Pesticides in PUFs

Analyte	Mean Lab Matrix Spike Recovery (%)	Mean Field Matrix Spike Recovery (%)	MDL (ng)	MDL (ng/m³)[1]
Diazinon	67.9	52.4	0.2	0.11
Chlorpyrifos	69.3	53.8	0.3	0.16
Dacthal	65.8	69.3	0.05	0.03
Imiprothrin	67.3	55.1	0.5	0.26
Piperonyl butoxide	65.6	77.4	0.05	0.03
Bifenthrin	77.7	85.1	0.2	0.11
Sumithrin	80.9	96.4	0.1	0.05
cis-Permethrin	63.7	68.5	0.05	0.03
trans-Permethrin	60.5	63.9	0.05	0.03
Cyfluthrin I	85.1	56.0	0.4	0.21
Cyfluthrin II	72.8	36.7	0.4	0.21
Cyfluthrin III	69.1	56.6	0.4	0.21
Cyfluthrin IV	76.3	44.8	0.4	0.21
Cypermethrin I	69.0	47.9	0.4	0.21
Cypermethrin II	65.5	43.6	0.4	0.21
Cypermethrin III/IV	118.1	59.2	0.4	0.21
Fenchlorphos*	84.5	105.3	.	.
13C16 trans-Permethrin*	79.4	104.8	.	.

[1] MDL in ng/m³ calculated with average total sample volume SVOCs (1.9 m³)

* Surrogate Recovery Standards

Table 135. Summary of RSDs for Two Duplicate Indoor Air Pesticide Measurements

	Mean RSD (%)	Standard Deviation of RSD (%)
Diazinon	74.6	94.4
Chlorpyrifos	7.1	6.9
Dacthal	106.1	50.0
Imiprothrin	0.0	0.0
Piperonyl butoxide	0.0	0.0
Bifenthrin	0.0	0.0
Sumithrin	0.0	0.0
cis-Permethrin	34.7	49.0
trans-Permethrin	18.5	23.9
Cyfluthrin	0.0	0.0
Cypermethrin	0.0	0.0

For three lab matrix spikes, the average recovery was 104.1% (SD=16.9). Duplicate pesticide analysis was performed on the two dust samples to assess precision in analytical methods (Table 136). Duplicate analysis was from dust collected at ECE#10 and 40. Duplicate dust analysis showed good precision with an average RSD of 4.3% (SD= 3.9). Pesticide dust method detection limits and analytical spike recoveries are presented in Table 137.

Table 136. Summary of the RSDs for Two Duplicate Pesticide Dust Analysis

	Mean RSD (%)	Standard Deviation of RSD (%)
Diazinon	6.1	8.6
Chlorpyrifos	5.4	0.5
Dacthal	4.2	2.8
Imiprothrin	1.4	2.0
Piperonyl butoxide	5.5	5.2
Bifenthrin	7.8	3.3
Sumithrin	0.0	0.0
cis-Permethrin	12.6	6.7
trans-Permethrin	4.2	3.1
Cyfluthrin	0.0	0.0
Cypermethrin	0.0	0.0

Table 137. Pesticide Lab Matrix Spike Recoveries (n=3) and MDLs in Dust

Analyte	Mean Lab Matrix Spike Recovery (%)	MDL (ng/g)
Diazinon	96.0	1
Chlorpyrifos	95.5	1
Dacthal	95.3	0.3
Imiprothrin	127.3	50
Piperonyl butoxide	99.1	0.3
Bifenthrin	99.6	0.5
Sumithrin	77.8	0.5
cis-Permethrin	99.8	1
trans-Permethrin	97.9	1
Cyfluthrin I	102.3	20
Cyfluthrin II	101.7	20
Cyfluthrin III	138.9	20
Cyfluthrin IV	147.4	20
Cypermethrin I	101.4	20
Cypermethrin II	101.1	20
Cypermethrin III/IV	103.4	40
Fenchlorphos *	96.0	1
13C16 trans-Permethrin*	94.1	1

* Surrogate Recovery Standard

Ultrafine Particle QA/QC

Figure 22 shows side-by-side measurements between CPCs at the beginning and end of the sampling period. The side-by-side measurements conducted at the beginning of the study were extremely close (Figure 22 and Table 138).

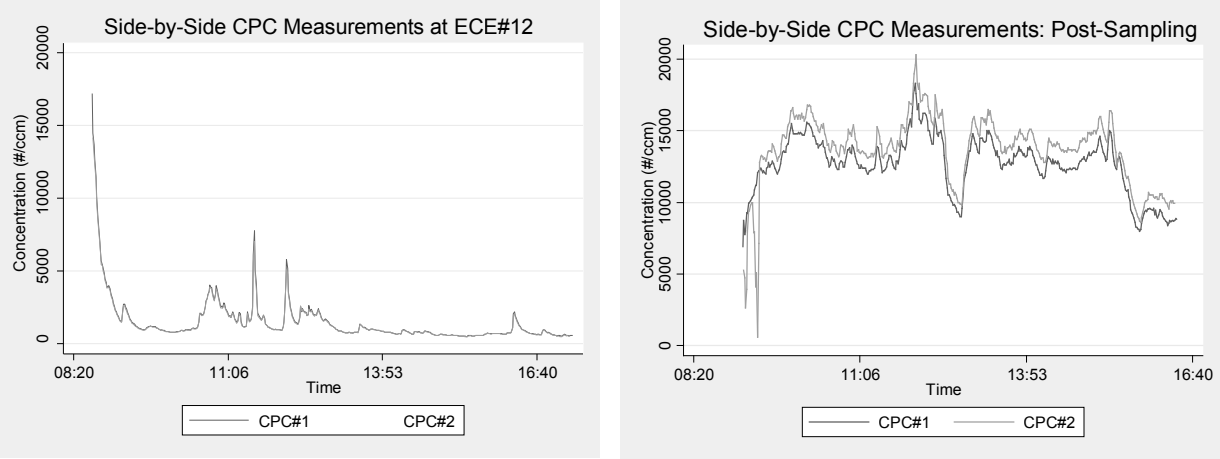


Figure 22. Side-by-side CPC measurements taken at ECE 12 on 7/8/2010 and taken in UCB office building at the conclusion of air sampling campaign on 5/19/2011

Table 138. Summary of Standard Deviations and RSDs for Side-by-Side CPC Measurements at ECE 12

	July 2010 QA/QC		May 2011 QA/QC	
	SD[1] (µg/m³)	RSD[2] (%)	SD (µg/m³)	RSD (%)
Mean	32.5	1.7	814.3	6.1
Median	14.4	1.4	848.5	6.2
Maximum	565.7	9.2	1909.2	11.6
SD	58.3	1.3	227.7	1.7

[1,2]Standard deviation and RSD measure variability between CPC1 and CPC2 minute-by-minute data points.

RealTime $PM_{2.5}$ QA/Q

Prior to sampling, DustTrak 1 was compared to CARB's Monitoring and Laboratory Division (MLD) ambient air $PM_{2.5}$ samples collected on Teflon filters in Sacramento, California. Note, the Teflon filter method is intrinsically different from the light scattering method used in the DustTrak. Thus, some differences between the two methods are to be expected. DustTrak 1 was run for 27 hours next to the ambient monitor and hourly $PM_{2.5}$ data between the two methods was compared to assess DustTrak 1 performance. The mean relative standard deviation between the duplicate measurements was 38.9% and the standard deviation was 32.1%. Results showed a bias between measurement techniques with DustTrak 1 measuring higher concentrations of $PM_{2.5}$ than the MLD unit. A linear regression comparing the two measurements produced a line, MLD=1.9 + 0.44(DT1) with a standard error of 0.07. The $PM_{2.5}$ levels between the two machines were strongly correlated (R^2=0.62 [r=0.79]), DustTrak 1 generally measured higher $PM_{2.5}$ concentrations than results from MLD (Table 139). Figure 23 presents the hourly trend between CARB's MLD and DustTrak 1 $PM_{2.5}$ measurements along with a scatter plot with a linear fit line. Tables 139 and 140 present a summary of the results and analysis of precision.

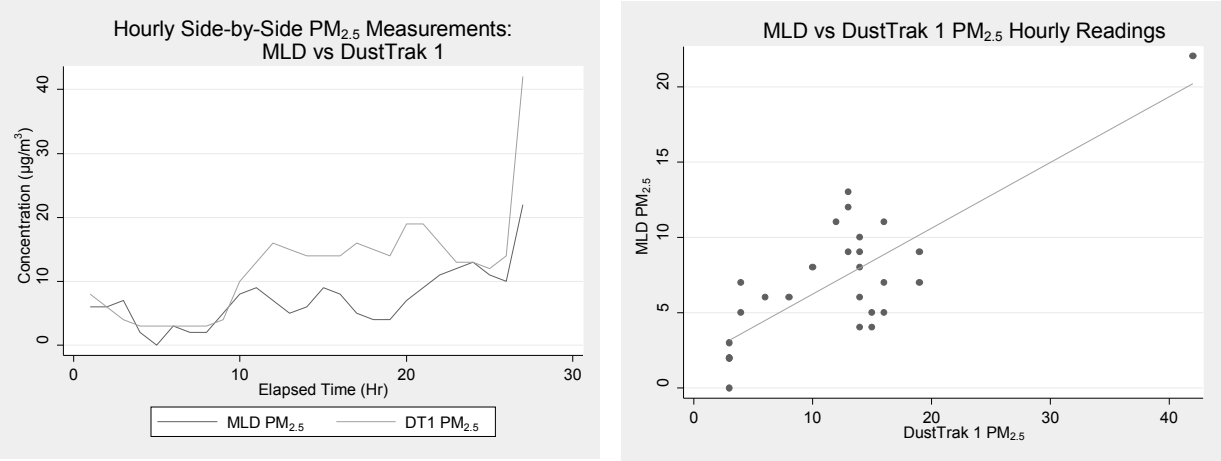


Figure 23. Graphs showing hourly trend between MLD and DustTrak 1 $PM_{2.5}$ measurements (left) and MLD and DustTrak 1 measurements plotted against each other with a linear fit line

Table 139. Summary of MLD and DustTrak 1 $PM_{2.5}$ Measurements

	MLD $PM_{2.5}$ ($\mu g/m^3$)	DustTrak 1 $PM_{2.5}$ ($\mu g/m^3$)
Mean	7.2	12.1
Median	7.0	13.0
Standard Deviation	4.4	8.0
Min	0.0	3.0
Max	22.0	42.0

Table 140. Summary of Standard Deviation and RSD between MLD and DustTrak 1 $PM_{2.5}$ Measurements

	SD $PM_{2.5}$ (µg/m³)	RSD $PM_{2.5}$ (%)
Mean	3.7	38.9
SD	3.5	32.1

DustTrak 2 was rented in January 2011, and was a more recent model (DustTrak 8520) Side-by-side comparisons between the two DustTraks were performed in a UC Berkeley office building before sending DustTrak 2 into the field and post-sampling. Figure 24 presents the side-by-side measurements between DustTrak 1 and DustTrak 2 prior to sampling and post-sampling. Figure 25 presents a scatter plot of the duplicate measurements fitted with a linear line. Tables 141 and 142 present the summary statistics and measurements of precision. Side-by-side measurements between DustTrak1 and DustTrak2 show a strong correlation (R^2=0.80); however, there was a consistent bias between DustTrak1 and DustTrak2 (linear regression: DT1=-0.001 + 0.89(DT2), standard error=0.03) with an average difference in sample concentration of 7 µg/m³. Prior to sampling the mean RSD was 10.0% and the standard deviation was 1.9%. Post-sampling side-by-side DustTrak measurements also correlated well (R^2=0.95), but a bias persisted between the machines (linear regression: DT1=-0.001 + 0.84(DT2), standard error=0.01). DustTrak 1 was approximately 5 µg/m³ lower than DustTrak 2 throughout the sampling period. The post-sampling mean RSD was 17.4% and the standard deviation was 2.6%.

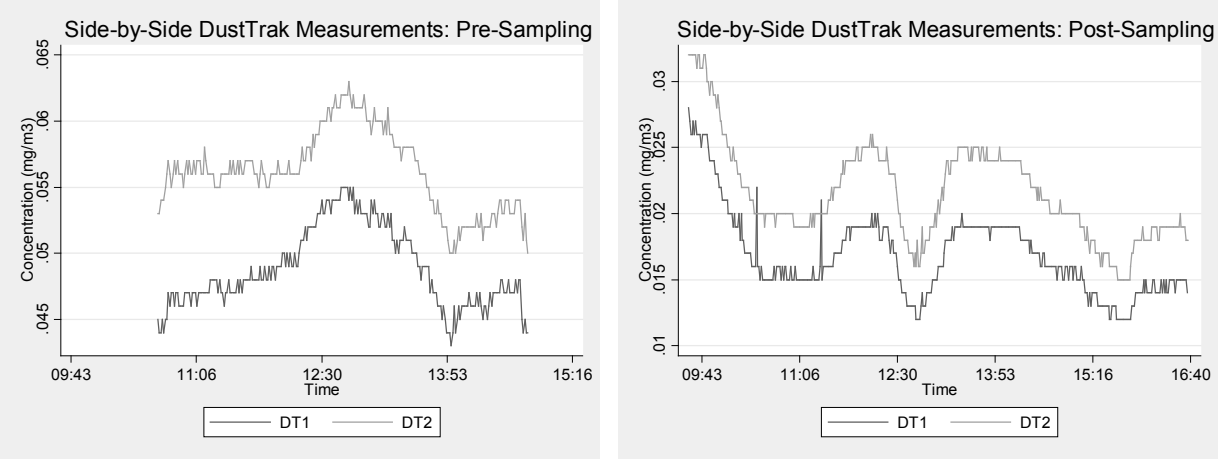


Figure 24. Side-by-Side DustTrak Measurements Taken in UC Office Building on 1/24/2011 and After Sampling (5/19/2011)

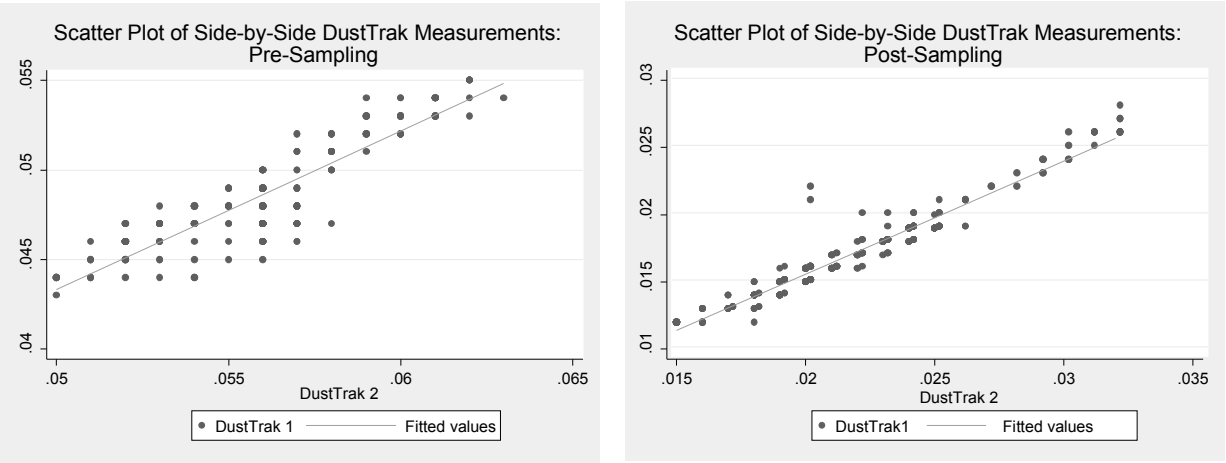


Figure 25. Scatter Plots of Pre- and Post-Sampling Side-by-Side DustTrak $PM_{2.5}$

Table 141. Summary Statistics for Side-by-Side DustTrak Measurements Pre- and Post-Sampling

	Pre-Sampling		Post-Sampling	
	DT1	DT2	DT1	DT2
N (# of minute measurements)	247	247	426	426
Average (µg/m³)	4.9	5.6	1.7	2.2
Median (µg/m³)	4.8	5.6	1.6	2.0
Std Dev (µg/m³)	3.0	3.0	3.0	4.0
Minimum (µg/m³)	4.3	5.0	1.2	1.5
Maximum (µg/m³)	5.5	6.3	2.8	3.2

Table 142. Summary of Standard Deviations and RSDs for Side-by-Side DustTrak Measurements Pre- and Post-Sampling

	Pre-Sampling		Post-Sampling	
	SD (µg/m³)	RSD (%)	SD (µg/m³)	RSD (%)
N (# of minute measurements)	247	247	426	426
Mean	5.0	10.0	3.0	17.4
SD	1.0	1.9	1.0	2.6

Gravimetric PM QA/QC

Field blanks (n=18) were analyzed by LBNL for QA/QC purposes. Field blanks were weighed prior to sampling, taken into the field by a technician without exposing the PEM, and then returned to LBNL for post-weighing. Field blank summary statistics are presented in Table 143. An MDL of 14.4 µg was calculated by computing three times the standard deviation of

blank filters. For 2 and 4 lpm PEMs and assuming an 8-hour sampling time, total air volume was approximately 0.96 and 1.92 m³. Reported data was blank corrected.

Table 143. Summary Statistics of the of Field Blank Weights

	2 and 4 lpm PEMs (µg)
Mean	2.3
Median	1.0
St. Deviation	4.8
Max	14.6

Integrated PM was to be sampled only using 2 lpm PEMs. However, during the pilot stage (ECE#10-14) of the project, filter contamination occurred due to the gaskets in some of the 2 lpm PEM bodies failing and shedding mass onto the filters during the loading and unloading process. This did not occur in all the filters but it was not possible, in retrospect, to determine which filters were contaminated. Upon finding this flaw, all 2 lpm PEM bodies were reconditioned and confirmed that weight change of the filters during loading and unloading was within acceptable limits (i.e., less than 3 µg change between measurements). Although the 2 lpm PEMs were reconditioned, 4 lpm PEMs were purchased to increase the sample volume and accuracy of measurements.

Four duplicate measurements were collected indoors for each $PM_{2.5}$ and PM_{10} for comparison. Due to flowmeter manifold set-up, the "field samples" were pulled through 4 lpm PEMs while "duplicate samples" were pulled through 2 lpm PEMs (Table 144). Standard deviations and RSDs were calculated to quantify the precision of measurements. For $PM_{2.5,}$ the mean RSD was 47.5% and a standard deviation of 16.2%. For PM_{10}, the mean RSD was 6.1% (SD=3.6). The larger RSDs for $PM_{2.5}$ are probably due the measurements being below/close to the MDL.

Table 144. Field and Duplicate Sample Concentrations with Standard Deviations and RSDs for $PM_{2.5}$

	$PM_{2.5}$				PM_{10}			
ECE#	Field Conc. (µg/m³)	Duplicate Conc. (µg/m³)	SD (µg/m³)	RSD (%)	Field Conc. (µg/m³)	Duplicate Conc. (µg/m³)	SD (µg/m³)	RSD (%)
45	5.3	10.6	3.7	46.7	15.1	16.6	1.0	6.4
46	5.3	15.9	7.5	70.5	25.1	29.2	2.9	10.8
47	16.3	26.7	7.3	34.1	77.4	73.1	3.0	4.0
49	10.4	18.2	5.5	38.5	50.0	52.0	1.4	2.8

As part of an additional QA analysis, mean DustTrak $PM_{2.5}$ concentration and integrated $PM_{2.5}$ concentrations were compared. At 35 ECE facilities, a DustTrak and PEM with a 2.5 µm size selectors were deployed. The mean RSD was 24.2% (SD= 21.1). Mean and median results across the 35 facilities with both measurements show consistent results (Table 145). The spearman rank test also indicates a strong correlation between the results ($R=0.73$, $p<0.00005$).

Table 145. Summary Comparison of Mean DustTrak PM2.5 and PEM $PM_{2.5}$ Concentrations ($\mu g/m^3$)

	DustTrak	PEM
N	35	35
Mean	20.0	19.3
25^{th} %	10.9	11.7
Median	14.8	16.2
75^{th} %	23.8	23.3
Maximum	89.4	54.9

Metals QA/QC

Table 146 presents the individual metal MDL in µg/ml and in µg/g assuming 0.5 gram dust sample extracted into a final volume of 50 ml.

Table 146. MDLs for Metal Dust Analysis

	MDL (µg/ml)	MDL (µg/g)
Al	0.026	2.6
Cd	0.001	0.1
Cr	0.001	0.1
Cu	0.003	0.3
Fe	0.029	2.9
Mn	0.001	0.1
Pb	0.075	7.5
Zn	0.006	0.6

The wavelengths used for metals analysis by ICP-MS were:

Sc 361.383 nm
Y 371.029 nm
Al 308.215, 394.401, and 396.153 nm
Cd 214.440, 226.502, and 228.802 nm
Cr 267.716 and 283.563 nm
Cu 224.700, 324.752, and 327.393 nm
Fe 238.204, 239.562, and 259.539 nm
Mn 257.610 and 260.568 nm
Pb 217.000 and 220.353 nm
Zn 202.548 and 206.200 nm

QTrak QA/QC

Both QTraks were calibrated by CARB in Spring 2010 prior to air sampling. In addition, duplicate measurements were taken indoors in three facilities to test the precision of the measurements. Although the correlation between the two machines is very high (R^2=0.98), QTrak 1 systematically reported higher levels of CO_2 concentrations than QTrak 2 (Table 147). The mean RSD between the duplicate measurements was 6.4% (SD=2.9) (Table 148).

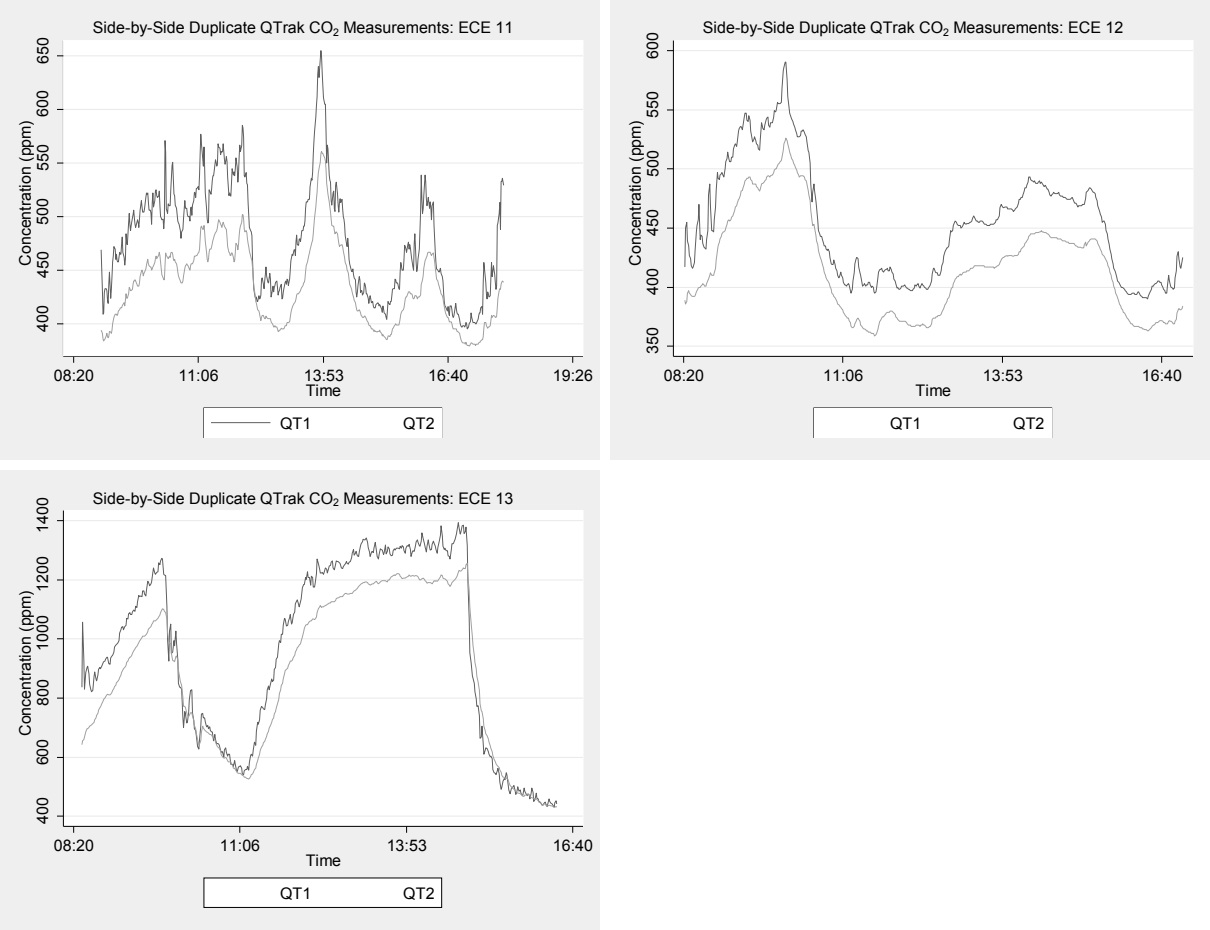


Figure 26. Side-by-side QTrak measurements at ECE 11, 12, and 13

Table 147. Summary Statistics for Side-by-Side QTrak CO_2 Measurements

	QTrak 1	QTrak 2
N (# of minute measurements)	1537	1537
Mean (ppm)	621	568
Median (ppm)	491	447

Table 148. Summary of Standard Deviations and RSDs between Duplicate Real-time CO_2 Measurements

	Standard Deviation (ppm)	RSD (%)
Mean	40.1	6.4
SD	30.1	2.9

List of Real-Time Malfunctions

Three real-time malfunctions occurred during the sampling period (Table 149). CPC 1 did not log at one facility (ECE #40); therefore, ultrafine measurements were recorded at a total of thirty-nine facilities. Two outdoor QTrak measurements were not logged. This impact was minor due to outdoor QTrak measurements only used for CO_2 inputted into ventilation calculations. For the facilities where the QTrak failed to log, average outdoor CO_2 measurements across all facilities were used.

Table 149. Descriptions of Real-time Malfunctions

ECE	Type	Description
40	Outdoor QTrak 2	Outdoor QTrak 2 did not log for unknown reasons.
46	Indoor CPC 1	Indoor CPC did not log data for unknown reasons.
49	Outdoor QTrak 2	Outdoor QTrak 2 did not log for unknown reasons.

APPENDIX D- Analysis of VOC Unknowns

Table 150. Surrogate Compounds and EI/TI Conversion Factors

Class[1]	Surrogate compound[2]	EI_x/TI_x[3]		EI_s/TI_s
		Average	St. Dev	
Aldehydes	Butanal	0.33	0.12	0.19
	Hexanal	0.22	0.05	
	Heptanal	0.16	0.03	
	Octanal	0.11	0.02	
	Nonanal	0.15	0.02	
	Decanal	0.11	0.02	
Alkanes	Octane	0.20	0.05	0.26
	Undecane	0.29	0.06	
	Dodecane	0.29	0.06	
	Tetradecane	0.27	0.05	
	Hexadecane	0.25	0.04	
Alkoxy	2-Butoxyethanol	0.43	0.05	0.36
	2-Ethyl-1-hexanol	0.36	0.06	
	Texanol	0.26	0.04	
	TXIB	0.24	0.03	
Aromatics	Benzene	0.48	0.11	0.39
	Toluene	0.45	0.04	
	Ethylbenzene	0.43	0.03	
	m/p-Xylene	0.47	0.02	
	o-Xylene	0.38	0.01	
	1,2,4-Trimethylbenzene	0.27	0.10	
	1,2,3-Trimethylbenzene	0.38	0.01	
	Butylbenzene	0.39	0.01	
Halogenated	Tetrachloroethylene	0.38	0.01	0.17
Phthalate	Dimethyl phthalate	0.17	0.01	0.51
	Diethyl phthalate	0.45	0.03	
	Dibutyl phthalate	0.41	0.03	
Siloxane	D3	0.62	0.04	0.36
	D4	0.52	0.02	
	D5	0.33	0.09	
Terpene	3-Carene	0.27	0.02	0.19
	d-Limonene	0.23	0.02	
	a-Terpineol	0.16	0.01	
Toluene	Toluene			0.43

[1] Dominant classes of chemicals identified in the indoor air. Each chemical was assigned to one of these classes.
[2] Chemicals included in the standard calibration method for the project that were selected as surrogates for the specific class.
[3] The average (and standard deviation) of all conversion factors for the given chemical across all calibration runs preformed during the project.

Table 151. Spearman Rank Correlation Test Results for VOC Analyte Concentrations Between Quantified and Semi-Quantified Analysis Methods

Analyte	Spearman's rho	p-value	Analyte	Spearman's rho	p-value
Hexane	0.92	<0.005	1,2,3-Trimethylbenzene	0.82	<0.005
Benzene	0.91	<0.005	g-Terpinene	0.52	0.002
Butanal	0.84	<0.005	Benzaldehyde	0.79	<0.005
Heptane	0.94	<0.005	Octanal	0.86	<0.005
Octane	0.95	<0.005	Undecane	0.92	<0.005
Toluene	1.00	<0.005	Butylbenzene	0.27	0.13
Hexamethylcyclotrisiloxane	0.71	<0.005	Decamethylcyclopentasiloxane	0.89	<0.005
Tetrachloroethylene	0.90	<0.005	2-Ethyl-1-hexanol	0.29	0.11
Hexanal	0.73	<0.005	Nonanal	0.98	<0.005
Ethylbenzene	0.99	<0.005	Dodecane	0.91	<0.005
m/p-Xylene	0.99	<0.005	Decanal	0.18	0.31
a-Pinene	0.93	<0.005	a-Terpineol	-0.52	0.12
o-Xylene	0.99	<0.005	Tetradecane	0.72	<0.005
Octamethylcyclotetrasiloxane	0.99	<0.005	Texanol	0.63	<0.005
Heptanal	0.97	<0.005	Hexadecane	0.39	0.028
Decane	0.79	<0.005	Dimethyl phthalate	0.75	<0.005
2-Butoxyethanol	0.97	<0.005	TXIB	0.88	<0.005
3-Carene	0.98	<0.005	Diethyl phthalate	0.68	<0.005
1,2,4-Trimethylbenzene	0.58	<0.005	Dibutyl phthalate	0.86	<0.005
d-Limonene	0.96	<0.005			

Table 152. Summary of Unknown VOC Concentrations (ng/m³) Using Semi-Quantitative Method of Analysis

Analyte	Det. Freq. (%)	N	Min	25th %	Median	75th %	90th %	95th %	Max
Pentane	54.5	22	0.0	0.0	40.9	95.0	187.5	394.0	417.8
1,3-Pentadiene, (Z)-	95.5	22	0.0	246.4	367.3	614.3	753.2	951.8	1,959.8
Ethanol	95.5	22	0.0	82.9	215.6	901.1	2,906.2	3,547.4	8,537.7
Isopropyl Alcohol	100.0	32	262.9	731.7	1,551.8	3,821.4	6,045.7	12,673.5	485,339
Hexane, 2-methyl-	100.0	32	50.4	111.9	242.3	598.9	1,100.3	1,532.1	1,858.1
Cyclohexane	100.0	32	40.3	96.8	221.0	403.9	645.8	1,403.3	1,514.9
Hexane, 3-methyl-	96.9	32	0.0	141.5	275.3	593.4	1,232.0	1,725.2	1,852.1
Ethyl Acetate	96.9	32	0.0	143.3	250.5	628.7	2,302.7	3,242.2	3,411.6
Silanol, trimethyl-	100.0	32	62.4	102.9	140.5	181.3	281.7	1,775.4	2,538.7
Cyclohexane, methyl-	100.0	32	47.6	95.0	292.5	410.8	905.7	1,118.9	2,372.1
2-Propanol, 1-methoxy-	71.9	32	0.0	0.0	131.3	319.7	933.4	2,176.0	11,417.8
1-Butanol	100.0	32	168.6	638.3	847.5	1,316.0	2,115.1	3,504.6	3,949.7
Pentanal	100.0	32	199.7	331.8	410.9	581.8	896.2	1,156.9	3,697.7
Acetic acid	87.5	32	0.0	215.4	764.9	1,954.4	4,146.1	7,142.1	10,550.8
Acetic acid, 2-methylpropyl ester	75.0	32	0.0	13.2	106.5	357.3	505.1	955.7	1,492.4
Acetic acid, butyl ester	96.9	32	0.0	245.8	389.4	777.2	1,862.1	6,490.0	6,997.0
Nonane	100.0	32	89.3	147.6	241.2	397.4	635.8	1,017.1	1,102.5
2-Pentanol, acetate	78.1	32	0.0	23.3	63.5	292.4	450.2	622.1	744.6
2-Propanol, 1-propoxy-	81.3	32	0.0	77.7	266.8	7,074.4	9,638.5	28,161.6	31,818.5
Propylene Glycol	100.0	32	1,002.7	4,273.0	7,357.4	15,519.7	17,631.5	24,012.7	25,025.7
1-Propanol, 2-(1-methylethoxy)-	25.0	32	0.0	0.0	0.0	6.8	97.6	148.7	247.1
Styrene	100.0	32	44.7	144.8	300.9	568.4	826.0	1,116.4	1,327.9
Furfural	100.0	32	193.1	428.5	708.7	1,377.5	1,992.0	3,008.2	3,257.6
Heptanal	100.0	32	260.7	455.5	558.9	726.1	918.3	1,045.8	1,363.4
Decane	81.3	32	0.0	222.6	529.3	1,006.3	1,807.9	3,110.4	4,814.3
Bicyclo[3.1.1]heptane, 6,6-dimethyl-2-me	100.0	32	352.8	703.7	1,601.5	3,402.4	7,841.7	10,209.9	25,611.0

Table 152 Continued. Summary of Unknown VOC Concentrations (ng/m³) using Semi-Quantitative Method of Analysis

Analyte	Det. Freq. (%)	N	Min	25th %	Median	75th %	90th %	95th %	Max
Cyclohexanone	100.0	32	159.9	366.5	517.1	868.0	1,368.5	2,688.7	12,195.6
beta-Myrcene	90.6	32	0.0	291.3	789.6	2,147.6	3,455.3	6,103.0	7,876.5
2-Propanol, 1-butoxy-	78.1	32	0.0	28.1	121.4	510.9	1021.1	3,507.9	17,086.2
Decamethyl Tetrasiloxane	50.0	32	0.0	0.0	17.3	193.8	765.4	6,185.9	68,645.5
.alpha.-Phellandrene	70.0	10	0.0	0.0	89.1	425.9	470.0	502.5	502.5
Methyltris(trimethylsiloxy)silane	37.5	32	0.0	0.0	0.0	132.2	752.0	2,915.5	6,185.9
Trisiloxane, octamethyl-	43.8	32	0.0	0.0	0.0	106.5	1,186.2	1,873.6	81,221.3
Eucalyptol	100.0	32	83.9	158.6	327.9	1,072.5	1,967.9	2,670.1	66,970.3
5-Hepten-2-one, 6-methyl-	68.8	32	0.0	0.0	82.8	209.1	446.1	817.2	1,061.8
1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)	68.8	32	0.0	0.0	484.5	710.0	2,459.4	7,611.5	11,510.7
2-Propanol, 1-(2-methoxy-1-methylethoxy)	96.7	30	0.0	125.3	253.6	719.0	1,494.3	2,363.4	2,469.2
Dipropylene glycol monomethyl ether	96.8	31	0.0	134.9	268.5	803.0	1,525.8	2,542.7	16,100.1
Benzene, 1-ethyl-3,5-dimethyl-	20.0	5	0.0	0.0	0.0	0.0	172.0	172.0	172.0
2-Propanol, 1-(2-methoxypropoxy)-	100.0	32	99.4	603.0	1,229.9	5,517.0	6,637.2	11,049.1	27,623.9
7-Octen-2-ol, 2,6-dimethyl-	100.0	32	163.0	637.9	1,656.7	3,214.4	9,019.4	11,492.5	15,495.2
3-Octanol, 3,7-dimethyl-, (±)-	65.6	32	0.0	0.0	86.3	217.3	390.2	1,334.0	11,475.8
1 Octane, 2,6-dimethyl-	0.0	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,8-Nonanediol, 8-methyl-	100.0	10	126.7	190.0	403.2	518.1	593.0	653.4	653.4
1-Octanol	100.0	10	1,450.7	2,343.3	2,768.9	3,294.2	4,594.3	4,653.7	4,653.7
Pentasiloxane, dodecamethyl-	100.0	10	23.7	37.5	139.9	411.1	14,153.5	27,748.0	27,748.0
Acetophenone	100.0	32	478.3	971.4	1,099.9	1,162.2	1,405.1	1,950.3	2,144.3
Benzyl Alcohol	100.0	32	72.0	285.4	483.3	894.2	1,226.7	3,339.9	6,853.1
Ethanol, 2-(hexyloxy)-	75.0	32	0.0	25.9	214.6	1,256.7	1,699.4	4,000.1	8,727.5
Phenol	93.8	32	0.0	588.9	1,127.8	1,843.2	3,575.8	3,803.4	7,588.3
Tetradecane, 2,2-dimethyl-	30.0	10	0.0	0.0	0.0	402.0	464.6	478.9	478.9

Table 152 Continued. Summary of Unknown VOC Concentrations (ng/m³) using Semi-Quantitative Method of Analysis

Analyte	Det. Freq. (%)	N	Min	25th %	Median	75th %	90th %	95th %	Max
Hexadecane, 2,6,10,14-tetramethyl-	50.0	32	0.0	0.0	83.1	343.7	882.8	8,511.7	12,256.0
1-Octanol, 2,2-dimethyl-	31.8	22	0.0	0.0	0.0	150.8	508.4	3,548.8	5,881.0
Camphor	93.8	32	0.0	188.6	338.8	696.0	1,126.1	1,689.4	22,410.8
Octane, 2,3,6,7-tetramethyl-	40.0	10	0.0	0.0	0.0	123.5	2,208.3	2,527.3	2,527.3
3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)	50.0	10	0.0	0.0	64.7	2,273.5	3,059.1	3,724.4	3,724.4
Decane, 2,2,4-trimethyl-	40.6	32	0.0	0.0	0.0	580.9	2,516.4	2,613.5	4,246.3
Cyclohexasiloxane, dodecamethyl-	100.0	32	291.0	978.5	1,885.5	3,448.6	4,066.4	7,165.8	16,681.6
Tetradecane, 2,2-dimethyl-	70.0	10	0.0	0.0	236.4	4,857.0	7,736.6	10,297.9	10,297.9
Acetic acid, phenylmethyl ester	100.0	32	77.9	188.3	366.4	897.3	1,336.9	4,041.6	7,525.1
Cyclohexanol, 5-methyl-2-(1-methylethyl)	100.0	32	86.4	235.0	466.5	829.1	2,074.7	4,529.4	8,239.4
Decane, 3,7-dimethyl-	30.0	10	0.0	0.0	0.0	30.0	233.7	391.2	391.2
Undecane, 6-ethyl-	50.0	10	0.0	0.0	79.6	464.1	1,473.9	2,435.7	2,435.7
1-Hexacosanol	30.0	10	0.0	0.0	0.0	914.1	1,190.6	1,223.4	1,223.4
3-Cyclohexene-1-methanol, alpha	87.5	32	0.0	135.8	232.5	870.7	2,069.2	3,467.8	10,565.3
Naphthalene	96.9	32	0.0	212.5	341.9	572.0	739.5	1,118.0	3,832.8
Nonane, 2-methyl-5-propyl-	70.0	10	0.0	0.0	1,491.3	2,343.3	3,977.3	5,556.8	5,556.8
Ethanol, 2-(2-butoxyethoxy)-	62.5	32	0.0	0.0	242.7	924.1	3,656.5	7,118.7	10,793.8
Tridecane, 3-methyl-	20.0	10	0.0	0.0	0.0	0.0	147.5	198.6	198.6
Octane, 2,5,6-trimethyl-	46.9	32	0.0	0.0	0.0	424.5	1,698.9	7,674.6	18,279.7
Undecane, 6,6-dimethyl-	70.0	10	0.0	0.0	470.4	10,105.5	16,802.1	21,933.2	21,933.2
Octane, 2,6-dimethyl-	80.0	10	0.0	82.0	307.9	4,541.9	7,117.5	9,482.7	9,482.7
Hexasiloxane, tetradecamethyl-	93.8	32	0.0	64.1	181.7	508.4	1,109.7	1,921.8	10,085.6
Decane, 2,2,6-trimethyl-	80.0	10	0.0	149.0	366.8	6,275.2	9,410.0	12,489.5	12,489.5
Hexane, 2,4-dimethyl-	80.0	10	0.0	196.3	324.0	4,553.1	6,812.0	9,054.9	9,054.9
Dodecane, 5,8-diethyl-	80.0	10	0.0	113.1	346.8	5,342.1	8,056.7	10,746.7	10,746.7

Table 152 Continued. Summary of Unknown VOC Concentrations (ng/m³) Using Semi-Quantitative Method of Analysis

Analyte	Det. Freq. (%)	N	Min	25th %	Median	75th %	90th %	95th %	Max
Dodecane, 2,6,10-trimethyl-	30.0	10	0.0	0.0	0.0	136.2	1,862.2	3,247.0	3,247.0
Decane, 2,2,8-trimethyl-	90.0	10	0.0	985.7	2,812.8	5,317.9	7,863.0	9,452.7	9,452.7
Cyclooctane	90.0	10	0.0	286.7	559.2	1,040.3	1,992.2	2,718.7	2,718.7
Decane, 2,2,7-trimethyl-	30.0	10	0.0	0.0	0.0	150.7	3,131.4	5,943.0	5,943.0
Tripropylene glycol (A)	28.1	32	0.0	0.0	0.0	26.1	139.5	5,718.7	10,766.3
Tripropylene glycol (B)	34.4	32	0.0	0.0	0.0	42.0	3,416.4	5,552.3	10,768.0
Tripropylene glycol (C)	50.0	32	0.0	0.0	15.2	868.4	2,089.0	5,940.5	6,515.5
Tripropylene glycol (D)	25.0	32	0.0	0.0	0.0	19.0	176.7	6,095.2	10,769.7
Ethanol, 2-phenoxy-	100.0	22	57.6	452.8	1,157.3	1,905.8	6,658.4	6,788.6	8,273.7
2-Propanol, 1-[1-methyl-2-(2-propenyloxy)-ethoxy]	18.2	22	0.0	0.0	0.0	0.0	31.0	62.6	10,782.2
2-Propanol, 1-[1-methyl-2-(2-propenyloxy)-ethoxy]	18.2	22	0.0	0.0	0.0	0.0	66.7	74.2	10,570.6
Decane, 2,2,9-trimethyl-	20.0	10	0.0	0.0	0.0	0.0	182.0	182.8	182.8
Dodecane, 2,7,10-trimethyl-	20.0	10	0.0	0.0	0.0	0.0	7,350.8	14,548.0	14,548.0
Benzaldehyde, 4-methoxy-	70.0	10	0.0	0.0	301.4	493.8	985.2	1,405.1	1,405.1
Octanol, 2-butyl-	40.0	10	0.0	0.0	0.0	186.1	371.0	489.2	489.2
Undecane, 2,8-dimethyl-	50.0	10	0.0	0.0	75.0	271.7	663.2	1,012.3	1,012.3
2-Propenal, 3-phenyl-	70.0	10	0.0	0.0	93.4	159.1	300.6	301.1	301.1
Caryophyllene	50.0	10	0.0	0.0	16.1	75.1	260.9	263.2	263.2
3-Methyl-4-isopropylphenol	50.0	10	0.0	0.0	10.5	36.1	577.4	1,073.7	1,073.7
Heptasiloxane, hexadecamethyl-	96.9	32	0.0	67.4	157.6	451.5	1,218.8	1,728.8	3,257.9
Benzoic acid, 2-hydroxy-, 3-methylbutyl	100.0	10	240.4	290.5	407.4	651.0	2,237.6	2,866.6	2,866.6
Pentadecane	100.0	10	646.6	1,209.9	1,646.4	2,453.3	6,693.6	10,837.4	10,837.4
Texanol(A)	93.8	32	0.0	1,241.4	2,372.8	3,733.0	7,465.7	11,312.6	45,730.9
Benzene, (1-butylhexyl)-	87.5	32	0.0	39.9	96.2	224.0	324.0	468.9	1,171.9
Cyclododecane	100.0	10	138.8	340.8	419.6	790.9	1,671.4	2,466.0	2,466.0

Table 152 Continued. Summary of Unknown VOC Concentrations (ng/m³) Using Semi-Quantitative Method of Analysis

Analyte	Det. Freq. (%)	N	Min	25th %	Median	75th %	90th %	95th %	Max
Benzene, (1-propylheptyl)-	81.3	32	0.0	40.1	79.6	191.8	287.8	1,185.8	2,976.0
Benzene, (1-ethyloctyl)-	71.9	32	0.0	0.0	50.3	116.7	198.0	1,104.1	2,739.0
Benzene, (1,1-dimethyldecyl)-	30.0	10	0.0	0.0	0.0	13.9	329.5	645.0	645.0
Naphthalene, 2-methoxy-	100.0	32	18.7	61.7	105.2	200.2	487.0	533.4	653.1
1-Penten-3-one, 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)	90.6	32	0.0	36.5	65.5	130.6	246.4	408.2	506.8
Heptasiloxane, hexadecamethyl-	20.0	10	0.0	0.0	0.0	0.0	216.9	379.8	379.8
Benzene, (1-methylnonyl)-	71.9	32	0.0	0.0	60.3	134.9	319.8	2,277.4	5,059.8
Benzene, (1-pentylhexyl)-	87.5	32	0.0	32.1	102.0	251.5	554.7	1,278.5	2,425.8
Benzene, (1-butylheptyl)-	87.5	32	0.0	114.9	190.1	332.1	687.2	2,745.1	4,902.4
Octane, 1,1'-oxybis-	93.8	32	0.0	191.0	511.8	891.7	1,564.6	1,697.1	3,106.2
Benzene, (1-propyloctyl)-	90.6	32	0.0	50.0	82.6	151.0	301.1	2,321.7	3,907.0
Benzene, (1-ethylnonyl)-	100.0	32	21.3	43.0	73.6	141.1	230.5	2,386.7	3,510.9
Benzene, (1,1-dimethylnonyl)-	31.3	32	0.0	0.0	0.0	16.9	24.2	137.0	858.3
Benzene, (1-methyldecyl)-	96.9	32	0.0	73.0	114.0	207.7	472.6	4,387.5	6,356.5
Benzene, (1-pentylheptyl)-	100.0	32	24.5	53.8	80.9	132.8	227.6	1,266.0	4,628.2
Benzene, (1-butyloctyl)-	96.9	32	0.0	54.4	80.1	138.1	229.4	1,266.0	4,584.1
Benzene, (1-propylnonyl)-	96.9	32	0.0	44.9	67.7	109.2	214.7	1,171.9	3,519.4
Benzene, (1-ethyldecyl)-	93.8	32	0.0	27.5	57.8	93.6	141.1	989.3	2,659.4
Tridecane, 2-methyl-2-phenyl-	40.0	10	0.0	0.0	0.0	58.5	535.1	1,008.9	1,008.9
Benzoic acid, 2-ethylhexyl ester	100.0	32	43.5	100.8	153.0	437.1	1,223.9	3,610.1	8,187.5
Benzene, (1-methylundecyl)-	90.0	10	0.0	38.3	54.8	82.5	1,951.9	3,812.2	3,812.2
Benzophenone	100.0	32	126.7	246.1	362.4	796.1	1,072.3	1,361.5	15,529.4
Benzene, (1-pentyloctyl)-	56.3	32	0.0	0.0	17.7	44.1	89.3	220.0	1,266.2
Benzene, (1-butylnonyl)-	37.5	32	0.0	0.0	0.0	14.5	52.7	222.8	727.9
Benzene, (1-propylheptadecyl)-	78.1	32	0.0	13.7	68.0	145.7	301.3	423.4	511.9

Table 152 Continued. Summary of Unknown VOC Concentrations (ng/m³) Using Semi-Quantitative Method of Analysis

Analyte	Det. Freq. (%)	N	Min	25th %	Median	75th %	90th %	95th %	Max
Nonadecane	100.0	32	54.9	123.0	158.6	209.6	336.4	342.8	450.9
2-Ethylhexyl salicylate	100.0	32	24.5	207.0	359.5	679.9	2,239.2	2,866.6	5,696.6
Homosalate	93.8	32	0.0	69.8	164.0	367.3	1,121.6	2,610.3	3,499.5

APPENDIX E- Chemical Inventory

Table 153. Inventory and Frequency of Active Ingredients Found in Products in Child Care Facilities

Active Ingredient	Frequency
Sodium Hypochlorite	37
N- Alkyl Dimethylbenzyl Ammonium Chloride	31
Ethanol	20
Alkyl Dimethylethylbenzyl Ammonium Chloride	14
Propane	14
Acetone	11
Pine Oil	11
Alkyl Dimethylbenzyl Ammonium Saccharide	9
Isobutane	9
Isopropanol	9
Petroleum Distillate	9
Didecyldimethylammonium Chloride	8
Sodium Dicholoro S-Triazinetrione Dihydrate	8
Butane	6
Hydrotreated Light Petroleum Distillate	6
Octyl Decyl Dimethyl Ammonium Chloride	6
D-Allethrin	5
D-Limonene	5
Dioctyl Dimethyl Ammonium Chloride	5
Pyrethrins	5
Sodium Dodecylbenzene Sulfonate	5
2-Butoxyethanol	4
Calcium Carbonate	4
Cypermethrin	4
Diethylene Glycol Monoethyl Ether	4
Glycol Ether	4
Hydrogen Chloride	4
Hydrogen Peroxide	4
Hydrotreated Heavy Naphthenic	4
Liquefied Petroleum Gas	4
Monoethanolamine	4
Nonoxynol	4
Piperonyl Butoxide	4
Sodium Carbonate	4
Sodium Hydroxide	4
Sodium Tetra Borate Decahydrate	4
Xylene	4
Difluoro Ethane	3
Ethoxylated Linear Alcohols	3
Imiprothrin	3
N-Octyl Bicycloheptene Dicarboximide	3

Table 153 Continued. Inventory and Frequency of Active Ingredients Found in Products in Child Care Facilities

Active Ingredient	Frequency
Permethrin	3
Poe Dodecyl Phenol Ether	3
Sodium Chloride	3
Sodium Lauryl Sulfate	3
Benzethonium Chloride	2
Benzylethyldimethylammonium Chloride	2
Boric Acid	2
Butyl Carbitol	2
Cocamidopropyl Betaine	2
Hydrocarbon Propellant	2
Lapao	2
Nonionic Surfactant	2
Sodium C14-16 Olefin Sulfonate	2
Sodium Silicate	2
Stoddard Solvent (Petroleum Distillate)	2
Tetramethrin	2
Thymol	2
Titanium Dioxide	2
Toluene	2
Triclosan	2
(S) Methoprene	1
2,4-D, Isooctyl Ester	1
2___(2___Butoxyethoxy)Ethanol	1
3-(Trimethoxysilyl)Propyldimethyloctade	1
Abamectin	1
Acephate	1
Acetaldehyde	1
Alkaline Builders	1
Ammonia	1
Ammonium Hydroxide	1
Arsenic Trioxide	1
Bifenthrin	1
Brodifacoum	1
Bromethalin	1
Calcium Carbonate (Limestone)	1
Calcium Sulfate Hemihydrate	1
Carbitol	1
Castor Oil	1
Chloroxylenol	1
Citric Acid	1
Crystalline Silica	1

Table 153 Continued. Inventory and Frequency of Active Ingredients Found in Products in Child Care Facilities

Active Ingredient	Frequency
Cyclohexane	1
Cycloryl Na	1
Dicamba	1
Dimethyl Ether	1
Dipropylene Glycol Monomethyl Ether	1
Diquat Bromide	1
Ethylbenzene	1
Ethylene Glycol	1
Glycerine	1
Glyphosate, Isopropylamine Salt	1
Hexonic Acid	1
Hexyloxyethanol	1
Imazapyr, Isopropylamine Salt	1
Imidacloprid	1
Isoparaphenic Hydrocarbon Solvent	1
L-Lactic Acid	1
Lactic Acid	1
Lambda- Cyhalothrin	1
Linseed Oil	1
Mecoprop-P	1
Metaldehyde	1
Methyl Acetate	1
Methyl Ethyl Ketone	1
Methyl Soyate	1
Mineral Oil	1
N,N-Dialkyl N-Dimethylammonium Chloride	1
Naphthegenic Distolent	1
Nepheline Syenite	1
Nonidet P-40	1
Octoxynol 9	1
Oleic Acid	1
Pentane	1
Phenothrin	1
Polyolimethyl Siloxane	1
Polyoxyethylene (5) Undecyl Ether	1
Potassium Hydroxide	1
Povidone-Iodine	1
Pp6-6 C12 15 Pareth- 12	1
Prallethrin	1
Propylene Glycol Propyl Ether	1
Resmethrin	1

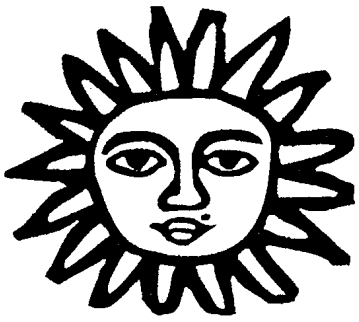
Table 153 Continued. Inventory and Frequency of Active Ingredients Found in Products in Child Care Facilities

Active Ingredient	Frequency
Silicone Emulsion	1
Sodium Polyacrylate	1
Sodium Polycarboxylate	1
Sodium Tripolyphosphate	1
Sulfuramid	1
Tall Oil Fatty Acids	1
Thyme Oil	1
Tralomethrin	1
Triethylene Glycol	1
Triforine	1
Tripropylene Glycol Methyl Ether	1
Tris (2-Butoxyethyl) Phosphate	1
Total	437

APPENDIX F- Questionnaire, Inspection, and Visit Material Packet

Environmental Exposures in Early Childhood Education Environments (ECE)

QC Review:	Date	ID
Initial EST	_ _/_ _/_ _	__ __
Final EST	_ _/_ _/_ _	__ __
Copied	_ _/_ _/_ _	__ __
Data entered	_ _/_ _/_ _	__ __



Questionnaire Form for Early Childcare Facilities

P1.	Date of Interview:	___ ___ /___ ___ /___ ___ MO DAY YR
P2.	Collector(s) who completed interview:	_____ __ __ **[Code]** _____ __ __ **[Code**

PRIOR TO STARTING THE INTERVIEW:

Thank you for participating in this important study about indoor/outdoor environments in child care facilities. With your permission, I would like to ask you a few questions about you and your facility. I want to get as much accurate information as possible and will therefore be reading you all of the possible responses to some questions. If you do not know the answer, please give me your best estimate or say you don't know. You may refrain from answering questions that make you uncomfortable. If you do not want to answer a question, let me know, and we will move to the next question. All of the information you provide will remain confidential.

Can we proceed with this questionnaire? Yes or No

A. TEACHER INFORMATION

1. What is your job here?

Director 1
Other Administrator 2
Teacher 3
Teacher Aide 4
Facility Manager 5
Custodial staff 6
Other 7
Please specify:_____ __ __
[CODE LATER]

2. How many years have you worked at this facility? **__ __Yrs __ __ Mo**

3. How many non-teaching staff are employed at this facility? These may include clerical, cleaning, and maintenance staff. ___ ___ ___

4. How many paid teachers are at this facility? Please include directors and paid teacher aids in your count. ___ ___ ___

5. In general, what is the education level of the teacher(s)?

None, or grade school (1st through 8th grade) 1
Grades 9-12 (high school, no diploma) 2
High school diploma/ GED/ equivalent 3
Technical school 4
Some college 5
College graduate or more 6
Don't know 9

B. INFORMATION ON CHILDREN WHO ATTEND THE CHILD CARE FACILITY

Now, I would like to ask you general questions about the children who attend this facility. No specific children will be identified in the following questions.

6. How many children attend this child care facility? ___ ___ ___

7. How many of children who attend this facility are less than 12 months old? ___ ___ ___

8. How many of children who attend this facility are 12 months to less than 24 months old? ___ ___ ___

9. How many of children who attend this facility are 24 months to less than 36 months old? ___ ___ ___

10. How many of children who attend this facility are 36 months old or older? ___ ___ ___

CHECK ANSWERS: ADD ANSWERS TO QUESTIONS 7, 8, 9, AND 10 AND MAKE SURE THEY EQUAL QUESTION 6. IF NOT, PLEASE REVIEW ANSWERS WITH PARTICIPANT.

11. How many children attend this center for less than 5 hours per day? ___ ___ ___

12. How many children attend this center for 5 to 8 hours per day? ___ ___ ___

13. How many children attend this center for more than 8 hours per day? ___ ___ ___

CHECK ANSWERS: ADD ANSWERS TO QUESTIONS 11, 12, AND 13 AND MAKE SURE THEY EQUAL QUESTION 6. IF NOT, PLEASE REVIEW ANSWERS WITH PARTICIPANT.

14. I would like to know about the racial/ethnic composition of your children. I am going to give several categories of races and ethnicities and I would like you to give me the number of children in each category.

Caucasian ..... ___ ___ ___

Black ..... ___ ___ ___

Hispanic ..... ___ ___ ___

Asian ..... ___ ___ ___

Native American..... ___ ___ ___

Multi-racial ..... ___ ___ ___

Any Other Ethnicity/ Race .... ___ ___ ___

Please Specify _____

[CODE LATER]

Don't know/ Do not want to answer 999

15. What percent of your children receive a government or other subsidy to pay for some or all of the cost of attending?

___ ___ ___%

16. <u>During this season</u>, about how many hours per day on average did your children spend outdoors at this facility? This includes outdoor lessons or playing outside.

Less than one …… 1

One to two …….. 2

Three to four …….. 3

Five to six …… 4

More than six …….. 5

Don't know …….. 9

C. BUILDING SYSTEMS

The next questions will be about your building's heating, ventilation, and air conditioning.

17. What kind of temperature control system is used?

Manual thermostat 1
Programmable thermostat 2
Temperature centrally controlled by building maintenance 3
Don't know 9

18. What type of heating system does this facility have?

None ..... (26.) 0
Central forced air 1
Wall mounted heaters 2
Baseboard heaters 3
Radiant floor heating 4
Portable (such as space heaters) 5
Floor mounted heaters 6
Other_____ __

Specify

[CODE LATER]

Don't know 9

19. How old is the heating system in this facility?

___ ___ ___Years

CODE 999 FOR DO NOT KNOW

20. What type of fuel is used for the heating system?

Gas 1
Propane 2
Electric 3
Wood 4
Other_____ __

Specify

[CODE LATER]

Don't know 9

21. How often is the building's heating system inspected and maintained by a professional?

Never 0
Less than once per year 1
At least once per year 2
Don't know 9

22. Is a furnace filter used?

No ..... (26.) 0
Yes 1
Don't know ..... (26.) 9

23. What type of furnace filter?

Pleated Filter (Not a High Efficiency Particulate Filter or HEPA) 1
High Efficiency Particulate Filter (HEPA) 2
Filter with activated carbon 3
Electrostatic precipitator 4
Ionizer 5
Ultraviolet/ UV Light 6

PCO USES UV LIGHT WITH A CATALYST LIKE TITANIUM DIOXIDE

Photocatalytic Oxidation (PCO) 7
Ozone generator 8
Other/ Combination _____ __

Specify

[CODE LATER]

Don't know 9

24. When were the furnace filters last changed?

DATE: __ __ / __ __ __ __
MO Year

CODE 99/9999 FOR DO NOT KNOW

25. How frequently are the furnace filters changed?

Never	0
Less than once a year	1
Annually	2
Quarterly	3
Monthly	4
Don't know	9

26. Does this facility have any gas-burning appliances? These appliances may include a gas water heater, a gas range, stoves, or gas clothes dryer.

No	(29.)	0
Yes		1
Don't know	(29.)	9

27. Is a gas stove or gas oven ever used to heat this facility?

No	0
Yes	1
Don't know	9

28. How often does a trained professional inspect your gas burning appliances?

Never	0
At least once a year	1
Less than once a year	2
Don't know	9

29. Does this facility ever use portable gas-burning appliances such as small propane or kerosene heaters?

No	(31.)	0
Yes		1
Don't know	(31.)	9

30. How often are the portable gas-burning appliances such as small propane or kerosene heaters used to heat the facility?

Once a month	1
Once a week	2
Once a day	3
Once a day in Winter	4
Don't know	9

31. Does this facility have a fireplace?

No	(34.)	0
Yes		1
Don't know	(34.)	9

32. What fuel does the fireplace use?

Wood	1
Gas	2
Don't know	9

33. During the cold season, how often is the fireplace used when children are present?

Never	0
More than once per month	1
Once per month	2
Don't know	9

34. Does this facility have a wood-burning stove?

No	(36.)	0
Yes		1
Don't know	(36.)	9

35. How often is the wood-burning stove used when children are present?

Never	0
More than once per month	1
Once per month	2
Don't know	9

36. Does this facility have air conditioning?

No	(44.)	0
Yes		1
Don't know	(44.)	9

37. How old is the air conditioning system in this facility?

___ ___ ___Years

CODE 999 FOR DO NOT KNOW

38. What type of air conditioning does this facility have?

Central Air Conditioning	.....	1
Window Unit	.....	2
Portable/ Stand Alone	.....	3
Swamp Cooler	.....	4
Other_____		__

Specify

[CODE LATER]

Don't know		9

39. How often is the air conditioning unit inspected and maintained by a trained professional?

Never	.....	0
At least once a year	.....	1
Less than once a year	.....	2
Don't know	.....	9

40. Does the air conditioning unit have a separate filter from the furnace filter?

No	.....(43.).....		0
Yes	.....		1
Don't know	.....(43.).....		9

41. When were the air conditioning filters last changed?

DATE: __ __ / __ __ __ __

MO Year

CODE 99/999 FOR DO NOT KNOW

42. How frequently are the air conditioning unit filters changed?

Never	.....	0
Less than once a year	.....	1
Annually	.....	2
Quarterly	.....	3
Monthly	.....	4
Don't know	.....	9

43. Have the air conditioning cooling coils and drip pan been cleaned in the last year?

No 0
Yes 1
Don't know 9

44. Does this facility have an active ventilation system? These are systems that actively bring in outside air into the building. Usually they are part of a central heating and air conditioning system, but not all central heating and air conditioning systems bring outside air into the building.

No .....(50.)..... 0
Yes 1
Don't know .....(50.)..... 9

45. How old is the ventilation system in this facility?

_____ Years

CODE 999 FOR DO NOT KNOW

46. How often is the building's ventilation system inspected and maintained?

Never 0
At least once per year..... 1
Less than once per year 2
Don't know 9

47. Does the ventilation system in this facility have a separate filter from the heater and air conditioning?

No .....(50.)..... 0
Yes 1
Don't know .....(50.)..... 9

48. When was the ventilation filter last changed?

DATE: __ __ / __ __ __ __

MO Year

CODE 99/999 FOR DO NOT KNOW

49. How frequently are the ventilation unit filters changed?

Never	0
Less than once a year	1
Quarterly	2
Annually	3
Monthly	4
Don't know	9

50. Who typically does the maintenance on your heating, ventilation, and air conditioning systems?

No one	0
You or another employee	1
Contractor	2
Don't know	9

51. Is it hard to control temperature in this facility?

No	0
Yes	1
Don't know	9

52. Does this facility use natural ventilation like open windows while children are in the facility?

No	0
Yes	1
Don't know	9

53. When children are present, is the kitchen stove fan used when preparing food?

No, the stove fan is not used	0
Yes, the stove fan is used	1
No stove fan in this facility	2
Don't know	9

54. When children are present, is the bathroom fan used when showering and/ or bathing?

No, the bathroom fan is not used	0
Yes, the bathroom fan is used	1
No bathroom fan in this facility	2
Showering and/or bathing does not occur while children are present	3
Don't know	9

55. Do windows "fog-up" during the heating season? This does not include when you cook.

No	0
Yes	1
Don't know	9

D. BUILDING MAINTENANCE

I am now going to ask you questions about this building's maintenance history.

55.A What year was this building originally constructed? — — — —

56. Have there been major renovations in the last five years? This may include an addition, new roof, new lighting, etc.

No.....(58.)	0
Yes	1
Don't know.....(58.)	9

57.	I am going to name specific items that could be renovated. Please tell me if this facility has renovated them in the PAST FIVE YEARS and how long ago it was installed?		**No**	**Yes**	**No. of Years ago?**
	(A.)	Addition.....	0	1	
	(B.)	Roof.....	0	1	
	(C.)	Lighting.....	0	1	
	(D.)	Heating, ventilation, and air conditioning (HVAC).....	0	1	
	(E.)	New Insulation	0	1	
	(F.)	Wall	0	1	
	(G.)	Electrical.....	0	1	
	(H.)	Foundation.....	0	1	
	(I.)	Plumbing.....	0	1	
	(J.)	Windows.....	0	1	
	(K.)	Other ..... **Please specify _____** **[CODE LATER] ___ ___**	0	1	

58. Has this facility applied new interior paint in the last year?

No .....(60.) 0
Yes 1
Don't know .....(60.) 9

59. How many months ago? ____ ____Months Ago

60. Has this facility applied new caulking in the last year?

No .....(62.) 0
Yes 1
Don't know .....(62.) 9

61. How many months ago? ____ ____Months Ago

62. Has this facility installed new pressed wood bookcases, desks, chairs, or cabinets in the last year? Pressed wood is also known as particle board hardwood plywood, and medium density fiberboard. It is made of wood veneer, particles or wood fiber bonded together with an adhesive.

No.....(64.) 0
Yes 1
Don't know.....(64.) 9

63. How many months ago? ____ ____Months Ago

64. Has this facility installed new vinyl-covered tack boards in the last year?

No.....(66.) 0
Yes 1
Don't know.....(66.) 9

65. How many months ago? ____ ____Months Ago

66. Has this facility installed new vinyl-covered walls in the last year?

No.....(68.) 0
Yes 1
Don't know.....(68.) 9

67. How many months ago? ____ ____Months Ago

68. Has this facility installed new floor coverings like carpet, vinyl, rubber, wood, or linoleum in the last year?

No.....(70.) 0
Yes 1
Don't know.....(70.) 9

69.	I am going to name different types of flooring. Please tell me what kind of new flooring was installed and how long ago it was installed?		**No**	**Yes**	**No. of Months ago?**
	(A.)	Carpet.....	0	1	
	(B.)	Vinyl.....	0	1	
	(C.)	Wood	0	1	
	(D.)	Rubber.....	0	1	
	(E.)	Linoleum	0	1	
	(F.)	Other..... **Please specify _____** **[CODE LATER]**	0	1	

70. Have wood floors been sanded and/or refinished in the last year?

No wood floors .....(72.) 99

No .....(72.) 0

Yes..... 1

Don't know.....(72.) 9

71. How many months ago? ____ ____Months Ago

72. Has this facility ever had mold remediation work done?

No .....(74.) 0

Yes..... 1

Don't know.....(74.) 9

73. How was the mold removed?

With detergent 1
With disinfectant 2
Source removal 3
Combination of Methods 4
Other_____ —
Specify
[CODE LATER]
Don't know 9

E. SMALL APPLIANCES

I will now ask you questions about small appliances.

74. Is a humidifier or vaporizer ever used in this facility?

No .....(79.) 0
Yes 1
Don't know.....(79.) 9

75. How often is the humidifier or vaporizer used?

Daily 1
Weekly 2
Monthly 3
Yearly 4
Don't know 9

76. How often is the humidifier or vaporizer cleaned?

Never 0
Weekly 1
Monthly 2
Yearly 3
Don't know 9

77. Do you use a humidifier or vaporizer that has any special features such as a high efficiency particulate air filter or others that help clean the air?

No (79.)	0
Yes	1
Don't know (79.)	9

78. What kind of feature does your humidifier or vaporizer use to clean air?

Pleated Filter (Not a High Efficiency Particulate Filter or HEPA)	1
High Efficiency Particulate Filter (HEPA)	2
Electrostatic precipitator	3
Ionizer	4
Ultraviolet/ UV Light	5
Photocatalytic Oxidation (PCO)	6
Ozone Generator	7
Other	__

Specify

[CODE LATER]

79. Is a dehumidifier used in this facility?

No (84.)	0
Yes	1
Don't know (84.).	9

80. How often is the dehumidifier used?

Daily	1
Weekly	2
Monthly	3
Yearly	4
Don't know	9

81. How often is the dehumidifier cleaned?

Never	0
Yearly	1
Monthly	2
Weekly	3
Don't know	9

82. Do you use a dehumidifier that has any special features such as a high efficiency particulate air filter or others to help clean the air?

No (84.)	0
Yes	1
Don't know (84.)	9

83. What kind of special feature does your dehumidifier use to clean air?

Pleated Filter (Not a High Efficiency Particulate Filter or HEPA)	1
High Efficiency Particulate Filter (HEPA)	2
Electrostatic precipitator	3
Ionizer	4
Ultraviolet/ UV Light	5
Photocatalytic Oxidation (PCO)	6
Ozone Generator	7
Other	__

Specify

[CODE LATER]

84. Are any portable air cleaning or filtering appliances used in this facility when kids are present?

No (88.)	0
Yes	1
Don't know (88.)	9

85. What is the portable air cleaner type?

Pleated filter (not a high efficiency particulate air filter) 1
High Efficiency Particle Air Filter (HEPA) ... 2
Electrostatic precipitator. 3
Ionizers 4
Ultraviolet/ UV Light 5
Photocatalytic Oxidation (PCO) 6
Ozone Generator 7

Other or combinations .....

Please Specify _____

[CODE LATER]

Don't know 9

86. How often are the filter components of the portable air cleaner removed and replaced?

Never 0
Yearly 1
Monthly 2
Weekly 3
Not applicable 4
Don't know 9

87. How often are the fans and other interior components of the portable air cleaner cleaned?

Never 0
Yearly 1
Monthly 2
Weekly 3
Not applicable 4
Don't know 9

F. CLEANING, MAINTENANCE, AND HYGIENE PRACTICES

I will now ask you questions about the cleaning and maintenance practices observed at this facility.

88. Does this facility have any drapes?

No	(91.)	0
Yes		1
Don't know	(91.)	9

89. Are the drapes ever dry cleaned?

No	(91.)	0
Yes		1
Don't know	(91.)	9

90. How often are the drapes dry cleaned?

Monthly	1
Every six months	2
Yearly	3
Don't know	9

91. How often are the furniture, shelves, and windowsills cleaned with a wet cloth or other wet dusting method?

Never	0
Less than once per month	1
Once per month	2
Twice per month	3
Once per week	4
Few times per week	5
At least once per day	6
Don't know	9

92. Does this facility contain any carpet?

No	(100.)	0
Yes		1
Don't know	(100.)	9

93. How often are the carpets in this facility vacuumed?

Never	0
Less than once per month	1
Once per month	2
Twice per month	3
Once per week	4
Few times per week	5
At least once per day	6
Don't know	9

94. Do you use a vacuum that has any special features such as a high efficiency particulate air filter or others that enhance their cleaning ability?

No	(96.)	0
Yes		1
Don't know	(96.)	9

95. What is the special feature?

Pleated Filter (Not a High Efficiency Particulate Filter or HEPA)	1
High Efficiency Particulate Filter (HEPA)	2
Electrostatic precipitator	3
Ionizer	4
Ultraviolet/ UV Light	5
Ozone Generator	6
Other or combination	

Please Specify _____

[CODE LATER]

96. How many times in a year are the carpets in this facility deeply cleaned by either staff or a professional? By this I mean, steam cleaned, shampooed, sent out to cleaner, or other wet cleaning method.

Never	0
Less than once per year	1
Once per year	2
Every six months	3
Every three months	4
Every other month	5
At least once per month	6
Don't know	9

97. Has any "dry cleaning" process been applied to the carpets?

No	0
Yes	1
Don't know	9

98. Were any of the rugs or carpets in this facility labeled or marketed as "stain resistant?"

No	0
Yes	1
Don't know	9

99. Have any products been applied to the rugs or carpets to make them more stain resistant?

No	0
Yes	1
Don't know	9

100. Does this facility have uncarpeted floors? By uncarpeted, I mean linoleum, hardwood, vinyl, etc.

No	(104.)	0
Yes		1
Don't know	(104.)	9

101. How often are the uncarpeted floors in this facility swept or vacuumed?

Never 0
Less than once per month 1
Once per month 2
Twice per month 3
Once per week 4
Few times per week 5
At least once per day 6
Don't know 9

102. How often are the uncarpeted floors in this facility mopped?

Never 0
Less than once per month 1
Once per month 2
Twice per month 3
Once per week 4
Few times per week 5
At least once per day 6
Don't Know 9

103. How often is a disinfectant or sanitizer used to mop the floors?

Never .....(104.) 0
Less than once per month 1
Once per month 2
Once per week 3
Few times per week 4
Every time the floors are mopped 5
Don't know 9

104. Is a disinfectant or sanitizer used to clean surfaces or items in this facility? These surfaces or items could include counter tops, table tops, diaper changing area, toys, etc.

No ..... (109.) 0
Yes 1
Don't know ..... (109.) 9

105. When using disinfectants or sanitizers, are the manufacturer's instructions followed?

No 0
Yes 1

106.	I am going to name a surface or item. Please tell me how often the surface or item is washed, disinfected, or sanitized. I will read you the answer choices.	**No area/item in facility**	**At least every day**	**Every other day**	**Once a week**	**Less than once a week**
(A.)	Diaper changing area					
(B.)	Food eating area					
(C.)	Sinks used to wash children					
(D.)	Items "mouthed" by children like toys and blankets					
(E.)	Linens used on or by children					

107. Does this facility use hand sanitizers

No ..... (109.) 0
Yes 1
Don't know ..... (109.) 9

108. On average, how often are hand sanitizers used on children?

Less than once per month 1
Once per month 2
Twice per month 3
Once per week 4
Few times per week 5
At least once per day 6
Don't Know 9

G. POTENTIAL EXPOSURES TO KNOWN BUILDING HAZARDS (LEAD, RADON, ASBESTOS, AND CARBON MONOXIDE)

I am now going to ask you question about potential building hazards.

109. Does the facility have any surfaces that have ever been painted using lead paint?

No 0
Yes 1
Don't know 9

110. Has the facility ever been tested for lead in paint dust or soil?

No .....(113.)..... 0
Yes 1
Don't know.....(113.)..... 9

111. Did the lead levels require abatement and removal?

No .....(113.)..... 0
Yes 1
Don't know.....(113.)..... 9

112. How long ago did the abatement occur? _____ Yrs _____Months Ago

113. Have any children who attend this day care facility ever been tested for lead?

No 0
Yes 1
Don't know 9

114. Has this facility ever been checked for radon?

No .....(117.)..... 0
Yes 1
Don't know.....(117.)..... 9

115. How long ago was the facility checked? _____ Yrs _____Months Ago

116. If the facility was checked, was the radon level:

Greater than 4 pCi/L	1
Less than 4 pCi/L	2
Less than 2 pCi/L	3
Don't know	9

117. Has this building ever been checked for asbestos?

No (124.)	0
Yes	1
Don't know (124.)	9

118. Has this facility been found to contain asbestos?

No (124.)	0
Yes	1
Don't know (124.)	9

119. How is asbestos monitored during any building repairs, renovations or construction activity?

No one is responsible for monitoring asbestos during these activities	0
Facility staff are responsible for monitoring asbestos during these activities	1
Licensed asbestos inspector is responsible for monitoring asbestos during these activities	2
Don't know (124.)	9

120. Has asbestos ever been removed by other than a trained professional?

No (124.)	0
Yes	1
Don't know (124.)	9

121. How long ago? _____ Yrs _____ Months Ago

122. Has asbestos ever been professionally removed?

No .....(124.)..... 0
Yes..... 1
Don't know.....(124.)..... 9

123. How long ago? _____ Yrs _____ Months Ago

124. Do you have a carbon monoxide detector in your facility?

No .....(126.)..... 0
Yes..... 1
Don't know.....(126.)..... 9

125. Do you or anyone else check the CO detector regularly to ensure that it is functioning properly?

No 0
Yes..... 1
Don't know..... 9

H. POTENTIAL EXPOSURES TO CHEMICAL AND BIOLOGICAL AGENTS

I am now going to ask you questions about possible chemical and biological irritants.

126. What do children nap on?

No napping equipment..... (128.)..... 0
Floor mats..... 1
Cots..... 2
Other .....
Please Specify _____
[CODE LATER]
Don't know..... (128.) 9

127. Is the napping equipment made out of foam?

No..... 0
Yes..... 1
Don't know..... 9

128. Does anyone who works in this facility smoke during a break from work?

No ..... (130.) 0
Yes 1
Don't know ..... (130.) 9

129. Where does smoking occur?

Anywhere, there are no restrictions 1
Only outside where children are not present 2
It is not permitted anywhere on the property 3
Don't know 9

130. Do you ever burn candles while children are present?

No ..... (134.) 0
Yes 1
Don't know ..... (134.) 9

131. How often are lit candles present?

Once per day or more 1
Few times per week 2
Once per week 3
Several times a month 4
Once per month 5
Less than once per month 6

132. Do you ever burn votive candles while children are present?

No ..... (134.) 0
Yes 1
Don't know ..... (134.) 9

133. How often are votive candles lit?

Once per day or more 1
Few times per week 2
Once per week 3
Several times a month 4
Once per month 5
Less than once per month 6

134. Are air fresheners used in this facility?
By air fresheners I mean scented spray, potpourri, Incense, etc.

No .....(137.)..... 0

Yes..... 1

Don't know .....(137.)..... 9

135.	In what rooms are the air fresheners used?		**No**	**Yes**
	(A.)	Bathroom.....	0	1
	(B.)	Kitchen	0	1
	(C.)	Children's area	0	1
	(D.)	Other ..... **Please Specify _____ [CODE LATER]**	0	1

136.	I am going to name different types of air fresheners. Please tell me how often these items are used inside this facility. I will read you the answer choices.	**Never**	**Less than once a week**	**Once a week**	**Few times a week**	**At least once a day**	**Continu-ously used**
(A.)	Spray air fresheners.....						
(B.)	Continuous release (like a plug in device)						
(C.)	Potpourri						
(D.)	Incense						
(E.)	Any other type of air freshener ..... **Please Specify_____ [CODE LATER]**						

137.	I am going to name some items. Please tell me how often these items are used inside this facility. I will read you the answer choices.	**Never**	**Less than once a week**	**Once a week**	**A few times a day**	**At least once a day**
(A.)	Oil/acrylic paints					
(B.)	Permanent markers or art pens					
(C.)	Whiteboard markers					
(D.)	Correction fluid					
(E.)	Rubber cement.....					
(F.)	Epoxy or “superglue”					
(F.)	Non-stick pans.....					

138.	Have you or any other staff seen evidence of any of the following unwanted pests inside this facility?		**NO**	**YES**	**DK**
	(A.)	Cockroaches.....	0	1	9
	(B.)	Ants	0	1	9
	(C.)	Flies.....	0	1	9
	(D.)	Fleas.....	0	1	9
	(E.)	Head lice.....	0	1	9
	(F.)	Mice or rats.....	0	1	9
	(G.)	Spiders	0	1	9
	(H.)	Termites.....	0	1	9
	(I.)	Any Other Pests..... **Please specify** _____ **[CODE LATER]**	0		

139. Have you or any other staff seen a live cockroach during the day?

No..... 0
Yes 1

140. Are any pets currently housed in this facility?

No.....(142.) 0
Yes 1

141.	Which of the following pets are housed in this facility?		NO	YES	IF YES INDICATE # BELOW	DK
	(A.)	Bird ……..…….....	0	1	_____	9
	(B.)	Cat…….....…….....	0	1	_____	9
	(C.)	Dog…….....…	0	1	_____	9
	(D.)	Gerbil…….....…	0	1	_____	9
	(E.)	Hamster…….....…	0	1	_____	9
	(F.)	Guinea Pig…….....…	0	1	_____	9
	(G.)	Other ..... **Please Specify** _____ **[CODE LATER]**	0		_____	

I. HEALTH AND SAFETY (INJURY PREVENTION MEASURES)

I am now going to ask you questions about health and safety.

142. Is your garbage service collection frequent enough to prevent nuisance odors and littering?

No 0
Yes..... 1
Don't know 9

143. Is the staff trained to use fire extinguishers?

No 0
Yes..... 1
Don't know 9

J. PESTICIDE USE

I am now going to ask you questions about pesticide use.

144.	**Who decides when and how to control indoor and outdoor pest problems at your child care facility? Please check all that apply.**		**No**	**Yes**
	(A.)	Director	0	1
	(B.)	Another staff member	0	1
	(C.)	The landlord	0	1
	(D.)	The custodial staff	0	1
	(E.)	A pest control company	0	1
	(F.)	Other **Please Specify _____** **[CODE LATER]**	0	1
		Don't know	9	

145. Have pesticides or insecticides ever been applied inside or outside this facility in the last year?

No .....(151.)..... 0
Yes..... 1
Don't know .....(151.)..... 9

146. Are pesticides applied when children are present?

No 0
Yes..... 1
Don't know 9

147. How often are pesticides applied by a professional exterminator?

Never .....(150.)..... 0
Sometimes 1
Always..... 2
Don't know 9

148. Do you know the name(s) of the pesticide used by the professional exterminators? Or is there any way of finding out what pesticides were used like with receipts or contacting the pesticide company?

No .....(150.)..... 0

Yes..... 1

Don't know.....(150.)..... 9

149. What are the names?

*Now I would like to ask you more specific questions about pesticides or insecticides that have been applied by you or your staff in the **PAST 12 MONTHS** in and around the facility. Please include pesticides or insecticides used in outdoor play areas or garden. Pesticides can come in the form of sprays, bombs, poison pellets or bait, powder, chalk, roach motels, traps, or ant stakes.*

150.	*A. Have pesticides or insecticides been used in or around your facility to kill* **[INSERT PEST]**:	*B. Was this pesticide in the form of …* NO ……0 YES…..1 DK…....9	*C. Was/were* **[INSERT B]** *used inside or outside the facility?* INSIDE…….1 OUTSIDE…2 BOTH……...3 DK.……..9	*D. How many times total in the past 12 months has/have* **[INSERT B]** *been applied?*	*E. Was/ were* **[INSERT B]** *applied in the last week?* NO …..0 YES…..1 DK…....9	*F. Who applied the* **[INSERT B]?** You……1 Other Staff Member…..2 Professional Applicator...3
A.	**Rodents?** NO..(next pest)…0 YES…..(→)…....1 DK..(next pest)…9	*Poison pellets or baits?…….___* *Poison powder?…...___* *Other?…….___* ***Specify**:* _____ **[CODE LATER]**	___ ___ ___	___ ___ ___ ___ ___ ___ ___ ___ ___	___ ___ ___	___ ___ ___
B.	**Fleas, including treatments to pets?** NO..(next pest)…0 YES…..(→)…....1 DK..(next pest)…9	*Sprays?……..___* *Bombs?……..___* *Powder?……___* *Spot Treatment* ____ *Other?……...___* ***Specify**:* _____ **[CODE LATER]**	___ ___ ___ ___	___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___	___ ___ ___ ___	___ ___ ___ ___
C.	**Termites?** NO…(next pest)..0 YES…..(→)…....1 DK..(next pest)…9	*Sprays?…….___* *Bombs?……..___* *Powder?……..___* *Other?……..___* ***Specify:*** _____ _ **[Code later]**	___ ___ ___ ___	___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___	___ ___ ___ ___	___ ___ ___ ___

	A. Have pesticides or insecticides been used in or around your facility to kill **[INSERT PEST]***:*	*B. Was this pesticide in the form of …* NO ……0 YES……1 DK……..9	*C. Was/were* **[INSERT B]** *used inside or outside the facility?* INSIDE……1 OUTSIDE…..2 BOTH……..…3 DK……..9	*D. How many times total in the past 12 months has/have* **[INSERT B]** *been applied?*	*E. Was/ were* **[INSERT B]** *applied in the last week?* NO ……0 YES……1 DK……9	*F. Who applied the* **[INSERT B]?** You……1 Other staff Member…… 2 Professional Applicator...3
D.	**Flying insects, ants, roaches or other crawling insects?** NO..(next pest)..0 YES…..(→)…....1 DK..(next pest)..9	*Sprays……*____ *Bombs?……*____ *Powder/chalk.*____ *Roach motels/traps/ ant stakes/bait?* *Pest strip?.*____ *Other?…….*____ ***Specify****:* **[CODE LATER]**	___ ___ ___ ___ ___ ___ ___	__ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __	___ ___ ___ ___ ___ ___ ___	___ ___ ___ ___ __ ___ ___
E.	**Fungus, weeds, snails, or slugs?** NO..(next pest)..0 YES…..(→)… …1 DK..(next pest)..9	*Sprays?…..*___ *Pellets? ….. ___* *Other?…….*___ ***Specify****:* **[CODE LATER]**	___ ___ ___	__ __ __ __ __ __ __ __ __	___ ___ ___	___ ___ ___

K. Attitudes and Beliefs

I am now going to ask you questions about environmental exposures and environmental health. When I use the term "environmental exposures," I mean the physical, biological, and chemical exposures humans receive from their environments. When I use the term "environmental health" in this section, I mean the health impacts of physical, biological, and chemical agents on humans. Do you have any questions about the definitions I will be using?

151. **Do you incorporate concern about children's environmental exposure in your purchasing decisions? i.e. purchasing low toxicity cleaners.**

No 0
Yes 1

152.	**Does this facility have written policies addressing any of the following subjects concerning children's environmental health**?	**NO**	**YES**	**DK**
	(A) Purchasing or using low toxicity cleaners	0	1	9
	(B.) Purchasing building materials that do not emit chemicals into the environment	0	1	9
	(C.) Facility disinfection and sanitization requirements	0	1	9
	(D.) Facility cleaning requirements including wet dusting and mopping	0	1	9
	(E.) Pesticide use and application	0	1	9
	(F.) Heating, Ventilation, and Air Conditioning Maintenance Requirements	0	1	9
	(G.) List of items that are prohibited to be used while children are present	0	1	9
	(H.) Any other written environmental health policies? **Please specify**	0	1	9

153. **Do you provide training in children's environmental health to your staff?**

No .....(155.)..... 0
Yes..... 1
Don't Know..... 9

154. **What subjects do you address in your training on children's environmental health?**

155. **If given the opportunity, would you like to learn more about children's environmental health?**

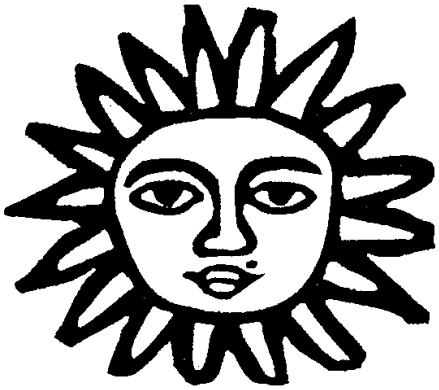
No ..... (157.) 0
Yes 1
Don't Know..... (157.) 9

156. **In what area would you like to receive more training on children's environmental health?**

157.	**Which of the following formats do you think would be the best way for to learn about environmental health?**		No	Yes
	A.	Workshops.....	0	1
	B.	Web content.....	0	1
	C.	News letter.....	0	1
	D.	Other..... **Please specify [CODE LATER]**	0	1

158. **Do you have anything that you would like to mention or add to this questionnaire?**

Thank you for taking the time to complete this questionnaire. We can now move to the facility inspection. Do you have any questions?



Inspection Form for Early Childcare Facilities

P1.	Date of Interview:	___ ___ /___ ___ /___ ___ MO DAY YR
P2.	Collector(s) who completed Interview:	_____[**Code]** _____**[Code]**

EQUIPMENT THAT WILL BE NECESSARY TO COMPLETE FACILITY INSPECTION:	
• FLASHLIGHT	• GLOVES
• GPS	• BLUE WATERPROOF PEN
• COMPASS	• CLIPBOARD
• FIRE ALARM TESTER	• EXTRA BATTERIES FOR GPS
• STREET MAP	• BOOTIES

DIRECTIONS: ALL INSPECTOR DIRECTIONS WILL BE "BOXED." ALL OBSERVATIONAL QUESTIONS ARE CAPITALIZED. *ALL SPOKEN QUESTIONS AND INSTRUCTIONS IN ITALICIZED PRINT*. **ALWAYS ASK PERMISSION BEFORE ENTERING A ROOM.**

Thank you for participating in the facility inspection. I will now perform a building inspection in which I will be compiling information about the characteristics of the indoor/ outdoor environments. In addition to the inspection, I will also be completing a sketch of this facility.
May I proceed with the facility inspection? ***Yes or No***

A. BUILDING CHARACTERISTICS

1. CENTER LOCATION?

ALAMEDA COUNTY	1
MONTERREY COUNTY	2

2. TYPE OF FACILITY?

SINGLE FAMILY DETACHED HOME	1
DUPLEX	2
APARTMENT	3
SCHOOL (TRADITIONAL)	4
SCHOOL (PORTABLE)	5
MANUFACTURED HOUSING (MOBILE HOME)	6
CHURCH	7
OFFICE BUILDING	8
OTHER _____	

SPECIFY
[CODE LATER]

3. BUILDING INCLUDES RESIDENTS?

NO	0
YES	1
DON'T KNOW	9

B. CHEMICAL INSPECTION

At this time, I will ask you some questions and then ask for you to show me to a specific room or area.

4. *Are there any cleaners, disinfectants, or sanitizers stored in or around this facility?*

Can you please show me?

No ..... (8.)	*0*
Yes	*1*
No Access ..... (8.)	*9*

INSTRUCTIONS: Be sure to USE GLOVES when handling chemical containers. DO NOT handle any open or leaking containers. Make sure to list all chemicals found in facility or yard. IF MORE THAN 3 CHEMICALS ARE PRESENT, COMPLETE APPENDIX I

		CHEMICAL 1	**CHEMICAL 2**	**CHEMICAL 3**
5.	A. BRAND NAME	____________________	____________________	__________________
	B. TYPE OF CHEMICAL CLEANER ....1 DISINFECTANT 2 SANITIZER 3	______	______	______
	D. ACTIVE INGREDIENT(S) **[CODE LATER]** **[CONFIRM CAS# WHEN CODING]**	NAME_____________ __________________ CAS#______________ CODE ______ _____ NAME_____________ __________________ CAS#______________ CODE ______ _____ NAME_____________ __________________ CAS#______________ CODE ______ _____	NAME______________ ____________________ CAS#_______________ CODE ______ _____ NAME______________ ____________________ CAS#_______________ CODE ______ _____ NAME______________ ____________________ CAS#_______________ CODE ______ _____	NAME______________ ___________________ CAS#______________ CODE ______ _____ NAME______________ ___________________ CAS#______________ CODE ______ _____ NAME______________ ___________________ CAS#______________ CODE ______ _____
	E. GREEN PRODUCT CERTIFICATION? NO ....0 GREENSEAL ....1 ECOLOGO 2	______	______	______

	F. CHEMICALS STORED? OUTSIDE .....(H) .....1 INSIDE .....2 OFF PROPERTY .....3 **NEXT CHEMICAL**	_____	_____	_____
	G. ROOM CHEMICALS ARE STORED? KITCHEN .....1 CHILDCARE ROOM.....2 CLOSET.....3 BATHROOM .....4 HVAC ROOM....5 OTHER ..... **SPECIFY [CODE LATER]**	_____	_____	_____
	H. INACCESSIBLE TO CHILDREN? (OUT OF REACH OR LOCKED) NO .....0 YES.....1	_____	_____	_____

6. *Which disinfectants or sanitizers are used most frequently when mopping the floors?*

7. *Which of the disinfectants or sanitizers are used to clean surfaces and items? These surfaces or items could include counter tops, table tops, diaper changing area, toys, etc* **[CODE LATER]**

8. *Are there <u>any</u> pesticides or insecticides stored anywhere in or around your facility? This includes insect sprays, ant and roach motels, flea powder or sprays for your pet, Chinese chalk, etc.*

Please show me

No .....(11)..... 0

Yes..... 1

.....

No access.....(11)..... 9

		PESTICIDE 1	PESTICIDE 2	PESTICIDE 3
9.	A. BRAND NAME	_____	_____	_____
	B. TARGET PEST ANTS..... 01 ROACHES ..... 02 FLEAS..... 04 FLYING INSECTS..... 05 TERMITES ..... 06 APHIDS..... 07 OTHER INSECTS..... 08 SNAILS/ SLUGS ..... 09 FUNGUS ..... 10 WEEDS..... 11 RODENTS..... 12	___ ___ ___ ___ MARK ALL THAT APPLY	___ ___ ___ ___ MARK ALL THAT APPLY	___ ___ ___ ___ MARK ALL THAT APPLY
	C. EPA REGISTRATION #s **If not present, code (999)**	_____ _____	_____ _____	_____ _____
	D. ACTIVE INGREDIENT(S) **[CODE LATER]** **[CONFIRM CAS# WHEN CODING]**	NAME_____ _____ CODE ___ ___ NAME_____ _____ CODE ___ ___ NAME_____ _____ CODE ___ ___	NAME_____ _____ CODE ___ ___ NAME_____ _____ CODE ___ ___ NAME_____ _____ CODE ___ ___	NAME_____ _____ CODE ___ ___ NAME_____ _____ CODE ___ ___ NAME_____ _____ CODE ___ ___

	E. PESTICIDES STORED? OUTSIDE ...(G)..... 1 INSIDE 2	_____	_____	_____
	F. ROOM PESTICIDES ARE STORED? KITCHEN..... 1 CHILDCARE ROOM 2 CLOSET..... 3 BATHROOM..... 4 HVAC ROOM ..... 5 OTHER..... **SPECIFY** **[CODE LATER]**	_____	_____	_____
	G. INACCESSIBLE TO CHILDREN? (OUT OF REACH OR LOCKED) NO..... 0 YES..... 1	_____	_____	_____

10. *Have any pesticides or insecticides other than the ones we looked at today been used in your facility? Please exclude professional pesticides application.*

Can you please show me?

No *0*

Yes ..... (9) *1*

YES, COMPLETE BEST AVAILABLE INFORMATION IN PESTICIDE GRID EVEN IF CONTAINER NOT AVAILABLE.

11. *Are any other chemicals stored anywhere in or around this facility? By other chemicals, I mean paints, solvents, glues, etc.*

Can you please show me?

No ..... (13) *0*

Yes *1*

No Access ..... (13) 9

		CHEMICAL 1	CHEMICAL 2	CHEMICAL 3
12.	A. BRAND NAME	_____	_____	_____
	B. TYPE OF CHEMICAL PAINT..... 1 SOLVENT..... 2 GLUE ..... 3 OTHER..... **SPECIFY _____** **[CODE LATER]**	___ ___	___ ___	___ ___
	D. INGREDIENT(S) **[CODE LATER]** **[CONFIRM CAS# WHEN CODING]** **Code 999 if CAS# unknown**	NAME_____ _____ CAS#_____ CODE _____ ____ NAME_____ _____ CAS#_____ CODE _____ ____ NAME_____ _____ CAS#_____ CODE _____ _____	NAME_____ _____ CAS#_____ CODE _____ _____ NAME_____ _____ CAS#_____ CODE _____ _____ NAME_____ _____ CAS#_____ CODE _____ _____	NAME_____ _____ CAS#_____ CODE _____ _____ NAME_____ _____ CAS#_____ CODE _____ _____ NAME_____ _____ CAS#_____ CODE _____ _____
	E. GREEN PRODUCT CERTIFICATION? NO.....0 GREENSEAL....1 ECOLOGO 2	_____	_____	_____
	F. CHEMICALS STORED? OUTSIDE ... (H)1 INSIDE 2	_____	_____	_____

	G. ROOM WHERE CHEMICALS ARE STORED? KITCHEN.....1 CHILDCARE ROOM .....2 CLOSET .....3 BATHROOM.....4 HVAC ROOM ...5 OTHER..... **SPECIFY [CODE LATER]**	_____	_____	_____
	H. INACCESSIBLE TO CHILDREN? (OUT OF REACH OR LOCKED) NO.....0 YES 1	_____	_____	_____

C. ROOM BY ROOM ASSESSMENT

I will now do a facility inspection for the next hour in which I will be inspecting the main child care room, the kitchen, and the bathroom most used by children.

INSTRUCTIONS: ALWAYS ASK FOR PERMISSION BEFORE ENTERING ROOM. INSPECT CHILD CARE ROOM WHERE TESTING WILL OCCUR. INSPECT BATHROOM MOST USED BY CHILDREN. IF ANSWER IS NOT APPLICABLE PLEASE CODE "99."

			A. CHILDCARE ROOM (WHERE TESTING WILL OCCUR)	B. KITCHEN/ FOOD PREP AREA	C. BATHROOM (USED BY CHILDREN)
13.	DOES THIS FACILITY HAVE A _____?	**0-** NO **1-** YES **2-** NO ACCESS	____	_____	_____
14.	TYPE OF FLOOR COVERING? HARD=LINOLEUM, TILE, WOOD, ETC)	**1-** HARD **2-** WALL TO WALL⇒16 **3-** HARD+AREA RUG(S **4-** WALL TO WALL +AREA RUG(S) ⇒16	____	_____	_____
15.	TYPE OF HARD FLOOR?	**1-** VINYL **2-** WOOD **3-** RUBBER **4-** TILE OTHER -> **SPECIFY [CODE LATER]**	_____	_____	_____
16.	CARPETS WORN OR SOILED?	**0-** NO **1-** YES **99 NOT PRESENT**	_____	_____	_____
17.	IF AREA RUGS PRESENT, ARE THEY SOILED?	**0-** NO **1-** YES **99 NOT PRESENT**	_____	_____	_____
18.	HOLES IN INTERIOR WALLS/CEILING?	**0-** NO **1-** YES	_____	_____	_____
19.	HOLES IN FLOOR?	**0-** NO **1-** YES	_____	_____	_____
20.	VINYL WALL COVERINGS PRESENT?	**0-** NO **1-** YES	_____	_____	_____
21.	UPHOLSTERED FURNITURE PRESENT?	**0-** NO **1-** YES	_____	_____	_____

			A. CHILDCARE ROOM (WHERE TESTING WILL OCCUR)	B. KITCHEN/ FOOD PREP AREA	C. BATHROOM (USED BY CHILDREN)
22.	FURNITURE CONTAINING A LARGE AMOUNT OF FOAM PADDING? **NOT INCLUDING NAPPING EQUIPMENT**	**0-** NO **1-** YES	_____	_____	_____
23.	CONDITION OF FURNITURE? **99 if not present**	**1-** BAD, TEARS, WORN. **2-** GOOD, FREE OF TEARS	_____	_____	_____
24.	PRESSED-WOOD FURNITURE? (E.G. DESKS, BOOKCASES, CABINETS, ETC. MADE FROM PLYWOOD OR PARTICLEBOARD)	**0-** NO **1-** YES	_____	_____	_____
25.	KIND OF NAPPING EQUIPMENT?	**0-** NONE⇒ 28 **1-** FLOOR MATS **2-** COTS OTHER -> **SPECIFY [CODE LATER]**	_____		
26.	NAPPING EQUIPMENT MADE OUT OF FOAM?	**0-** NO **1-** YES	_____		
27.	CONDITION OF NAPPING EQUIPMENT?	**1-** BAD, TEARS, WORN. **2-** GOOD, FREE OF TEARS	_____		
28.	ANY OF THE FOLLOWING ITEMS PRESENT? MARK ALL THAT APPLY.	**0-** NONE **1-** FOAM PILLOWS **2-** MATTRESSES **3-** MATTRESS PADS OTHER ITEMS WITH FLAME RETARDANTS? **SPECIFY [CODE LATER]**	_____		
29.	WINDOWS IN ROOM?	**0-** NO⇒ 36 **1-** YES	_,____	_____	_____
30.	WINDOWS HAVE SCREENS?	**0-** NO⇒33 **1-** YES	_____	_____	_____
31.	WINDOWS HAVE SECURE SCREENS?	**0-** NO **1-** YES	_____	_____	_____
32.	WINDOW SCREENS' CONDITION?	**1-** BAD, TEARS **2-** GOOD, FREE OF TEARS	_____	_____	_____

			A. CHILDCARE ROOM (WHERE TESTING WILL OCCUR)	B. KITCHEN/ FOOD PREP AREA	C. BATHROOM (USED BY CHILDREN)
33.	WINDOWS OPEN?	**0-** NO **1-** YES	_____	_____	_____
34.	ANY WINDOW COVERINGS?	**0-** NO⇒36 **1-** YES	_____	_____	_____
35.	WHAT TYPE OF COVERING?	**1-** SHADES **2-** CURTAINS **3-** HEAVY DRAPES **4-** BLINDS	_____ _____ MARK ALL THAT APPLY	_____ _____ MARK ALL THAT APPLY	_____ _____ MARK ALL THAT APPLY
36.	WATER DAMAGE/ INTRUSION IN ROOM? SUCH AS STAINS ON WALL, CEILING, OR FLOOR.	**0-** NO⇒38 **1-** YES	_____	_____	_____
37.	WATER DAMAGE/ INTRUSION LOCATION?	**1-** WALL **2-** CEILING **3-** FLOOR OTHER -> **SPECIFY [CODE LATER]**	_____	_____	_____
38.	MOLD PRESENT?	**0-** NONE⇒40 **1-** MINIMAL **2-** MODERATE **3-** EXTENSIVE	_____	_____	_____
39.	LOCATION OF MOLD?	**1-** WINDOW **2-** CARPET **3-** CLASSROOM ITEM **4-** CABINET **5-** WALL **6-** CEILING **7-** FURNITURE **8-** PLUMBING STRUCTURES OTHER -> SPECIFY [CODE LATER]	_____ _____ _____	_____ _____ _____	_____ _____ _____
40.	PLUMBING LEAKS UNDER SINK?	**0-** NO **1-** YES 99 NO SINK IN ROOM	_____	____	____
41.	ROTTING WOOD IN ROOM?	**0-** NO **1-** YES	_____	_____	_____
42.	UNPLEASANT ODORS?	**0-** NO⇒44 **1-** YES	_____	_____	_____

			A. CHILDCARE ROOM (WHERE TESTING WILL OCCUR)	B. KITCHEN/ FOOD PREP AREA	C. BATHROOM (USED BY CHILDREN)
43.	TYPE OF ODOR?	**1-** MUSTY/ MILDEW **2-** CHEMICAL **3-** SEWAGE **4-** TOBACCO SMOKE OTHER -> SPECIFY [CODE LATER]	____	____	____
44.	PEELING PAINT IN ROOM?	**0-** NO **1-** YES	____	____	____
45.	PAINT CHIPS ON FLOOR?	**0-** NO **1-** YES	____	____	____
46.	EVIDENCE OF MICE, RATS, OR RODENTS? (I.E. DROPPINGS, BAITS, ETC.)	**0-** NO **1-** YES	____	____	____
47.	EVIDENCE OF COCKROACHES?	**0-** NO **1-** YES	___	___	___
48.	VISIBLE DUST?	**0-** NO **1-** YES	___	___	___
49.	BURNING CANDLES?	**0-** NO **1-** YES	___	___	___
50.	AIR FRESHENERS PRESENT?	**0-** NO⇒52 **1-** YES	___	___	___
51.	TYPE OF AIR FRESHENERS?	**1-** SPRAY **2-** CONTINUOUS RELEASE (PLUG IN) **3-** POTPOURRI **4-** INCENSE OTHER -> SPECIFY [CODE LATER]	___	___	___
52.	MOTH BALLS OR MOTH CAKES PRESENT?	**0-** NO **1-** YES	___	___	___
53.	TACKBOARDS PRESENT?	**0-** NO **1-**YES, UPHOLSTERED **2-** YES, VINYL-COVERED **3-** YES, CORKED	___	___	
54.	FOOD STORED TO PREVENT PEST ACCESS? **99 if not present**	**0-** NO **1-** YES	___	___	
55.	TV PRESENT?	**0-** NO **1-** YES	___	___	

			A. CHILDCARE ROOM (WHERE TESTING WILL OCCUR)	B. KITCHEN/ FOOD PREP AREA	C. BATHROOM (USED BY CHILDREN)
56.	COMPUTER PRESENT?	**0-** NO **1-** YES	____	____	
57.	COMPUTER PRINTER PRESENT?	**0-** NO **1-** YES	____	____	
58.	COPY MACHINE PRESENT?	**0-** NO **1-** YES	____	____	
59.	Other electronics present?	**0-** No **1-** Yes	____	____	
60.	FIRE EXTINGUISHER?	**0-** NO **1-** YES	____	____	____
61.	SMOKE DETECTOR?	**0-** NO⇒**63.** **1-** YES	____		
62.	SMOKE DETECTOR FUNTIONING?	**0-** NO **1-** YES	____		
63.	CARBON MONOXIDE DETECTOR?	**0-** NO⇒**65.** **1-** YES	____		
64.	CO DETECTOR FUNCTIONING?	**0-** NO **1-** YES	____		
65.	SHOWER PRESENT?	**0-** NO **1-** YES			____
66.	FAN PRESENT? **[CONSIDER STOVE FAN OR OVERHEAD BATHROOM FAN ONLY] [CHECK IF IT WORKS]**	**0-** NO FAN⇒68. **1-** NOT FUNCTIONING **2-** FUNCTIONING		____	____
67.	IS FAN VENTED TO THE OUTSIDE?	**0-** NOT VENTED **1-** VENTED **9-** DON'T KNOW/ UNCONFIRMED		____	____
68.	TYPE OF STOVE IN KITCHEN?	**0-** NONE ⇒**71** **1-** ELECTRIC ⇒**71** **2-** GAS **3-** PORTABLE GAS (CAMPING) STOVE⇒**71** OTHER -> **SPECIFY [CODE LATER]**		____	
69.	STOVE PILOT BURNING?	**0-** NO **1-** YES		____	
70.	GAS SMELL?	**0-** NO **1-** YES		____	

			A. CHILDCARE ROOM (WHERE TESTING WILL OCCUR)	B. KITCHEN/ FOOD PREP AREA	C. BATHROOM (USED BY CHILDREN)
71	TYPE OF OVEN IN KITCHEN?	**0-** NONE⇒**73.** **1-** GAS **2-** ELECTRIC⇒**73.**		____	
72.	OVEN PILOT BURNING?	**0-** NO **1-** YES		____	
73.	ANY OF THE FOLLOWING COMBUSTION SOURCES PRESENT IN ROOM OR ADJACENT TO ROOM?	**0-** NO **1-** GAS WATER HEATER **2-** UNVENTED GAS SPACE HEATER **3-** CHARCOAL FOR HEATING OR COOKING **4-** OPEN FLAME GAS WALL HEATER **5-** GAS COOK TOP OR OVEN **6-** UNVENTED KEROSENE HEATER **7-** WOOD STOVE	____ ____ ____ MARK ALL THAT APPLY	____ ____ ____ MARK ALL THAT APPLY	____ ____ ____ MARK ALL THAT APPLY
74.	SOLID WASTE CONTAINERS WITH TIGHT FITTING LIDS?	**0-** NO **1-** YES	____	____	____
75.	DIAPERS PRESENT?	**0-** NO **1-** YES, UNSCENTED **2-** YES, SCENTED	____	____	____
76.	DIAPER WIPES?	**0-** NO **1-** YES, UNSCENTED **2-** YES, SCENTED	____	____	____
77.	URINAL CAKES IN BATHROOM?	**0-** NO **1-** YES			____
78.	GENERAL CLEANLINESS?	**1-** LESS CLEAN **2-** FAIR **3-** CLEAN	____	____	____

FOR THE NEXT QUESTIONS, YOU WILL NEED TO FIND THE INTERVIEWEE.

D. MOLD AND WATER DAMAGE

79. A. *Have you seen any water damage inside your facility? By water damage I mean water stains on the ceiling or walls, or flaking sheetrock or plaster.*
Can you please show me?

No ..... (80) *0*

Yes *1*

B. ALL WATER DAMAGE RECORDED?

NO ..... *(*36.*)*..... 0

YES 1

80. *A. Have you seen any mold or mildew on walls or other surfaces, other than food, inside your facility?*
Can you please show me?

No ..... *(*81.*)*..... *0*

Yes *1*

B. ALL MOLD/MILDEW RECORDED?

NO ..... *(*38.*)*..... 0

YES 1

E. BUILDING SYSTEMS

81. **[EITHER ASK OR OBSERVE THE FOLLOWING:]**
Does this facility have a hot water heater located inside the facility?

Please Show Me

No ..... *(83)* *0*

Yes..... *1*

82. GAS WATER HEATER?

NO..... (83.) 0

YES..... 1

NO ACCESS 9

83. **[EITHER ASK OR OBSERVE THE FOLLOWING:]**
Is there any clothes dryer inside this facility?

Please Show Me

No .....(86)..... 0
Yes..... 1
No Access.....(86)..... 9

I can fill in the rest of the inspection by myself. I will come find you when I am finished.

84. GAS CLOTHES DRYER?

NO..... 0
YES..... 1
NO ACCESS 9

85. DRYER VENTED TO OUTSIDE?

NO..... 0
YES..... 1

NOTE: NEED TO CONFIRM BY INSPECTING BEHIND THE DRYER AND OUTSIDE AT VENT TERMINUS. FEEL THE AIR FLOW AND LOOK FOR SIGNS OF LINT BUILD UP IN BACK OF DRYER. VENT HOSE OFTEN LEAKS OR IS BLOCKED.

NO ACCESS 9

86. TYPE OF HEATING SYSTEM?

NONE.....(90)..... 0
CENTRAL..... 1
WALL 2
FLOOR..... 3
PORTABLE 4
OTHER _____

SPECIFY

[CODE LATER]

NO ACCESS .....(90)..... 9

87. TYPE OF FUEL USED TO HEAT THE FACILITY?

GAS 1
PROPANE..... 2
ELECTRIC..... 3
WOOD..... 4
NO ACCESS 9

88. TYPE OF FURNACE FILTER?

NONE.....(90.) 0
PLEATED FILTER (NOT HEPA) 1
HIGH EFFICIENCY PARTICULATE FILTER (HEPA)..... 2
FILTER WITH ACTIVATED CARBON 3
ELECTROSTATIC PRECIPITATOR..... 4
IONIZER..... 5
ULTRAVIOLET (UV) LIGHT 6

PCO USES UV LIGHT ALONG WITH A CATALYST LIKE TITANIUM DIOXIDE (TiO2)

PHOTOCATALYTIC OXIDATION (PCO)..... 7
OZONE GENERATOR 8
WASHABLE FILTER 9
OTHER _____
SPECIFY[CODE LATER]
NO ACCESS .....(90.) 9

89. HOW SOILED IS THE FURNACE FILTER?

MINIMAL 1
MODERATE 2
EXTENSIVE 3
NOT APPLICABLE 4
NO ACCESS 9

89a.. FURNACE FILTER PROPERLY INSTALLED? I.E. APPROPRIATE SIZE AND CORRECTLY POSITIONED IN HVAC SYSTEM.

NO..... 0
YES 1

90. COOLING METHOD?

NONE 0
CENTRAL AC 1
WINDOW AC 2
FANS 3
WINDOW 4
PORTABLE/ STAND ALONE 5
SWAMP COOLER 6
NO ACCESS 9

91. AIR CONDITIONING FILTER DIFFERENT FROM FURNACE FILTER?

NO ..... (94) 0
YES 1
NO ACCESS ..... (94) 9

92. TYPE OF AIR CONDITIONING FILTER?

NONE 0
PLEATED FILTER (NOT HEPA) 1
HIGH EFFICIENCY PARTICULATE FILTER (HEPA) 2
FILTER WITH ACTIVATED CARBON 3
ELECTROSTATIC PRECIPITATOR 4
IONIZER 5
ULTRAVIOLET (UV) LIGHT 6

PCO USES UV LIGHT ALONG WITH A CATALYST LIKE TITANIUM DIOXIDE (TiO2)

PHOTOCATALYTIC OXIDATION (PCO) 7
OZONE GENERATOR 8
WASHABLE FILTER 9
OTHER_____

SPECIFY
[CODE LATER]

NO ACCESS 9

93. HOW SOILED IS THE AIR CONDITIONING FILTER?

NONE	0
MINIMAL	1
MODERATE	2
EXTENSIVE	3
NOT APPLICABLE	4
NO ACCESS	9

94. ACTIVE VENTILATION SYSTEM PRESENT?

NO	(98)	0
YES		1
NO ACCESS	(98)	9

95. VENTILATION SYSTEM FILTER DIFFERENT FROM FURNACE FILTER?

NO	(98)	0
YES		1
NO ACCESS	(98)	9

96. TYPE OF VENTILATION FILTER?

NONE	0
PLEATED FILTER (NOT HEPA)	1
HIGH EFFICIENCY PARTICULATE FILTER (HEPA)	2
FILTER WITH ACTIVATED CARBON	3
ELECTROSTATIC PRECIPITATOR	4
IONIZER	5
ULTRAVIOLET (UV) LIGHT	6

PCO USES UV LIGHT ALONG WITH A CATALYST LIKE TITANIUM DIOXIDE (TiO2)

PHOTOCATALYTIC OXIDATION (PCO)	7
OZONE GENERATOR	8
WASHABLE FILTER	9
OTHER_____	
SPECIFY	
[CODE LATER]	
NO ACCESS	9

97. HOW SOILED IS THE VENTILATION FILTER?

NONE 0
MINIMAL 1
MODERATE 2
EXTENSIVE 3
NO ACCESS 9

98. MOLD PRESENT IN HVAC SYSTEM (e.g. COILS, DRIP PAN, OR DUCT-WORK)?

NO 0
MINIMAL 1
MODERATE 2
EXTENSIVE 3
NOT APPLICABLE 4
NO ACCESS 9

99. VISIBLE ASBESTOS? I.E. POPCORN ASBESTOS, DUCTWORK ASBESTOS, ETC?

NO 0
YES 1

F. <u>INDOOR SAFETY</u>

100. ELECTRICAL CORDS FOR EXTENSIONS/ APPLIANCES IN UNSAFE CONDITION?

NO 0
YES 1
NO ACCESS 9

101. STAIRS, WALLS, RAILINGS, PORCHES, OR BALCONIES IN POOR CONDITION?

NO 0
YES 1
NO ACCESS 9

102. UNPROTECTED WALL HEATERS?

NO … 0
YES 1
NOT APPLICABLE 9

103.	OVERALL, DOES THE INDOOR ENVIRONMENT SEEM DANGEROUS TO CHILDREN? IN THE FOLLOWING SCALE, 0 INDICATES THAT THERE IS NO DANGER AND 3 INDICATES THAT IT IS VERY DANGEROUS	0	1	2	3

H. EXTERIOR BUILDING CHARACTERISTICS

104. BUILDING FOUNDATION?

BELOW GRADE 1
SLAB ON GRADE 2
RAISED FLOOR 3
OTHER _____
SPECIFY [CODE LATER]

105.	BUILDING EXTERIOR?		NO	YES
		WOOD	0	1
		BRICK	0	1
		STUCCO	0	1
		METAL	0	1
		STONE.....	0	1
		OTHER _____ **SPECIFY [CODE LATER]**	0	1

106. PEELING PAINT ON EXTERIOR?

NO..... 0
YES..... 1

107. LARGE CRACKS ON EXTERIOR

NO..... 0
YES..... 1

108. GENERAL CONDITION OF BUILDING EXTERIOR?

POOR 1
FAIR..... 2
GOOD 3

109. SOIL WITH NO GRASS OR MULCH?

NO..... 0
YES..... 1

110. UNPLEASANT SMELLS AROUND EXTERIOR?

NO.....(112)..... 0
YES..... 1

111. TYPE OF SMELL?

SEWAGE 1
MUSTY..... 2
CHEMICAL..... 3
SMOKE 4
OTHER _____ _

SPECIFY

[CODE LATER]

112. ARE OBSTRUCTIONS BLOCKING THE FRESH AIR INTAKES (NESTING BIRDS, ETC)?

NO..... 0
YES..... 1
NO ACCESS 9

113. ARE POTENTIAL POLLUTANTS (IDLING CARS OR TRUCKS) LOCATED NEAR THE FRESH AIR INTAKES?

NO..... 0
YES..... 1
NO ACCESS 9

114. ATTACHED GARAGE?

NO.....(116)..... 0
YES..... 1

115. CAR STORED IN ATTACHED GARAGE?

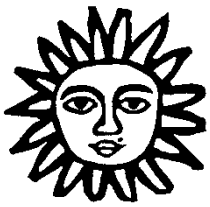
NO..... 0
YES..... 1

116.	FACILITY NEIGHBORHOOD?		**No**	**Yes**
	A.	COMMERCIAL	0	1
	B.	RESIDENTIAL.....	0	1
	C.	AGRICULTURAL.....	0	1
	D.	SUBURBAN	0	1
	E.	OTHER ..... _____ SPECIFY	0	

117.	DAYCARE LOCATED WITHIN 1/4TH MILE TO THE FOLLOWING PLACES?	**NO**	**YES**	**DK**
	(A.) NAIL SALON OR BEAUTY SHOP	0	1	9
	(B.) DRY CLEANER	0	1	9
	(C.) AUTO REPAIR SHOP	0	1	9
	(D.) AGRICULTURAL FIELD	0	1	9
	(E.) GOLF COURSE	0	1	9
	(F.) GAS STATION	0	1	9
	(G.) INDUSTRIAL FACILITY **TYPE OF INDUSTRIAL FACILITY _____ [CODE LATER]**	0	1	9
	(H.) PARKING LOT	0	1	9
	(I.) ABANDONED BUILDINGS	0	1	9
	(J.) BUSY ROADWAY	0	1	9
	(K.) TRUCK DEPOT	0	1	9
	(L.) TRAIN STATION	0	1	9
	(M.) AIRPORT	0	1	9
	(N.) BUS STOP	0	1	9

ADDITIONAL OBSERVATIONS:

BE SURE TO THANK PARTICIPANTS FOR THEIR PARTICIPATION AND ASK IF THEY HAVE ANY ADDITIONAL QUESTIONS.



Environmental Exposures in Early Childhood Education Environments

Visit Materials Packet

Child Care First Site Visit

Pre-First Visit Activities Checklist

Prior to the first visit to the child care center complete the following:

- ☐ Contact Child Care Director and confirm site visit two days prior to first site visit.
  - o Ensure access to HVAC system

- ☐ Compile facility binder with appropriate forms
  - ☐ 2 Full Study Consent Forms
  - ☐ Dust Collection Form and Procedure
  - ☐ Questionnaire
  - ☐ Inspection Form
  - ☐ TrustLine Background Check Certificates

- ☐ Compile all appropriate equipment for inspection
  - ☐ Flashlight
  - ☐ GPS
  - ☐ Compass
  - ☐ Fire alarm tester
  - ☐ Street Map
  - ☐ Gloves
  - ☐ Blue waterproof pen
  - ☐ Clipboard
  - ☐ Extra batteries for GPS
  - ☐ Booties
- ☐ Wash and prepare HVS3 Vacuum and parts
- ☐ Compile all appropriate equipment for dust sample
  - ☐ HVS3

- ☐ Tubing
- ☐ 2-3 iChem Amber bottles (1 for sample, 1 extra, 1 for QC -if applicable)
- ☐ Washed Silica gel for blanks (if applicable)
- ☐ Extension cord
- ☐ Tape
- ☐ Measuring tape
- ☐ Ziplock® bags
- ☐ Tool Box + tools
- ☐ Ice chest with blue ice
- ☐ Outlet voltmeter
- ☐ Latex gloves

First Site Visit Checklist

All to be accomplished during the first site visit to the childcare center

- ☐ Review full consent form with participant
  - o Have participant sign both copies
  - o Give one to subject and keep one for records

- ☐ Complete questionnaire

- ☐ Complete Inspection form

- ☐ Complete GPS form

- ☐ Collect dust sample

- ☐ Walk through facility and locate potential sites for air sampling
  - o Ask participant if he/she has preferred location
    Location:_____
  - o Available power supplies
  - o Find outdoor location and power supply, if applicable

- ☐ Arrange Second Site Visit

  - o DATE: _____
  - o Mark in calendar.
  - o Make sure date is a day children will be present and in facility.

Dust Collection Form

1. DATE: ..... __ __ / __ __ / __ __
2. ECE ID NUMBER: ..... __ __
3. ARRIVAL TIME: ..... __ __:__ __ am / pm
4. DEPARTURE TIME ..... __ __:__ __ am / pm
5. SAMPLE COLLECTOR(S): _____ ___ ___
   CODE
   _____ ___ ___
   CODE

6. CURRENT WEATHER CONDITION?

   SUNNY 1
   CLOUDY 2
   RAINY 3
   FOGGY 4
   OTHER .....
   SPECIFY _____
   (CODE LATER)

7. DUST SAMPLE COLLECTED?

   NO.....(18)..... 0

   YES..... 1

8. HVS3 NUMBER?
   (On Vacuum) _____
9. SAMPLE ID # (SEE SAMPLE CODE SECTION)
   _____
10. LOCATION OF SAMPLE:

    CHILDCARE ROOM..... 1
    OTHER..... _
    SPECIFY _____
    [CODE LATER]

11. IF NOT IN CHILDCARE ROOM, EXPLAIN CHOICE OF ROOM.
    _____
    _____

12. SAMPLE TAKEN FROM:

    CARPET..... 1
    UPHOLSTERED FURNITURE 2
    BARE FLOOR..... 3
    OTHER..... _
    SPECIFY _____
    [CODE LATER]

13. TOTAL AREA VACUUMED (M^2) ……_____X_____ = ___ . ___ ___ m^2

14. TOTAL ELAPSED TIME **(MINUTES)**…… ___ ___

ASK PARTICIPANT THE FOLLOWING QUESTIONS

15.When was the carpet, furniture, or other floor type last cleaned?

[READ CHOICES]

Today	1
Yesterday	2
2-3 days ago	3
4-7 days ago	4
More than 1 week ago	5
Don't know	9

16. How was the carpet, furniture, or other floor cleaned?

[READ CHOICES]

[CIRCLE ALL THAT APPLY]

	N	Y
Swept/carpet sweeper	0	1
Vacuumed	0	1
Cleaned by a wet method like steam cleaned or shampooed	0	1
Shaken out	0	1
Don't know	0	1

17. IF YOU SAMPLED ON FURNITURE, GIVE A DETAILED DESCRIPTION OF THE FURNITURE SAMPLED, I.E TYPE OF UPHOLSTERY, ETC.

18. DESCRIBE ANY DIFFICULTIES IN SAMPLING:

19. ADDITIONAL NOTES

ECE GPS FORM

Date: __ __ / __ __ / __ __

ECE# __ __

TAKE FIRST GPS READING AT START OF CENTER VISIT

GPS coordinates:	**Latitude** a.) N ____ ____ . ____ ____ . ____ ____ **Longitude** b.) W ____ ____ ____ . ____ ____ . ____ ____

TAKE SECOND GPS READING AT END OF CENTER VISIT. DO *NOT* COPY COORDINATES FROM ABOVE

GPS coordinates:	**Latitude** a.) N ____ ____ . ____ ____ . ____ ____ **Longitude** b.) W ____ ____ ____ . ____ ____ . ____ ____

Post First Visit Checklist

- ☐ Store dust sample in -20°C freezer
- ☐ Review that all information was recorded correctly
- ☐ If required, code answers that are not already coded in questionnaire and inspection forms
- ☐ Input contact information into Participation Identification file
- ☐ Wash HVS3 and all parts according to cleaning protocol

Second Site Visit

Pre-Second Visit Activities

To be done 5 day prior to visit:

- ☐ Call center to confirm time and date of site visit
- ☐ Ensure working order of pumps and instruments
- ☐ Check VOC conditioned
- ☐ Ensure 37mm Teflon filters are conditioned and pre-weighed

To be done 1 day prior to visit:

- ☐ Review site visit binder to make sure all appropriate logs and protocols are included
- ☐ Compile all appropriate equipment and supplies (see supplies and equipment list)
- ☐ Look up address and confirm driving directions
- ☐ Sync QTrak and DustTrak Internal Clocks with Computer

Supplies and equipment checklist

- ☐ Ziplock® Bags
- ☐ **Non-powdered** latex or neoprene gloves
- ☐ Kimwipes® (large and small)
- ☐ Aluminum Foil
- ☐ Time Piece
- ☐ Tape
- ☐ Zip ties
- ☐ Tool Box+ Tools
- ☐ Ice chest with blue ice
- ☐ Camera
- ☐ Extension Cords (2)
- ☐ Power Strips (3)
- ☐ Outlet Voltmeter
- ☐ Kiddie Corral
- ☐ Tripods (4)
- ☐ Vacuum Pump with Manifold
  - o PUF cartridges (3)
  - o Tenax-TA® only sorbent tubes (3)
  - o Carbosieve® only(3)
  - o XPoSure Aldehyde Sampler (3)
  - o Ozone Scrubber (2)
  - o Personal Environmental Monitors (PEMs) with Teflon filters (2)
  - o PEM calibration fitting (1)
  - o Extra tubing
- ☐ 2 Q-Traks
- ☐ DustTrak (2)
- ☐ Water CPC (2)
  - o DI water
  - o Computer cord
- ☐ Laptop
- ☐ Calculator
- ☐ Sample Labels
- ☐ 75$ Gift Certificate
- ☐ CO2 Cylinder
- ☐ Sampling table (2)

Second Visit Timeline

SET UP

- □ Set up interior location and outside location (if applicable)
- □ Turn on all real time instruments to warm-up
- □ Set up all air sampling pumps

LAUNCH

- □ Launch real time instruments when they have warmed up
- □ Fill out real time log sheet
- □ Check start flow rates
- □ Fill out indoor air field logs

MONITOR

- □ Measure and diagram sampling room dimensions
- □ Fill out ventilation, occupancy, and site monitoring logs
- □ Photograph sampling locations
- □ Release CO2 when children are not present

BREAKDOWN

- □ Start breakdown instruments at _____ pm
  - o Upload Data
  - o Check flowmeter locations
  - o Remove all instruments at _____ pm

Sample Collection Forms

Air Sampling Field Log

QC Review:	Date	ID
Initial EST	_ _/_ _/_ _	__ __
Final EST	_ _/_ _/_ _	__ __
Copied	_ _/_ _/_ _	__ __
Data entered	_ _/_ _/_ _	__ __

1. FIELD SAMPLING TECHNICIAN _____
_____
_____

2. ECE ID# ____ ____ DATE _____ / _____ / _____

3. LOCATION OF SAMPLING TRAIN?

CHILDCARE ROOM 1
OTHER ROOM ..... __

SPECIFY _____
[CODE LATER]

3A. IF NOT IN CHILDCARE ROOM, EXPLAIN CHOICE OF SAMPLING LOCATION.

_____
_____
_____
_____

3. WEATHER CONDITION?

SUNNY 1
PARTLY CLOUDY 2
CLOUDY 3
FOGGY 4
RAINY 5
WINDY 6
OTHER .....
PLEASE SPECIFY_____

ADDITIONAL NOTES:

Data Log Instructions

Please fill in the following information in the data log integrated sampler table:

1. **Sample ID-** Place the appropriate code label next to the sample type. Sample types are as follows:
    a. Indoor Sample- Sample that is taken in the child care center playroom
    b. Outdoor Sample- Sample taken outside of the child care center
    c. Duplicate- sample collected in parallel with the primary sample.
    d. Replicate- sample collected from same house as the primary sample but at a different time and/or location
    e. Field Blank- indicate a sample that was removed from its storage container, mounted on sampler without collecting sample (no flow) then removed and returned to storage container.
2. **Number on Tube**- This is a number written on sample tube container that the laboratory who prepares the sample uses to identifies their samples.
3. **Pump Number**- Is a number which identifies which pump is pulling the samples. Pump number can be found on the vacuum pump.
4. **Location in Building and QAmate**- Very briefly describe location of sample i.e. child care room, kitchen. For duplicate and breakthrough samples, indicate the "Qamate" or the sample that the QA is associated with.
5. **Start Time**- Write the time air began to pass through sample tube/ filter. Please write in military time, i.e. 5:00 am = 05:00 and 4:45pm = 16:45.
6. **Start Flow**- If not using flowmeter, mark the start flow obtained from calibration device.
7. **End Flow**- If not using flowmeter, mark the end flow obtained from calibration device.
8. **End Time**- Write the time air stopped passing through the tubes/filters in military time (see above).

Please fill in the following information in the Flow Check tables:

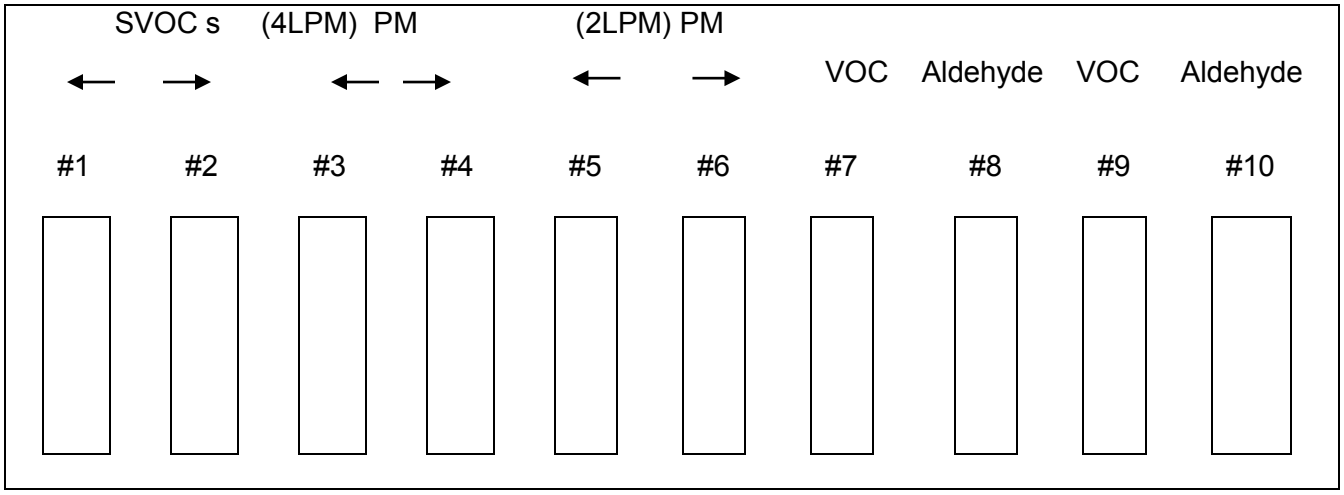
1. **Sample ID**- Place a copy of the sample code label in this field
2. **Flowmeter #-** Each flowmeter on the manifold has a corresponding number (see manifold instructions/diagram for more instructions). Please write this number in this field
3. **Original Location**- According to the **FLOWMETERS,** note the location of the center of the ball (mm) for each sample at the start of sampling.
4. **2 Hours into Sampling, 4 Hours into Sampling, 6 Hours into Sampling, 8 Hours into Sampling-** Please write down the location of the center of the ball in the flowmeters at the end of 2, 4, 6, and 8 hours into sampling. If the values vary, do not change the flow, just observe.

Vacuum Pump and Flowmeter Instructions

A vacuum pump attached with 10 flowmeters attached to a manifold will be used for air sampling. There will be 10 inlets that will allow for the sampling of SVOCs, Particle Mass, Carbonyls, and VOCs. Specific flowmeters/inlets are to be used for specific analytes measured.

Directions

Manifold Diagram



Each number represents a flowmeter. Flowmeters 1-2 are for SVOCs, 3-4 are for 4 LPM PEMs, 5-6 are for 2 LPM PEMs, 7 and 9 are for VOCs, and 8 and 10 are for carbonyls.

Set Up Procedure:

1. Set up tripods about 4 feet apart
2. Clamp down bottom bracket between tripod
3. Place manifold on bottom bracket
4. While holding manifold up-right, place top bracket onto manifold and clamp down
5. Ensure manifold is level by viewing “bubble leveler” and making sure bubble is in the center of device. If not make corrections to configuration
6. Place vacuum pump below manifold and attach yellow tubing from pump to the manifold
7. To power, plug in pump to power source (no on/off switch)
8. Attach all appropriate dummy tubes to tripods using zip ties.
9. Ensure tubes are facing either down or parallel to ground (not up)
10. Check and set appropriate flow of dummy tubes with calibration device
11. Note flow and flowmeter location on data log sheets
12. Remove dummy and install real sample tube
13. Note any change in flow from flowmeter

Note: Please read individual analyte sampling procedures for specific sampling requirements.

Take Down Procedure

1. Unplug pump from power source
2. Detach yellow tubing from manifold system
3. Unclamp and remove top bracket **while still holding manifold**

4. Remove manifold and place in storage container
5. Unclamp and remove bottom bracket
6. Disassemble tripods
7. Put all equipment in proper storage containers

Data Log Sheets for PBDEs

Date: _____ Operator's initials _____ (start) _____(end) ECE ID: _____

PBDE Integrated Samplers

Pollutant/ Sampler Type	**Sample ID**	**Flow-meter Number**	**Location in building and QAmate**	**Start Time watch/pump**	**Start Flow* (ml/min)**	**End Flow (ml/min)**	**End Time watch/pump**
Indoor Sample Tube							
Outdoor Sample Tube							
Duplicate Tube							
Replicate Tube							
Breakthrough Tube							
Field Blank Tube							

***Start Flow should be ~4 LPM. Flowmeter location = 65mm.**

Flow Checks from Flowmeters

Sample ID	**Flowmeter#**	**Original Location (mm)**	**2 hours into Sampling**	**4 hours into Sampling**	**6 hours into Sampling**	**8 hours into Sampling**

Data Log Sheets for Phthlates/ Pesticides/ Other Flame Retardants

Date: _____ Operator's initials _____ (start) _____(end) ECE ID: _____

Pesticides Integrated Samplers

Pollutant/ Sampler Type	**Sample ID**	**Flow-meter Number**	**Location in building and QAmate**	**Start Time watch/pump**	**Start Flow* (ml/min)**	**End Flow (ml/min)**	**End Time watch/pump**
Indoor Sample Tube							
Outdoor Sample Tube							
Duplicate Tube							
Replicate Tube							
Breakthrough Tube							
Field Blank Tube							

***Start Flow should be ~4 LPM. Flowmeter location = 65mm.**

Flow Checks from Flowmeters

Sample ID	**Flowmeter#**	**Original Location (mm)**	**2 hours into Sampling**	**4 hours into Sampling**	**6 hours into Sampling**	**8 hours into Sampling**

Data Log Sheets for PM2.5 and PM10

Date: _____ Operator's initials _____ (start) _____(end) ECE ID: _____

ALD Integrated Samplers

Pollutant/ Sampler Type	**Sample ID**	**Number on PEM**	**Flow-meter Number**	**Location in building and Qamate**	**Start Time watch/pump**	**Start Flow (ml/min)***	**End Flow (ml/min)**	**End Time watch/pump**
Indoor PM2.5								
Indoor PM10								
Outdoor PM2.5								
Outdoor PM10								
Duplicate PM2.5								
Duplicate PM10								
Replicate PM2.5								
Replicate PM2.5								
Field Blank Filter								

***Flow should be set to 4 LPM. Flowmeters should be set at 65mm.**

Flow Checks from Flowmeters

Sample ID	**Flowmeter#**	**Original Location (mm)**	**2 hours into Sampling**	**4 hours into Sampling**	**6 hours into Sampling**	**8 hours into Sampling**

Data Log Sheets for VOC

Date: _____ Operator's initials _____ (start) _____(end) ECE ID: _____

VOC Integrated Samplers

Pollutant/ Sampler Type	**Sample ID**	**Number on tube***	**Flow-meter Number**	**Location in building and QAmate**	**Start Time watch/pump**	**Start Flow (ml/min)** **	**End Flow (ml/min)**	**End Time watch/pump**
Indoor Sample Tube								
Outdoor Sample Tube								
Duplicate Tube								
Replicate Tube								
Breakthrough Tube								
Field Blank Tube								

*** This is the serial number on the VOC tube itself. LBNL uses this number for tracking purposes.**

** **Total volume for Tenax only tubes = 6 Liters. i.e. For 8 hours, set at 0.0125 LPM or a flowmeter location of 67mm. Total sample volume for CarboTrap only tubes = 1 Liter. So for 1 hour, sample at 0.0167 LPM or a flowmeter location of 76 mm.**

VOC Flow Checks from Flowmeters

Sample ID	**Flowmeter#**	**Original Location (mm)**	**2 Hours into Sampling**	**4 Hours into Sampling**	**6 Hours into Sampling**	**8 Hours into Sampling**
Sample ID	**Flowmeter#**	**Original Location (mm)**	**1 Hour into Sampling**			

Data Log Sheets for Carbonyls

Date: _____ Operator's initials _____ (start) _____(end) ECE ID: _____

ALD Integrated Samplers

Pollutant/ Sampler Type	**Sample ID**	**Flow-meter Number**	**Location in building and QAmate**	**Start Time watch/pump**	**Start Flow (ml/min)***	**End Flow (ml/min)**	**End Time watch/pump**
Indoor Sample Tube							
Outdoor Sample Tube							
Duplicate Tube							
Replicate Tube							
Breakthrough Tube							
Field Blank Tube							

***Total volume sampled should be 120 liters. If sampling for 8 hours, pull at a rate of 0.25 LPM or a flowmeter location of 102mm.**

Aldehyde Flow Checks from Flowmeters

Sample ID	**Flowmeter#**	**Original Location (mm)**	**2 hours into Sampling**	**4 hours into Sampling**	**6 hours into Sampling**	**8 hours into Sampling**

Real Time Log Sheets

ECE ID:____ ____ Date: ___ / ___ / _____

Indoor Real Time

Instrument	Equipment Number	Start Time	End Time	Uploaded? Y/N	Data File Name?*	Notes
Q-Trak						
DustTrak for PM2.5						
CPC						

***Please see section on "Data File Naming Conventions."**

Outdoor/ Duplicate Real Time

Instrument	Equipment Number	Start Time	End Time	Uploaded? Y/N	Data File Name?*	Notes
Q-Trak						
DustTrak for PM2.5						
CPC						

***Please see section on "Data File Naming Conventions."**

Room Volume Calculation

Please measure the volume (length x width x height) of the following parameters:

Where Sampler is Located:

Total Room Volume	**ROOM VOLUME**	**_____meters^3**
Non-Accessible Space Volume Where Sampler is Located (This is measure of how much of the room's volume is taken up by objects in the room like desks, refrigerators, etc. This is typically 10% of the volume)	**VOLUME OF NON-ACCESSIBLE SPACE**	**_____meters^3**
Total Volume of the Air in Room Where Sampler is Located (This is total room volume – non accessible space volume)	**TOTAL AIR VOLUME**	**_____meters^3**

ECE Occupancy Log

ECE ID:____ ____ Date: ___ / ___ / _____

ON CONTINUOUS BASIS- FILL IN FOLLOWING INFORMATION:

AT THE START OF AIR SAMPLING, COUNT TOTAL NUMBER OF OCCUPANTS, THEN BREAKDOWN OCCUPANCY INTO NUMBER OF PRE-SCHOOL CHILDREN (0-5 YEARS OLD), NUMBER OF OTHER CHILDREN (5-18 YEARS OLD), AND NUMBER OF ADULTS. **NOTE THE DIFFERENCE IN AMOUNT OF PEOPLE IN EACH CATEGORY** AND NOTE THE TIME ON A CONTINUOUS BASIS. FOR ACTIVITY, USE SCALE: SLEEPING, PASSIVE, LOW, MODERATE, OR HIGH ACTIVITY.

Time	Elapsed time (Starting from zero)	Total Occupancy	Number of Pre-School Children 0-5 years old	Number of Other Children (5-18 years old)	Number Childcare Staff	Number of ECE study staff	Notes (Please note activity level of individuals i.e. nap time, playing, etc.)	Tech Initials

Time	Elapsed time (Starting from zero)	Total Occupancy	Number of Pre-School Children 0-5 years old	Number of Other Children (5-18 years old)	Number Childcare Staff	Number of ECE study staff	Notes (Please note activity level of individuals i.e. nap time, playing, etc.)	Tech Initials

ECE Ventilation Log

ECE ID# ___ ___ Date: ___ / ___ / _____

AT THE BEGINNING OF SAMPLING, NOTE THE NUMBER AND AREA OF WINDOWS AND DOORS OPEN TO THE OUTSIDE. IF THE NUMBER OR OPEN AREA OF THE WINDOWS/DOORS CHANGES DURING SAMPLING, NOTE TIME AND NEW AREA.

Time	Elapsed Time	Number of Windows Open	Area of Open Windows (m^2)*	Number of Doors Open to Outside	Area of Open Doors to Outside (m^2)*	Number of Passage** Doors Open	Area of Open Passage Doors (m^2)	Notes on which Windows are Open	Tech Initials

*If “swinging” type, measure area of the plane defined by the outer edge of the swinging glass pane and the outer edge of the window opening.
** Passage doors are doors that lead to other rooms in facility/ house.

MAKE A SKETCH OF THE INTERIOR LAYOUT OF THE AIR SAMPLING ROOM AND ADJACENT ROOMS WITH CONNECTING DOORS THAT ARE CONSTANTLY OPEN. FIRST, DRAW OUTLINE OF ROOM. NEXT, DRAW A RECTANGLE WITH AN "E" AND A UNIQUE NUMBER INSIDE THE RECTANGLE FOR EACH DOOR THAT LEADS TO THE EXTERIOR. THEN, DRAW A RECTANGE WITH A "P" AND A UNIQUE NUMBER INSIDE OF IT FOR EACH DOOR THAT LEADS TO ANOTHER ROOM (A PASSAGE DOOR). NEXT, MARK AN OVAL FOR EACH WINDOW WITH A UNIQUE NUMBER INSIDE. IF PRESENT, MARK AN "X" FOR COMBUSTION SOURCE. NOTE ANY OTHER POSSIBLE EMISSION SOURCE.

ECE Sample Site Monitoring Log

ECE ID# ___ ___ Date: ___ / ___ / _____

Technician ID _____

_____

Any of the events observed during the sampling period?

	Yes	No	Time(s)	Notes
Tobacco Smoke?				
Cooking or Baking?				
Adhesives, glues, correction fluid, art supplies, etc?				
Painting?				
Pesticide use?				
Cleaners used?				
Printer, photocopier, fax used?				
Heater turned on?				
Fan turned on? Extra ventilation?				
Any other events? Please describe.				

Any of the following odors observed in use during the sampling period?

	Yes	No	Time(s)	Notes/ Description
Tobacco Smoke?				
Cosmetics?				
Car or diesel exhaust?				
Chemical odor from cleaners, solvents, etc?				
Musty or mildew smell?				
Any other unpleasant odor?				

Estimating Air Exchange Rates with Released CO_2

Objective: Estimate ventilation rate from all sources using CO_2 release inside child care room at two time periods throughout the day. CO_2 should be released during the day and at the end of the day when children are not present.

1.0 Have MSDS for CO_2 available for your use and in case questions arise.

2.0 All CO_2 equipment should be kept out of reach of children and outside the facility when not in use.

3.0 Measure CO_2 levels at 2 locations

3.1. Outdoors: _____ ppm

3.2. Inside child care room: _____ ppm

4.0 Record time of 1st CO_2 release: __ __ : __ __ AM/PM (circle one)

5.0 Release CO_2 evenly throughout space until target concentration is reached (2,500ppm).

6.0 Ensure CO_2 is evenly released by walking through room with Qtrak to measure concentration

7.0 Record peak CO_2 concentration found in room: _____ ppm

8.0 Place Qtrak back onto sampling table. Test is done when CO_2 reaches about 200 ppm above normal room concentration.

9.0 If possible, repeat test.

10.0 Measure CO_2 levels at 2 locations

10.1. Outdoors: _____ ppm

10.2. Inside child care room: _____ ppm

11.0 Record time of 2nd CO_2 release: __ __ : __ __ AM/PM (circle one)

12.0 Release CO_2 evenly throughout space until target concentration is reached (2,500ppm).

13.0 Ensure CO_2 is evenly released by walking through room with Qtrak to measure concentration

14.0 Record peak CO_2 concentration found in room: _____ ppm

15.0 Place Qtrak back onto sampling table. Test is done when CO_2 reaches about 200 ppm above normal room concentration.

16.0 Remove all CO_2 from child care room and securely store equipment in study van.

17.0

ADDITIONAL NOTES:

Post-Second Visit Checklist

- ☐ Bring VOC, Carbonyl, and PEMs to LBNL
  - o Store VOCs and Carbonyls in freezer in Dr. Maddalena's lab
  - o Place PEMs on workbench in designated Child Care Study Area
  - o Send Dr. Maddalena VOC, Carbonyl, and PEM total volume calculations via email
- ☐ Store PUFs in -20°C freezer
  - o Arrange for dry ice transfer to Battelle Laboratory
- ☐ Review data collection sheets for errors
- ☐ Input Ventilation, Occupancy, and Total Room Volumes onto CCEHR server
  - o Send Dr. Maddalena Ventilation, Occupancy, and Total Room data
- ☐ Upload all real time data onto CCEHR server
  - o Send Dr. Maddalena Q-Trak CO2 data converted into elapsed time
- ☐ Put Visit Material Packet Materials into correct ECE file folder

Sample Code Naming Convention

Each air and dust sample will receive a unique sample code for. To maintain confidentiality, the sample identification code does not explicitly identify the facility. The sample code will contain the 2-digit ECE identification number and descriptive names for the type of sample, sample location/ QC code, and the date sample was taken.

___ ___ -- _____ -- _____ -- _____

ECE ID # Sample type Location/QC Code Date of Sample

Before the facility visit, the laboratory technician will print labels for each sample ID. Low-temperature polyester labels will be used for all field samples. The field technician will fix matching sample ID labels to the collection form and to the sample containers. The laboratory technician at the field office will check that the label(s) on the collection form to match the label(s) on the sample container(s).

ECE ID #

Code 10—98

For example, the first facility enrolled would be ECE ID # 10, the second facility enrolled would be ECE ID # 11. CCEHR will keep all electronic documents linking child care facility name with ECE ID# in a password protected database and all paper documents in locked file cabinets. Please see section on Data Storage and Backup for more information.

Code “99” for QA/QC prepared in laboratory

Sample Type Codes

CODE	TYPE
Dust	Dust- For all analysis
TEN	Air-Tenax® VOC Tube
CAR	Air- CARBOSIEVE® VOC Tube
ALD	Air Aldehyde and Acetones
PBDE	Air-PBDEs
PEST	Air- Pesticides/ Phthalates/ Other Flame Retardants
PM2.5	Air-PM2.5 Mass
PM10	Air-PM10 Mass

Location/ QC Codes

CODE	TYPE
IN	Indoor Sample
OUT	Outdoor Sample
INDUP	Indoor Duplicate
OUTDUP	Outdoor Duplicate
REP	Replicate
BRE	Breakthrough
BLA	Field Blank
SPI	Spike

- **Indoor sample** means that this sample was taken indoors and it's the primary indoor sample
- **Outdoor sample** means that this sample was taken outdoors and it's the primary outdoor sample
- **Indoor Duplicate** indicates a sample collected in parallel with the primary indoor sample.
- **Outdoor Duplicate** indicates a sample collected in parallel with the primary outdoor sample.
- **Replicate** indicates a sample collected from same house as the primary sample but at a different time and/or location
- **Breakthrough** indicates a backup tube mounted in series behind a primary sample tube
- **Field blank** tube indicates a tube that was removed from its storage container then returned to container, mounted on sampler without collecting sample (no flow) then removed and returned to storage container
- **Spike tube** indicates a laboratory prepared sample with a known amount of compound on the media

Date of Sample

Each sample label will have a 6 digit sample code that states the date of the sample was taken from childcare facility.

Sample Code Example

Given code: 12_ALD_IN_092310

One would read this as a sample taken in **child care facility number 12** (de-identified participant number). Cartridge will be analyzed for **aldehydes and acetones** taken from air. Sample was taken **indoors**. This sample was taken on **September 23rd 2010**.

Given code: 46_Dust_IN_071510

One would read this as a sample taken in **child care facility number 46**. Sample will be is the **dust sample**. Sample was taken indoors. Sample was taken on **July 15th 2010**.

Data Files Naming Convention

All data files should be named according to the following naming convention. **Data files should be named appropriately and saved in the appropriate folder immediately after sample completion.**

- The first two characters represent the unique ECE # given to each child care center or home.
- Third character should be an underscore
- The fourth and fifth characters will be letters that describe the instrument that took the measurements. Please see codes below:

Instrument	Code
QTrak	QT
DustTrak	DT
CPC	CP

- The next character should be an underscore
- The next character will be a number that will distinguish which particular instrument was used based on the label attached to each instrument. For example, we have two CPCs, one labeled 1, the other labeled 2. These labels are linked to the instruments serial code if the need arises.
- The next character should be an underscore
- The next characters will distinguish if the sample was taken inside, outside, or if it is a duplicate measure. Inside will be represented by "IN," outside represented by "OUT."
- The next character should be an underscore
- The last six characters will be digits that describe the date. The first two digits will be the month, the third and fourth digits will be the day, and the fifth and sixth digits will be the year.

Examples of coding:

A code of **13_CP_2_IN_061510** would tell you that this sample was taken at ECE# 13 using the CPC that is labeled # 2. This sample was taken inside on June 15th, 2010.

A code of **38_DT_1_OUT_082310** would indicate that the sample was taken at ECE# 38, with the DustTrak using a size selective inlet of 2.5. This is the DustTrak labeled #1 and sample was taken outside on September 23rd, 2010.

APPENDIX G- Sample Collection and Laboratory Analysis Standard Operating Procedures

Dust Collection Protocol

INSTRUCTIONS FOR DUST SAMPLING. FOLLOW SPECIFIC SOP RELATED TO EACH DUST SAMPLING. DUST SAMPLES SHOULD BE COLLECTED AT THE END OF THE SCHOOL DAY, AFTER ALL CHILDREN HAVE LEFT THE FACILITY.

SITE SELECTION

Choose a site in the central childcare area to collect the dust sample. Preferred location would a carpeted area in child care area. If not available, use upholstered furniture in child care area. If not available, vacuum hard floor in child care area.

SET UP

- Put on a pair of latex gloves.
- Remove cleaned amber jar from plastic bag and label the collection jar with proper ECE code.
- Screw into collection port on the vacuum.
- Attach clean collection head or furniture attachment onto vacuum unit.
- Attach additional tubing if necessary.
- Ensure that all seals are tight.
- Test outlet with voltmeter
- Plug in vacuum.

LEAK TEST

- Place a thick manila envelope or file folder underneath the nozzle to seal off flow..
- Turn on vacuum.
- Check the flow. The Magnehelic gauge should read between 0 to 0.02 inches of water. Use a 0.10 inch Magnehelic gauge if a good reading cannot be achieved with the flow Magnehlic gauge.
- If the gauge reads more than 0.02 inches of water, check that all connections of the gauge tubing are correct.
- If the gauge tubing is correct and flow is still above 0.02 inches of water, check the clamps and gaskets throughout the HVS3. Also, check the tightness of the catch bottle.

DUST COLLECTION

- Choose a square meter in the central childcare area. Measure with ruler or meter and mark off with masking tape.
- Adjust pressure drop and flow according to ASTM recommendations. Review chart below for appropriate flow rates.

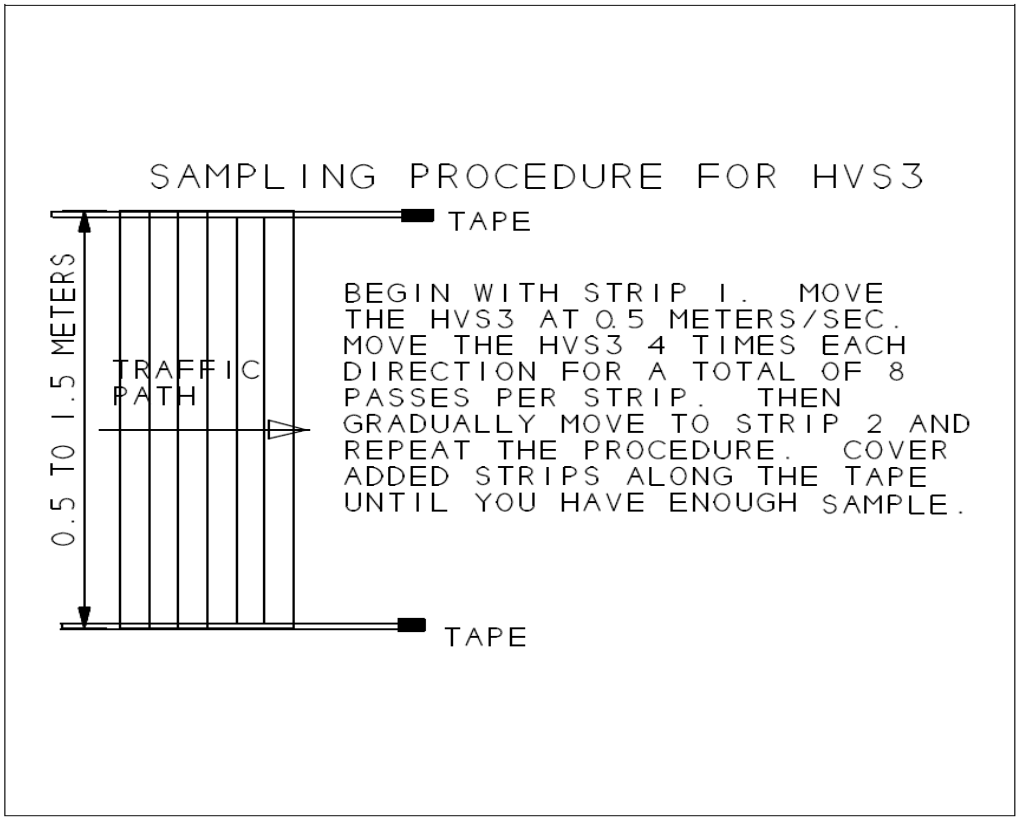
Carpet	Flow rate cfm (in. H2O)	Nozzle Press. Drop, in. H2O
Plush	20 cfm, 8 inches H2O	9 inches H2O
Level Loop	16 cfm,5 inches H O	10 inches H O

- Vacuum the square meter in such a manner that four double passes of the entire surface are performed. Two in one direction, and two at 90 degrees.
- Ensure that the sampler has collected enough dust to fill the bottle at least a third of the way.
- If not enough sample collected in first round, sample another square meter.

- Once enough sample is collected, record sampling time.
- Carefully unscrew amber collection jar, re-cap, and place in plastic bag.

HANDLING AND TRANSPORT

- Fill out all relevant fields of data collection form.
- Place all samples in cooler with gel refrigerant packs for transport back to field office.
- Store samples in -20°C freezer



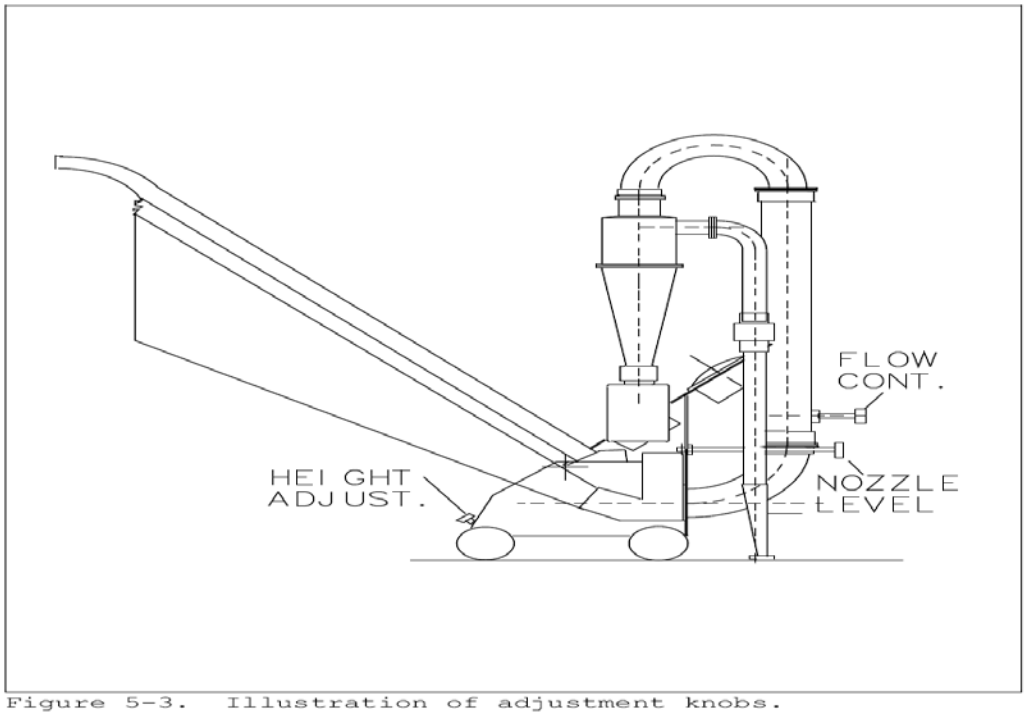


Figure 5-3. Illustration of adjustment knobs.

HVS3 Cleaning Protocol

ESTs clean all attachments and collection heads from cleaning bag, and the HVS3 sampling train, as follows:

1. Place the sampler in a well-ventilated cleaning area that is free from dust. The surface should be level and covered with clean plastic.
2. Take care to avoid knocking dirt or dust onto clean plastic. Do not put sampler down except on plastic surface in transport box.
3. Remove the cyclone cone, bellows connector, and elbow at the tip of the nozzle tubing from the sampler.
4. Wearing gloves, dismantle gaskets and bellows. Rinse and brush bellows, gaskets, and sample bottle cap with deionized water (DI), detergent, DI again, and isopropanol (IPA), then store in wide-mouth jar or HDPE cleaning tray.
5. Rinse all interior sections of the sampling train with DI, detergent, and then DI. Brush all interior surfaces, rinsing with IPA between brushing. Rinse again with DI and then IPA.
6. Clean brush by rinsing with DI, detergent, DI again, and IPA.
7. Clean catch bottle using same procedures, using the brush to carefully clean threads.
8. Wash wheels with IPA.
9. Dry sampling train with Kim-wipes. Retrieve gaskets and bellows with gloved hand. Assemble. This procedure should take about 30 minutes total.
10. Dry the sampler pieces in air for 20 minutes or by drawing air through the assembled sampler for 5 minutes.
11. Store clean HVS3 in new, large plastic bag.

DustTrak Protocol

SETTING UP DUSTTRAK

1- Plug in DustTrak to power source with power adapter.
2- Turn on DustTrak using ON/OFF switch.
3- Let DustTrak warm up for a minute.

ZERO CHECKING/ RE-ZEROING (DONE BEFORE EACH SAMPLING)

1- Attach zero filter onto aerosol inlet
2- Set the time-constant to 10 seconds. Press and hold the TIME CONSTANT key until “10” is displayed, then release.
3- Wait 10–60 seconds for displayed values to settle to zero.
4- If the displayed value is between -0.001 and +0.001 mg/m3, the DUSTTRAK monitor does not need adjustment. If the displayed value exceeds this limit, follow steps below to re-zero the instrument.
5- Press and hold the CALIBRATE key and wait for the displayed countdown to reach 0, then immediately release the key. The message “CALIBRATE ZERO” is displayed… if not, try again.
6- Press the SAMPLE key and wait for the 60-second countdown. When the countdown is completed, the current calibration constant will be displayed.
7- Press the CALIBRATE key again to return to survey mode. The rezeroing process is now completed.

OPERATING DUSTTRAK

1- After setting up and zero checking, press the SAMPLING MODE key. The SAMPLING MODE key allows you to select the appropriate sampling mode.
2- The display should read LOG 1 with the percentage of free memory.
3- Ensure that percentage of free memory equals 100%. If not turn erase memory by holding the CLEAR MEMORY button until countdown reaches 0.
4- Once display reads LOG 1 and 100% memory. Press SAMPLE
5- Display should read “RECORDING LOG 1” and “SAMPLE.”
6- Record sample start time on appropriate field log.
7- To prevent accidents, enable lockout switch. Lockout switch is on the backside of DustTrak monitor between the data port and the external power socket. It is a small slide switch and is recessed so that a pointed instrument must be used to move it. Use provided calibration screwdriver to enable lockout switch.
8- Once sampling is complete. Press SAMPLE again. This action will stop recording the measurements. The average, minimum, and maximum will be displayed once sampling is complete.
9- Note sampling stop time in appropriate field log.
10- Turn off machines using ON/OFF button.

Uploading DustTrak Data

1. Connect the DustTrak with the computer using the serial port cable with the USB adapter.
2. Turn on DustTrak
3. Start TrakPro software
4. Select **Instrument Setup**, then **Communications** in the TRAKPRO software
5. Select the correct serial port, then press **Test –** if communications are established the system display will confirm.
6. Select **OK** to accept set up (computer is now communicating with Qtrak)
7. Click **File,** then **Receive…**
8. Click on the tests you would like to import.
9. Click “Receive” and this will import the data into TrakPro.
10. Once in TrakPro, you must save the test by clicking **Save**
11. Name the file according to the ECE data file naming convention.
12. Once information is saved with the appropriate name, clear the memory of the DustTrak for the next use.

Q-Trak Protocol

Keys:

To lock keys: Move the keypad lockout switch to the “0” position. If this is done before logging begins Q-Trak will operate normally until logging starts, if it is done after logging begins all key presses will be ignored until switch is set to | position.

Displays:

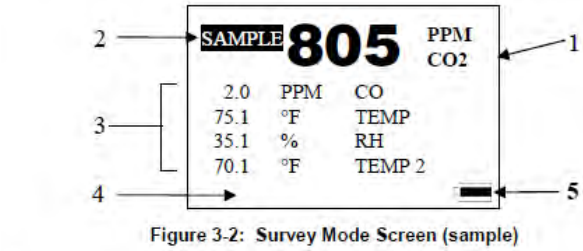
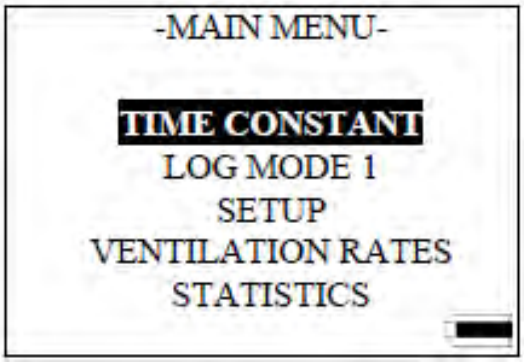


Figure 3-2: Survey Mode Screen (sample)

Ref	Description
1	Primary Parameter (CO_2 concentration is shown).
2	Sample mode. Used for capturing single data points.
3	Remaining parameters.
4	Status message area.
5	Battery status.



To Set a Log Interval

1. Power the Q-Trak with the AC Adaptor and turn on with Power button.
2. Wait until Q-Trak is showing data as in saving one data point
3. Press Escape to enter the main menu
4. Press the Down key and select “Log Mode 1”
5. Use the Up and Down keys to enter the log interval- from the device the options are 1 second, 1 minute, or 5 minutes (using TrakPro software you can choose your own interval)
6. Set the log interval to 1 minute
7. Press Enter to begin logging or log Q-trak from computer

To Upload Data to Computer

1. Locate RS-232 serial port (COM1 or COM2) on the computer and connect the RS 232 cable.
2. Connect RJ-45 cable to the Q-Trak communications port.
3. Turn on Q-Trak
4. Start TrakPro software
5. Select **Instrument Setup**, then **Communications** in the TRAKPRO software
6. Select the correct serial port, then press **Test –** if communications are established the system display will confirm.
7. Select **OK** to accept set up (computer is now communicating with Qtrak)
8. Click **File,** then **Receive…**
9. Click on the tests you would like to import.
10. Click “Receive” and this will import the data into TrakPro.
11. Once in TrakPro, you must save the test by clicking **Save**
12. Name the file according to the ECE data file naming convention.
13. Once information is saved with the appropriate name, clear the memory of the QTrak for the next use.

CPC Protocol

To Start Sampling:

1. Fill water source bottle with distilled water.
2. Place water source bottle into the bottle bracket on the back of the WCPC.
3. Insert connector from the source bottle into the “Water” connector on the back of the panel on the WCPC.

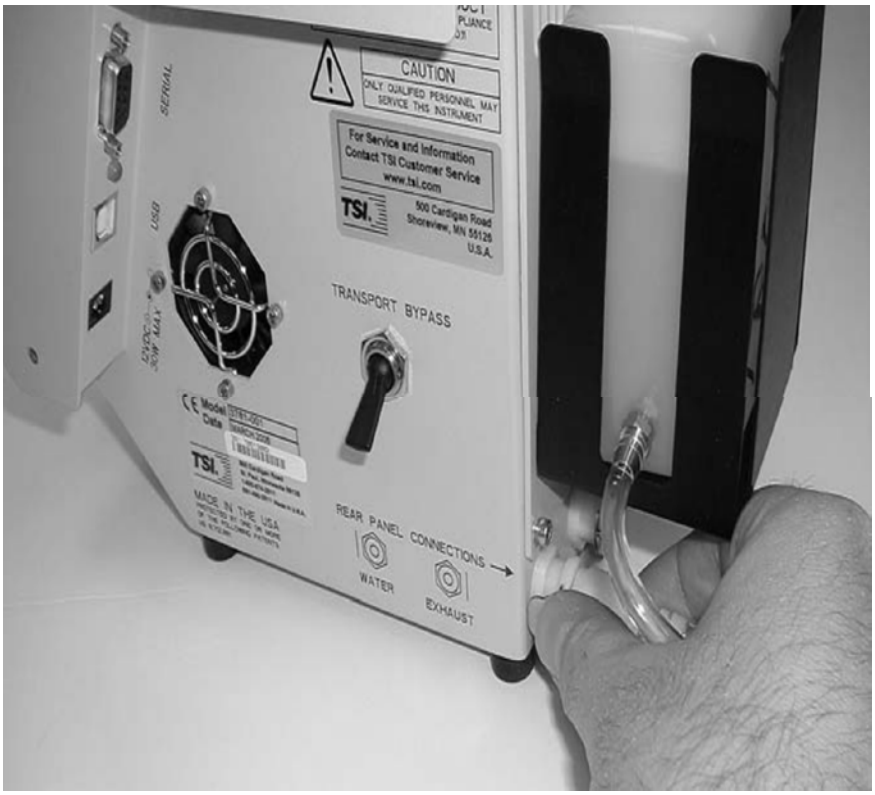


Figure 1- Fill Bottle Connection

4. Attach power cord to the AC power supply and connect the DC connector from this supply to the connector on the recess handle on the side of the WCPC.

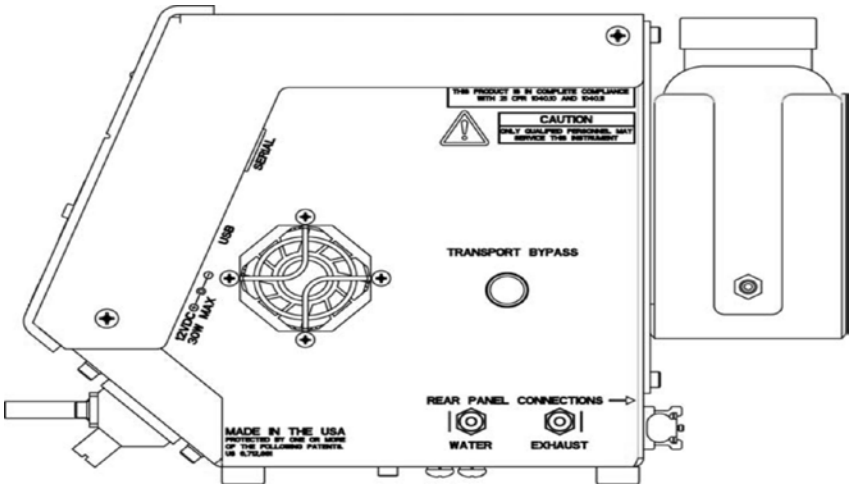


Figure 2 Connector Locations

5. Connect the AC cord to an AC source. **There is no power switch on the instrument.**
6. WARM-UP- Wait for the WCPC to warm-up and reach operating temperatures. The display will show a moving hyphen and the difference between set operation temperatures and actual measured temperatures which will tick down to 5.0˚C before the instrument leaves warm-up mode.
7. The “Status” light on the front panel will slowly blink until the final operating temperatures are reached, and then will be steady green.
8. If the “Flow” light on the front panel is off, turn on the pump (button on front panel).
9. Attach USB cable to WCPC and computer
10. Open AIM software
11. Click **File→3781 WCPC Import/ Logging**
12. Click on “Logging”
13. Click on “Clear Memory”
14. Click on “Synchronize” and make sure the time is correct on both the CPC and the computer.
15. Ensure that the “Average Interval (sec)” is set to 1 second
16. Click “Start” then exit out of that window.
17. Next to the logging button, an orange “ON” should appear.
18. Exit out of that window and then you can disconnect the USB cable from the CPC and computer.

To End Sampling and Import Data:

1. Reconnect the CPC with the computer using the USB cable
2. Click **File→3781 WCPC Import/ Logging**
3. Click on “Logging”
4. Click “Stop” then exit window
5. Click “Read Memory”
6. Select appropriate sample then press “Save As…”
7. Name the file according to the ECE data file naming convention.
8. All information has been saved and you may disconnect the USB cable.

PUF Collection Protocol

1. On-site setup
   1.1. Identify location for collecting sample(s)
      1.1.1. Preferably in child care room where children spend most of their time.
      1.1.2. Avoid drafts if possible.
   1.2. Setup sampler
      1.2.1. Set cartridge out of cooler and allow it to come to room temperature.
      1.2.2. Attach sample line to fitting and attach fitting to tripod or stand
      1.2.3. Attach other end of sample line to pump
      1.2.4. > 10 minutes before start of sampling, turn on pump and let warm up
      1.2.5. Install dummy PUF cartridge to sample fitting for flow setting/check
         1.2.5.1. Adjust flow if needed to get to desired value (target flow = 4 LPM) with dummy tube installed record initial sample flow rate on the data log sheet. Also check flowmeter level and record on data sheet.
      1.2.6. Remove dummy and place back in initial container.
2. Sample collection
   2.1. Record details on data log sheets
      2.1.1. Affix sample code labels to data log sheet
      2.1.2. Record all other required information
   2.2. When ready to start collecting sample, clean your hands with a pre-packaged IPA wipe then proceed to remove one clean PUF cartridge from the bubble wrap and zip seal bag.
   2.3. Remove both end caps and foil from the PUF cartridge. Do not touch the exposed PUF. Keep the bubble wrap and end caps in the zip seal bag for use after air sampling is complete.
   2.4. Attach PUF cartridge on sample fitting
      2.4.1. .If the cartridge must be set down on a surface, be sure to place it on a piece of muffled aluminum foil.
   2.5. Affix a sample code label on flexible tubing
   2.6. Record start time on data log sheet
   2.7. If a field blank or field spike sample is to be taken at the residence, simply leave the prepared cartridges in the cooler they were brought to the facility in and transport them back to the field office unopened.

3. While sampling

   3.1. Check the pump regularly during sampling.

   3.2. At the beginning and every 2 hours, note the rate on the flowmeters for each sample on data logs.

4. Terminate sampling

   4.1. Note end location of ball in flowmeter.

   4.2. Clean hands by using the pre-packaged alcohol pads. Put on a clean pair of latex gloves. Disconnect the cartridge from the tubing.

   4.3. Place a new piece of muffled aluminum foil over the ends of the cartridge. Carefully place the end caps over the foil, taking care not to rip the foil.

   4.4. Place the cartridge in bubble wrap then place into the zip seal bag. Use the bag and bubble wrap that were taken off the cartridge prior to sampling. Store the cartridge in a cooler packed with blue ice packs for transport back to the field office.

   4.5. Return dummy PUF cartridge to sample fitting and check air flow.

      4.5.1. Record air flow

      4.5.2. Note location of ball in flowmeter (if changed)

   4.6. Remove dummy PUF and place in container

   4.7. Store all samples in -20°C freezer until shipment.

   4.8. Ship to the following address:

      ATTN: Marcia Nishioka
      Battelle Memorial Institute
      505 King Ave
      Columbus, OH 43201

VOC Collection Protocol

1. On-site setup
   1.1. Identify location for collecting sample(s)
      1.1.1. Preferably in child care room where children spend most of their time.
      1.1.2. Avoid drafts and strong sunlight if possible (if direct sunlight will be on sampler then wrap them in foil)
   1.2. Setup sampler
      1.2.1. Attach sample line to fitting and attach fitting to tripod or stand
      1.2.2. Attach other end of sample line to pump
      1.2.3. > 10 minutes before start of sampling, turn on pump and let warm up
   1.3. When ready to start collecting sample:
      1.3.1. Remove tubes from plastic holder.
      1.3.2. Place sample labels on plastic holder
      1.3.3. Note tube serial number on data log sheets
      1.3.4. Hand tighten the Teflon compression fitting
      1.3.5. Check that tubes are in the correct direction.
      1.3.6. The sample tube can be facing out (horizontal orientation) or down (vertical orientation)
      1.3.7. Set flowmeters to desired location for correct flow rate (target volume= 7 liters).
      1.3.8. Record start time on data log sheet
      1.3.9. Place a sample code label on flexible
2. While sampling
   2.1. Check the pump regularly during sampling.
   2.2. At the beginning and every 2 hours, note the location on the flowmeters for each sample on data logs.
3. After sampling
   3.1. At the stop time, remove the sample tube and return to hard plastic sleeve with Teflon cap. Place tube back in secondary sleeve with red cap. **Tape on the red cap** and place in ice chest with blue ice.
   3.2. Record stop time on data log sheet

4. After sampling campaign

   Package samples in blue ice and deliver to the following address:

   Marion Russell or Randy Maddalena
   Indoor Environment Department
   Environmental Energy Technologies Division
   Lawrence Berkeley National Lab
   1 Cyclotron Road, room 70-222
   Berkeley CA 94720

   510-486-4924

Aldehyde/Acetone Collection Protocol

1. On-site setup
    1.1. Identify location for collecting sample(s)
        1.1.1. Preferably in child care room where children spend most of their time.
        1.1.2. Avoid drafts if possible.
    1.2. Setup sampler
        1.2.1. Attach sample line to fitting and attach fitting to tripod or stand
        1.2.2. Attach other end of sample line to pump
        1.2.3. > 10 minutes before start of sampling, turn on pump and let warm up
        1.2.4. Install dummy cartridge to sample fitting for flow setting/check
            1.2.4.1. Plug tube inlet with finger to ensure no leaks.
                1.2.4.1.1. Flow should go to zero
                1.2.4.1.2. If not check all fittings an redo leak check
            1.2.4.2. Adjust flow if needed to get to desired value (target volume = 120 L) with dummy tube installed record initial sample flow rate on the data log sheet. Also check flowmeter level and record on data sheet.
        1.2.5. Remove dummy and install just the Sep-Pak Ozone Scrubber on sample inlet.
            1.2.5.1. Remove and store all caps of Sep-Pak Ozone Scrubber
            1.2.5.2. Place Sep-Pak Ozone Scrubber properly in line
        1.2.6. Flush the system for approximately 15 minutes at desired flow rate.
2. Sample collection
    2.1. Record details on data log sheets
        2.1.1. Affix sample code label to data log sheet
        2.1.2. Record all other required information
    2.2. When ready to start collecting sample, at start time, remove ozone scrubber and place the Waters Xposure Sampler on the sample tube inlet.
        2.2.1. Remove and store all caps to Waters Xposure Sampler
    2.3. Replace ozone scrubber upstream from Sep-Pak Xposure Sampler
    2.4. Affix a sample code label on flexible tubing
    2.5. Record start time on data log sheet
3. While sampling
    3.1. Check the pump regularly during sampling.
    3.2. At the beginning and every 2 hours, note the rate on the flowmeters for each sample on data logs.
4. After sampling

4.1. At the stop time, remove both the Sep-Pak Ozone Scrubber and Waters Xposure Sampler.

4.1.1. Record stop time on data log sheet

4.1.2. Put the caps back onto both the Waters Xposure Sampler® and Sep-Pak Ozone Scrubber®

4.1.3. Place sampler into metal zip lock bag in which it came

4.1.4. Attach a sample code label to metal zip lock bag containing Water Xposure Sampler®

4.1.5. Place metal bag into additional zip lock bag.

4.1.6. Store on blue ice in cooler

4.2. Return Dummy sampler and ozone scrubber to sample fitting and measure the final sample flow rate in triplicate and record average final flow rate on data log sheet

4.2.1. Ozone scrubber may be used a multiple of times for indoor sampling. Store in metal bag in which it came and note date of use.

4.2.2. Return dummy and scrubber to containers in which they came and store with other samples.

5. After sampling campaign

5.1. Package all samples on fresh blue ice and FedEx back to LBL. Shipping address is:

Marion Russell or Randy Maddalena
Indoor Environment Department
Environmental Energy Technologies Division
Lawrence Berkeley National Lab
1 Cyclotron Road, room 70-222
Berkeley CA 94720
510-486-4924

Gravimetric $PM_{2.5}$/ PM_{10} Collection Protocol

1. On-site setup
   1.1. Identify location for collecting sample(s)
      1.1.1. Preferably in child care room where children spend most of their time.
      1.1.2. Avoid drafts and strong sunlight if possible
   1.2. Setup sampler
      1.2.1. Attach sample line to fitting and attach fitting to tripod or stand
      1.2.2. Attach other end of sample line to pump
      1.2.3. > 10 minutes before start of sampling, turn on pump and let warm up
      1.2.4. Install dummy Personal Environmental Monitor (PEM) to sample fitting for flow setting/check
         1.2.4.1. Attach calibration fitting over PEM inlet.
         1.2.4.2. Verify no leaks by plugging end of inlet tube with finger and seeing if flowmeter location drops to 0.
         1.2.4.3. If there is a leak, check all connections and tighten screws on PEM.
         1.2.4.4. Perform leak checks until problem solved.
         1.2.4.5. Adjust flowmeter until flow is set at 2 LPM or 4LPM, depending on PEM
2. Sample collection
   2.1. Record details on data log sheets.
   2.2. When ready to start collecting sample, at start time, remove dummy and install sample PEM in fitting
      2.2.1. Perform leak by plugging inlet to PEM
      2.2.2. The PEM can be facing out (horizontal orientation) or down (vertical orientation)
      2.2.3. Record start time on data log sheet
      2.2.4. Record number inscribed on PEM on data log sheet
      2.2.5. Place a sample code label on flexible
3. While sampling
   3.1. Check the pump regularly during sampling.
   3.2. At the beginning and every 2 hours, note the location on the flowmeters for each sample on data logs.

4. After sampling

   4.1. At the stop time, remove the sample PEM and return to plastic bag. Place PEM in cooler with other samples to be brought back to LBNL.

   4.2. Record stop time on data log sheet

   4.3. Return Dummy PEM to sample fitting and measure the final sample flow rate in triplicate and record average final flow rate on data log sheet

5. After sampling campaign

   5.1. After all centers are tested, package all samples on fresh blue ice and FedEx back to LBL. Shipping address is:

   Marion Russell or Randy Maddalena
   Indoor Environment Department
   Environmental Energy Technologies Division
   Lawrence Berkeley National Lab
   1 Cyclotron Road, room 70-222
   Berkeley CA 94720
   510-486-4924

Standard Operating Procedure for Sieving Vacuum Cleaner Dust Prior to Analysis

1.0 **Scope and Applicability**

This standard operating procedure (SOP) describes the method for sieving vacuum cleaner dust prior to analysis for antigenic microbiologicals, metals, and perfluorinated organic compounds.

2.0 **Summary of Method**

Vacuum cleaner bags or dust from bagless vacuums shall be collected from child care centers Each dust sample shall be uniquely numbered and placed in a zip top polypropylene bag after collection. The samples shall be sent to the laboratory where they will be sieved to obtain fractions > 2mm, < 2mm but > 150 µm, and smaller than 150 µm. Three separate microfugal tubes shall be filled to approximately 25 mm with each of > 2mm, < 2mm but > 150 µm, and smaller than 150 µm dust fractions. The remaining dust fractions shall be stored in separate trace element-free polypropylene bottles in the dark pending analysis.

3.0 **Definition**

3.1 Vacuum Cleaner Dust: Dust collected into sample collection bottles from HVS3 Vacuum.

4.0 **Cautions**

Standard laboratory protective clothing and eye covering is required. All manipulation of the dust (e.g., sieving, transferring) shall be conducted in a glove box to minimize potential exposures to particulate matter.

Extreme care must be taken to avoid the use of metal- or Teflon-containing materials during this process as they may contaminate the samples.

5.0 **Responsibilities**

5.1 The project staff performing dust processing shall be responsible for obtaining the initial dust samples from the study sample coordinator, entering relevant tracking information in the laboratory record books (LRB), and sending final processed samples and spreadsheet to the collaborators (Battelle Institute and US EPA).

6.0 **Apparatus and Materials**

6.1.1 Vacuum Cleaner dust samples

6.1.2 150 m (No. 100) particle sieve, U.S. Standard Stainless Steel, 8 in diameter, 2 inch depth, Fisher Scientific Company, Cat. No. 04-881-10X or equivalent.

6.1.3 Sieve cover, stainless steel, 8 in diameter, Fisher Scientific Company, Cat. No. 04-887A, or equivalent.

6.1.4 Sieve receiver pan, stainless steel, 8 in diameter, 2 in depth, Fisher Scientific Company, Cat. No. 04-887B, or equivalent.

6.1.5 Syntron Jogger J-1 Sieve Shaker, Arthur H. Thomas, Philadelphia, PA, USA, or equivalent.

6.1.6 250 and 500 ml Polypropylene wide-mouth bottles, Fisher Scientific Company, Cat. No. 02-896D and 02-896E, acid-cleaned, trace element-free, or equivalent.

6.1.7 Shipping tubes, Corning Brand Microfuge 2 ml tubes, Fisher Scientific Company, Cat. No. 05-538-69C with cardboard shipping boxes.

6.1.8 Laboratory grade detergent, Versa-Clean, Fisher Scientific Company, Cat. No. 04-342, or equivalent.

6.1.9 Permanent marking pen, felt-tip, fine point, such as a Sanford, No. 30001, “Sharpie” brand, fine point, black, permanent marker, or equivalent, for marking sample tubes.

6.1.10 Labels, adhesive or computer-generated, to label sample bottles.

6.1.11 Methanol, reagent grade, for rinsing sieves.

6.1.12 Nitrogen, laboratory grade compressed, to assist in sieve drying when needed.

7.0 Sieving and Sample Transfer Procedure

7.1. Label and weigh 4 300 mL wide-mouth amber bottles (I-CHEM, item# 341-0250) that will be used to store the sieved sample fractions. These bottles shall be labeled for each analyte to be analyzed, PBDEs, PFCs, Phthalates, and Pesticides. Weight to the nearest 10 mg. Record the sample IDs and weights in the laboratory record book and on a spreadsheet.

7.2. Bring dust sample bottle to room temperature

7.3. Weigh the dust sample bottle with dust and record

7.4. Use a 150µm dust sieve

7.5. Add dust to sieve screen

7.6. Cover sieve and sieve for approximately 5 minutes

7.7. Aliquoting the 4 dust fractions.

7.7.1. For the BDE Sample, aliquot a total of 1 gram into I-CHEM amber bottle. Label and record total weight.

7.7.2. For the Pesticide, Phthalate, and Other Flame Retardants, a total of 0.5 grams of dust is needed for analysis. Label and record total weight.

7.7.3. For the PFC analysis, a total of .25 grams is needed for analysis.

7.7.4. Send the following samples to their appropriate places by 2 day delivery and enclose a copy of the sample spreadsheet and chain of custody form. No refrigeration is necessary.

PFC samples

Dr. Mark Strynar
US EPA ORD/ NERL
Chemical Services, Room E-178
Building E Loading Dock
109 Alexander Drive
RTP, NC 27709

BDE samples

Walter Weathers
US EPA: Human Exposure and Atmospheric Sciences Division
USEPA Mailroom
Mail Code E205-04
Research Triangle Park, NC 27711

Pesticides/ Phthalates/ Other Flame Retardants

Marcia Nishioka
Battelle Memorial Institute
505 King Ave
Columbus, OH 43201

7.7.5. The remaining dust shall be kept in -20°C freezer.

7.8. Cleanup

7.8.1. Scrupulous care must be taken to clean the sieve apparatus and all other equipment that comes in contact with each sample to assure that the possibility of sample-to-sample carryover or contamination is eliminated. All such surfaces shall be washed with a brush and mild laboratory grade detergent, thoroughly rinsed with deionized water, and then triple rinsed with reagent grade methanol prior to drying by air or with laboratory grade nitrogen.

8 Quality Control and Quality Assurance

Proper chain of custody records shall be kept documenting the initial receipt of the material by all staff handling sampling materials.

9 Reference

1. "Chemical Hygiene Plan", Office of Research and Development, US EPA, RTP, NC 27711, Revised June 2001.

Standard Operating Procedure For Extracting and Preparing Air Samples for Analysis of Pesticides

1. **Scope and Applicability**

This standard operating procedure (SOP) describes the method for extracting air samples for pesticides.

2. **Summary of Method**

This method describes the procedures for extracting air samples by accelerated solvent extraction using dichloromethane (DCM). The sample is then concentrated to 1 mL by KD concentration and then to 0.2 mL by N-evap concentration; the internal standard (IS) is spiked into the sample. The solution is transferred into a GC vial and the extract is analyzed.

3. Cautions

3.1. Appropriate laboratory safety equipment such as lab coats, safety glasses, and protective gloves should be worn when performing these procedures.

4. Responsibilities

4.1. The project staff performing the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation laboratory record books, and sending final extracts for analyses.

4.2. The Laboratory Team Leader (LTL), the QA Officer or designee, and Task Order Leader (TOL) will oversee the sample extraction operation and ensure that SOPs are followed by all project staff.

5. Reagents and Equipment

5.1. Reagents

6.1.1 Dichloromethane (DCM); distilled in glass
6.1.2 Nonane
6.1.3 Glass wool, muffled
6.1.4 Sodium sulfate (Na_2SO_4), analytical grade, muffled
6.1.5 Accelerated solvent extractor filters
6.1.6 pre-cleaned XAD-2; Supelco
6.1.7 27 mm Glass fiber filter (GFF); Pallflex

5.2. Equipment

5.2.1. Accelerated solvent extractor (ASE)
5.2.2. 33-mL ASE cells with end-caps
5.2.3. ASE collection vials, 60 mL, muffled
5.2.4. Syringes or pipettes for spiking samples and extracts
5.2.5. Kuderna-Danish (KD) glassware (25-mL tube, flask, macro and micro Snyder columns)
5.2.6. Boiling chips, Hengar

5.2.7. Air bath capable of maintaining temperature of 60-80 °C
5.2.8. Concentrator tube, glass, disposable
5.2.9. Nitrogen Evaporator
5.2.10. Vortex mixer

6. Procedure

6.1. Sample Extraction

6.1.1. Obtain an air sample (5 g XAD and 1 GFF). Prepare additional QC samples using 5 g of pre-cleaned XAD and 1 DCM-rinsed GFF.
6.1.2. For the matrix spike sample, spike 25 µL of the 0.2/0.4/1.0 µg/mL Pesticide Analyte Mix onto the filter (see SOP 6.101).
6.1.3. For the solvent method blank, use 30 mL of extraction solvent (DCM).
6.1.4. Obtain 33-mL ASE cells and end-caps. Screw on the bottom end-cap, insert filter.
6.1.5. Place the air sample in the ASE cell.
6.1.6. Spike 10 µL of the 0.5 µg/mL Pesticide SRS spiking solution onto the XAD (see SOP 6.1.1). The spiked level may be adjusted and the exact spiked amounts will be recorded in the laboratory record book (LRB).
7.1.7 Place the ASE cells and the 60 mL muffled collection vials on the ASE unit.

Pressure: 2000 psi
Temperature: 100 °C
Solvent: DCM
Static: 5 min
Flush: 100%
Purge: 60 seconds
Cycles: 2

The extraction time for each sample is ~20 mins and the collection volume is ~40 ml.

6.2. Concentration

6.2.1. Transfer extract to KD tube with DCM rinses.
6.2.2. Add 3-4 boiling chips to the KD apparatus and attach a Snyder column.
6.2.3. Concentrate the extract to ~1 mL in a 60-65 °C water bath.
6.2.4. Remove the sample from the bath and allow it to cool to room temperature.
6.2.5. Remove the Snyder column and rinse the lower joint with DCM allowing the rinse to go into the KD tube.
6.2.6. Remove the KD flask and rinse the lower joint with DCM allowing the rinse to go into the KD tube.
6.2.7. Add 100 µL nonane.
6.2.8. Spike the extract with 10 µL of 2 µg/mL dibromobiphenyl IS solution (see SOP 6.101). Mix on a vortex mixer.
6.2.9. Transfer the sample from the KD tube to a disposable tube.
6.2.10. Rinse the KD tube with two 0.5 mL aliquots of DCM; add rinses to the disposable tube.
6.2.11. Gently N-evap the extract to 0.2 ml.
6.2.12. Transfer the sample to an autosampler vial.
6.3. Store at ~-10 °C until analyzed.

7. Records

7.1. The samples will be assigned an LRB number; the field sample ID (if applicable) will be documented with the LRB number. The QC samples generated in the laboratory will be

assigned a laboratory record book number.

7.2. The date of extraction, the lot numbers of solvents, identification of spike solutions, matrix spike volumes, and internal standard volumes will be recorded in the LRB. The extraction activities of samples will be also recorded in the LRB. The LRB will be retained until the conclusion of the study and will be held for one year after completion of the study.

8. **Quality Control and Quality Assurance**

8.1. Three types of QC samples (laboratory method blank, duplicate sample aliquot, and matrix spiked sample) will be processed with the field samples. The laboratory method blank is to verify that minimal contamination occurs through sample preparation in the laboratory. The duplicate and matrix spiked samples are used for assessing the overall method precision and the accuracy, respectively.

8.2. Surrogate recovery values of 80-120% in blanks and actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than 80% and or greater than 120%, the data will be flagged.

8.3. If significant target analyte levels (>0.1 µg) are found in the laboratory blanks, the source of contamination must be identified and more laboratory blanks and storage blanks will be analyzed.

Standard Operating Procedure for Extracting and Preparing Dust Samples for Analysis of Pesticides

1. **Scope and Applicability**

   This standard operating procedure (SOP) describes the method for extracting dust samples for pesticides.

2. **Summary of Method**

   This method describes the procedures for extracting dust samples by sonication with SPE clean-up, derivitization and analysis. An aliquot of dust (0.5 g) is spiked with compound-specific surrogate recovery standards (SRSs), extracted in dichloromethane and solvent exchanged into acetonitrile (ACN). The samples is applied to stacked SPE columns(C18 and aminopropyl) and eluted with ACN. The sample is concentrated to 1 mL and the internal standard (IS) is spiked into the sample. The solution is transferred into a GC vial and the extract is analyzed.

3. **Definitions**

   3.1. LRB – laboratory record book

4. Cautions

   4.1. Appropriate laboratory safety equipment such as lab coats, safety glasses, and protective gloves should be worn when performing these procedures.

5. Responsibilities

   5.1. The project staff performing the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation laboratory record books, and sending final extracts for analyses.

   5.2. The Laboratory Team Leader (LTL), the QA Officer or designee, and Task Order Leader (TOL) will oversee the sample extraction operation and ensure that SOPs are followed by all project staff.

6. Reagents and Equipment

   6.1. Reagents

      6.1.1. Dichloromethane (DCM), distilled in glass
      6.1.2. Acetonitrile (ACN), distilled in glass
      6.1.3. C18 SPE column, 0.5 g, JT baker or equivalent
      6.1.4. Aminopropyl SPE column, 0.5 g, Supelco

   6.2. Equipment

      6.2.1. Centrifuge tubes, 50 mL
      6.2.2. Syringes or pipettes for spiking samples and extracts
      6.2.3. Serological pipette, capable of holding 10 mL of DCM

6.2.4. Pipette bulb
6.2.5. Sonication bath
6.2.6. Centrifuge, equipped with a rotor for the centrifuge tubes
6.2.7. TurboVap, low-volume
6.2.8. Sample collection tubes, 20 mL
6.2.9. Vortex mixer

7. Procedure

7.1. Extraction of Sieved Dust

7.1.1. Weigh 0.5 g aliquots of each sample into 50-mL centrifuge tubes. Weigh additional 0.5 g aliquots of a reference dust sample into 50-mL centrifuge tubes for QC samples.
7.1.2. For the matrix spike sample, spike 50 µL of the 2/4/10 µg/mL Pesticide Analyte Mix onto the dust (see SOP 6.101).
7.1.3. For the solvent method blank, add 12 mL of extraction solvent (DCM) to an empty centrifuge tube.
7.1.4. Spike 50 µL of the 0.5 µg/mL Pesticide SRS spiking solution onto each dust (see SOP 6.101). The spike level may be adjusted and the exact spike amounts will be documented.
7.1.5. Add 12 mL of extraction solvent (DCM) to the dust sample; shake or vortex mix to wet the dust thoroughly.
7.1.6. Place the tube in a rack in a sonication bath and sonicate for 15 minutes.
7.1.7. Centrifuge the sample at ~3000 rpm for 10 minutes.

7.2. Concentration

7.2.1. Transfer 10 mL of the extract to a TurboVap tube with a line drawn at the 1-mL mark.
7.2.2. Concentrate to 1 mL in a 45 C TurboVap bath. During the concentration step, periodically rinse the inside walls with DCM.
7.2.3. Add 5 mL ACN.
7.2.4. Concentrate the extract to 1 mL in a 65 C TurboVap bath. During the concentration step, periodically rinse the inside walls with ACN.
7.2.5. Add 4 mL ACN to bring the volume up to 5 ml.

7.3. Solid Phase Extraction (SPE)

7.3.1. Connect a 0.5 g C18 SPE column to the top of a 0.5 g aminopropyl SPE column.
7.3.2. Add 5 mL ACN and allow the solvent to pass through the columns and go to waste; the liquid level should be just above the sorbent bed.
7.3.3. Place a collection vial under the stacked SPE columns.
7.3.4. Add the 5 mL of extract and start collecting effluent.
7.3.5. Allow the solvent level to nearly reach the C18 sorbent bed.
7.3.6. Close the stopcock and allow the sample to sit on the column for 3 minutes.
7.3.7. Rinse the concentrator tube with 3x3 mL ACN.
7.3.8. Add the rinses to the stacked SPE columns and collect all effluent.

7.4. Concentration

7.4.1. Transfer the sample from the collection tube to a TurboVap tube.
7.4.2. Rinse the collection tube with two 0.5 mL aliquots of ACN; add rinses to the TurboVap tube.
7.4.3. Concentrate the extract to ~1 mL in a 65 C TurboVap bath.
7.4.4. Spike the extract with 10 µL of 10 µg/mL dibromobiphenyl IS solution (see SOP 6.101). Mix on a vortex mixer.
7.4.5. Transfer the sample to an autosampler vial.

7.5. Store at ~-10 C until analyzed.

8. **Records**

8.1. The samples will be assigned an LRB number; the field sample ID (if applicable) will be documented with the LRB number. The QC samples generated in the laboratory will be assigned a laboratory record book number.

8.2. The date of extraction, the lot numbers of solvents, identification of spike solutions, matrix spike volumes, and internal standard volumes will be recorded in the LRB. The extraction activities of samples will be also recorded in the LRB. The LRB will be retained until the conclusion of the study and will be held for one year after completion of the study.

9. **Quality Control and Quality Assurance**

9.1. Three types of QC samples (laboratory method blank, duplicate sample aliquot, and matrix spiked sample) will be processed with the field samples. The laboratory method blank is to verify that minimal contamination occurs through sample preparation in the laboratory. The duplicate and matrix spiked samples are used for assessing the overall method precision and the accuracy, respectively.

9.2. Surrogate recovery values of 80-120% in blanks and actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than 80% and or greater than 120%, the data will be flagged.

9.3. If significant target analyte levels (>0.1 µg) are found in the laboratory blanks, the source of contamination must be identified and more laboratory blanks and storage blanks will be analyzed.

Standard Operating Procedure for Determination of Pesticides in Sample Extracts by Gas Chromatography/ Mass Spectrometry

1.0 **Scope and Applicability**

This standard operating procedure (SOP) describes the method for detection and quantification of pyrethroid pesticides their associated surrogate recovery standard (SRS) by gas chromatography/mass spectrometry using multiple ion detection (GC/MS/MID) for sample extracts.

2.0 **Summary of Method**

This SOP describes the method used for the GC/MS/MID determination of target analytes in sample extracts. The analytical column (ZB-35) is installed in the instrument. The GC parameters and acquisition profile are set. A sequence consisting of calibration standards and sample extracts is run. The calibration curves for each analyte and surrogate recovery standard are obtained using the internal standard method and linear regression. The calibration curves are applied to the detected analytes to determine analyte concentration in the extract.

3.0 **Definitions**

3.1 Extract: The sample extract that contains native target analytes, surrogate recovery standard, and internal standard.

3.2 Surrogate Recovery Standard (SRS): The compound used for QA/QC purposes to assess the extraction efficiency obtained for individual samples. A known amount of the compound is spiked into the sample prior to extraction. The SRS is quantified at the time of analysis and its recovery indicates the probable extraction and recovery efficiency for native analytes that are structurally similar. The SRS is chosen to be as similar as possible to the native analytes of interest, but it must not interfere in the analysis.

3.3 Internal Standard (IS): The compound added to sample extracts prior to GC/MS analysis. The ratio of the detector signal of the native analyte to the detector signal of the IS is compared to ratios obtained for calibration curve solutions where the IS level remains fixed and the native analyte levels vary. The IS is used to correct for minor run-to-run differences in GC injection, chromatographic behavior, and MS ionization efficiency.

4.0 **Cautions**

4.1 Standard laboratory protective clothing, gloves, and eye covering is required.

4.2 The toxicity and carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references of laboratory safety and MSDS must be available for the information of the analyst.

5.0 **Responsibilities**

5.1 The project staff performing the GC/MS analyses will be responsible for obtaining sample extracts, analyzing the samples, maintaining instrument control and maintenance records, and entering relevant information in the laboratory record books.

5.2 The Battelle Task Order Leader (TOL), the QA Manager, or designees will oversee the sample analysis operations and ensure that SOPs are followed by all project staff.

6.0 **Apparatus and Materials**

6.1 Analytical Column - ZB-35ms (or equivalent), 30 m x 0.25 mm id fused silica, 0.25 µm film thickness.

6.2 Gas Chromatograph Mass Spectrometer System: The instrument should be operated in multiple ion detection (MID) mode, with a minimum of two ions monitored per analyte. The extracts will be analyzed in the MID mode.

6.2.1 GC/MS:Hewlett Packard 6890 GC equipped with a HP5973 mass selective detector and an autosampler or equivalent.

6.2.2 Operating Parameters:

Column Flow Rate: 1 mL/min Helium
Injection Port Temperature: 300 °C
Injection Volume: 2 µL splitless for 0.75 min
Oven Temperature Program: 100 C for 1 min; 100-130 @ 25°C/min, 130-340 @ 6 C/min; hold 340 for 5 min, 42.2 min run time
Transfer Line Temperature: 300 °C
MS Zone Temperatures: MS Quad – 150°C
MS Source – 230°C
Ions Monitored: see Table 1

The first ion listed is the target ion, which is used for quantitation. Subsequent ions are used as qualifier ions to confirm the identification of the analyte.

6.3. Microliter syringe, 10 µL, for injection of liquid standards and sample extracts into GC/MS system.

7.0 Procedure

7.1 GC/MS Instrument Set-Up. (NOTE: The set-up procedure may be different for different GC/MS systems).

7.1.1 The column is installed in the GC oven and the column flow is set. The GC column temperature program is set.
7.1.2 The MS is set according to the manufacturer's instructions. Once the entire GC/MS system has been set up, the system is calibrated as described in Section 7.3.
7.1.3 The autosampler, containing a 100-vial tray, is positioned on the injection port of the GC. Settings for the sample volume (1 - 5 µL), number of injections per sample (1 - 4), number of sample pre-washes (0 - 10), and number of solvent post-washes (0 - 10) are selected through data acquisition software.

7.2 GC/MS Tuning and Standardization.

7.2.1 The GC/MS system is tuned, according to the manufacturer's instructions, using the "autotune" function. The instrument is tuned each day a sample sequence is set up.
7.2.2 To tune the GC/MS, FC-43 is introduced directly into the ion source via the molecular leak. The instrumental parameters (i.e., lens voltages, resolution, etc.) are adjusted to give documented, standard relative abundance as well as acceptable resolution (i.e., baseline mass resolution) and Gaussian peak shape. If the instrument fails to tune under autotune conditions, then the ion source will require cleaning as per the manufacturer's instructions, or other corrective issues must be considered and carried out.
7.2.3 After tuning is complete, the autotune report is printed and the hard copy is placed in that instrument's autotune record book in the MS laboratory.

7.3 Calibration of the GC/MS system.

7.3.1 Before analyzing a sample set on a new column, a shortened column, or after the instrument has been vented for cleaning or maintenance, calibration runs are performed with one or more calibration standards, under the same conditions used to analyze the field samples.
7.3.2 All ions (quantification and qualifier) are entered into windows in the acquisition method. For the GC/MS, the identification window for each analyte is set at the RT ± 0.2 min.
7.3.3 A calibration curve for each analyte will be constructed with a minimum of 5 calibration standards that will encompass the calibration range. Reference Pyrethroids in Dust SOP 1.01 for calibration curve information.

7.3.3.3 The internal standard is dibromobiphenyl and is present in samples and standards at a concentration of 100 ng/ml.

7.3.4 The calibration curve will be generated using the theoretical analyte concentration vs the relative area (analyte area/IS area). The calibration curve may be forced through the origin. The correlation coefficient (r^2) of the curves must be ≥0.98. The % relative error (%RE) for recalculation of each calibration standard against the curve must be <25%, except for the lowest level standard, which must have a relative error <30%. If the correlation coefficient of any analyte is less than 0.98, or the %RE exceeds tolerance, then the calibration

curve can be fit to a second order equation, the top calibration point can be eliminated (if there are no samples at this level), and/or the GC/MS system is checked to determine the sources for this variation. Corrective actions for the instrument (i.e., clean source) will be taken and the sample set will be reanalyzed.

7.4 Analysis Sequence:

7.4.1 A higher level calibration standard is analyzed first to ensure retention times in the method are correct.
7.4.2 One to three standards are analyzed, followed by up to 5 sample extracts (some of which may be QC sample extracts).
7.4.3 A second calibration standard is analyzed.
7.4.4 Steps 7.4.2 and 7.4.3 are repeated until all samples have been analyzed.

7.5 Data processing involves: (1) generating a calibration curve for each target analyte and SRS compound(s) from the results of the standard analyses, (2) calculating the concentrations of target analytes and SRS(s) in the sample extracts and in standards with calibration curves using HP ChemStation software, and (3) manually reviewing each data file to ensure that the identification and integration of quantified target peaks are correct.

7.6 Analyte ID will be based on the following criteria: correct RT ± 0.02 min, using as a guide the RT of the two standards that bracket the sample in the GC/MS run order; correct ratio of quantification (quant) ion area to first qualifier (qual) ion area ± 20%; and co-maximizing peak shapes for the target ion and first qualifier ion. If the relative intensity of the first qual ion (with respect to the quant ion area) is lower than the acceptable range, then the ID cannot be confirmed; if the relative intensity of the first qual ion is higher than the acceptable range, then the ID may be confirmed using the second qualifier ion.

7.7 Calculations:

The instrument software will calculate ng/mL of the analytes and SRSs in the sample based on the calibration curve. A quantitation report will be generated for each sample or standard which will include these concentrations.

8.0 **Records**

8.1 All operations, maintenance, daily mass calibration, ion transmission balance, and multiplier gain are stored in each instrument's logbook.

8.2 All analytical results are logged in specific study folders.

8.3 Hardcopy output of QUAN reports will be generated after the qualified analyst reviews the data. For each analysis set, one file folder will be used to hold/archive the hardcopy output of QUAN reports (samples and standards), the calibration curve, copy of the analytical method, and analytical sequence. The QUAN report lists the file name and sample name together with the calculated concentrations.

8.4 All data files are stored on disks or tapes for permanent record. The disks or tapes are stored permanently in the GC/MS laboratory as part of the GC/MS laboratory records.

8.5 Final calculations of the data are performed and/or recorded in the study database.

8.6 A separate data record will be prepared for each sample analysis as part of the electronic data file submitted to the database. Each record must contain, at a minimum, the following information:

8.6.1 The sample ID code.
8.6.2 The sample analysis date.
8.6.3 A code to indicate whether this is a reanalysis for a diluted sample extracts
8.6.4 A code to indicate the overall acceptability of the analysis result.
8.6.5 A code to indicate the type of sample (SMB, DS1, DS2, etc).
8.6.6 The analysis result for the surrogate standard(s).
8.6.7 The percent recovery result for the surrogate standard.
8.6.8 The analysis result for the target analytes as analyzed in the extract.

9.0 **Quality Control and Quality Assurance**

9.1 The absolute response levels for the internal standard must be recorded for each analysis. If IS areas decrease throughout a sample set or if a difference is observed in the area of the IS in samples and in standards, but the SRS recoveries in samples remain within the acceptance range, then no action will be taken. If IS areas decrease or if a difference is observed in the area of the IS in samples and in standards, and the SRS recoveries in samples do not remain within the acceptance range, then corrective action will be taken. These actions will include: cleaning the GC/MS injector, liner, and/or ion source, and removing the first meter of the column, and reanalyzing the sample set.

9.2 Samples will be re-analyzed when the calibration curve data cannot be fit to either a first or second order equation with fit parameter r^2>0.98 or when the recalculation of the standards against the curve does not meet the tolerances set in section 7.3.4. Corrective action, as listed in Section 9.1 will be undertaken before samples are reanalyzed.

9.3 Surrogate recovery values of 70-120% in the actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than the minimum goal the data will be flagged. For recoveries greater than the maximum goal, the concentration of the surrogate spiking solution will be checked against a calibration curve to determine whether inadvertent solvent loss has resulted in higher spike levels.

10.0 **Extract Storage**

Extracts are stored protected from light at -20°C except during analysis. Holding times have not been established for sample extracts.

Table 1. Analyte List

Analyte Group	Analyte	Retention Time, min	Primary Ion	Secondary Ion(s)	Ion Ratios
Pesticides	Bifenthrin	23.75	181	165, 166	100, 25, 26
	Chlorpyrifos	17.48	314	316	100, 75
	Cyfluthrin I	28.22	163	226	100, 65
	Cyfluthrin II/III	28.35	163	226	100, 45
	Cyfluthrin IV	28.49	163	226	100, 55
	Cyhalothrin-lambda	25.57	209	197, 181	100, 260, 370
	Cypermethrin I	28.88	163	181	100, 100
	Cypermethrin II/III	29.03	163	181	100, 85
	Cypermethrin IV	29.18	163	181	100, 90
	Diazinon	14.09	276	199, 304	100,210,223
	Imiprothrin	22.90	151	318, 123	100, 10, 650
	Permethrin – cis	27.36	183	163	100, 15
	Permethrin - trans	27.58	183	163	100, 35
	Piperonyl butoxide	23.17	176	177	100, 35
	Sumithrin	25.02	183	123	100, 180
Internal Standard	Dibromobiphenyl	18.36	312	314	100, 50
Surrogate Standards	Fenchlorphos	16.37	285	287	100, 70
	Permethrin – trans 13C6	27.56	189	190	100, 10

Standard Operating Procedure for Extracting and Preparing Air Samples for Analysis of Phthalates

1. Scope and Applicability

This standard operating procedure (SOP) describes the method for extracting air samples for phthalates.

2. Summary of Method

This method describes the procedures for extracting air samples by accelerated solvent extraction (ASE) using dichloromethane (DCM). The sample is then concentrated to 2 mL and the internal standard (IS) is spiked into the sample. The solution is transferred into a GC vial and the extract is analyzed.

3. Cautions

3.1. Appropriate laboratory safety equipment such as lab coats, safety glasses, and protective gloves should be worn when performing these procedures.

4. Responsibilities

4.1. The project staff performing the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation laboratory record books, and sending final extracts for analyses.

4.2. The Laboratory Team Leader (LTL), the QA Officer or designee, and Task Order Leader (TOL) will oversee the sample extraction operation and ensure that SOPs are followed by all project staff.

5. Reagents and Equipment

5.1. Reagents

5.1.1. Dichloromethane (DCM); distilled in glass
5.1.2. Sodium sulfate (Na_2SO_4), analytical grade, muffled
5.1.3. Accelerated solvent extractor filters
5.1.4. pre-cleaned XAD-2, Supelco
5.1.5. Glass fiber filter (GFF), DCM rinsed; Pallflex

5.2. Equipment

5.2.1. Accelerated solvent extractor (ASE)
5.2.2. 33-mL ASE cells with end-caps
5.2.3. ASE collection vials, 60 mL, muffled
5.2.4. Syringes or pipettes for spiking samples and extracts
5.2.5. Kuderna-Danish (KD) glassware (25-mL tube, flask, macro and micro Snyder columns)
5.2.6. Boiling chips, Hengar
5.2.7. Water bath capable of maintaining temperature of 60-80 °C
5.2.8. Concentrator tube, glass, disposable
5.2.9. Nitrogen Evaporator (N-evap)

5.2.10. GC autosampler vials
5.2.11. Vortex mixer

6. Procedure

6.1. Sample Extraction

6.1.1. Obtain air samples (5 g XAD and 1 GFF) for a sample batch (10-20 samples). Prepare QC samples (e.g., instrument blank and matrix spike) using 5 g of pre-cleaned XAD and 1 DCM-rinsed GFF.
6.1.2. For the matrix spike sample, spike 10 µL of 0.5 mg/mL Phthalate Analyte Mix onto the XAD. [See SOP 6.401 for Phthalate Analyte Mix preparation.]
6.1.3. For the solvent method blank, use 30 mL of extraction solvent (DCM).
6.1.4. Obtain 33-mL ASE cells and end-caps. Screw on the bottom end-cap, insert filter.
6.1.5. Place the air sample in the ASE cell.
6.1.6. Spike 20 µL of the Phthalate surrogate recovery standard (SRS) spiking solution (5 µg/mL) onto the sample. The spiked level may be adjusted and the exact spiked amounts will be recorded in the laboratory record book (LRB). [See SOP 6.401 for Phthalate SRS preparation.]
7.1.7 Place the ASE cells and the 60 mL muffled collection vials on the ASE unit. Extract with the following conditions

Pressure: 2000 psi
Temperature: 100 °C
Solvent: DCM
Static: 5 min
Flush: 100%
Purge: 60 seconds
Cycles: 2

The extraction time for each sample is ~20 mins and the collection volume is ~40 ml.

6.2. Concentration
6.2.1. Transfer extract to KD tube with DCM rinses.
6.2.2. Add 3-4 boiling chips to the KD apparatus and attach a Snyder column.
6.2.3. Concentrate the extract to ~2 mL in a 60-65 °C water bath.
6.2.4. Remove the sample from the bath and allow it to cool to room temperature.
6.2.5. Remove the Snyder column and rinse the lower joint with DCM allowing the rinse to go into the KD tube.
6.2.6. Remove the KD flask and rinse the lower joint with DCM allowing the rinse to go into the KD tube.
6.2.7. Adjust the volume to 2 mL with N-evap.
6.2.8. Draw off 1.0 mL of the extract to another KD tube.
6.2.9. Add 5 mL of hexane.
6.2.10. Concentrate the extract to 1 mL with N-evap.
6.2.11. Spike the extract with 10 µL of dibromobiphenyl IS solution (10 µg/mL). Mix on a vortex mixer. [See SOP 6.401 for Phthalate IS preparation.]
6.2.12. Transfer the sample to an autosampler vial.
6.3. Store at ~-10 °C until analyzed.

7. Records

7.1. The samples will be assigned an LRB number; the field sample ID (if applicable) will be documented with the LRB number. The QC samples generated in the laboratory will be

assigned a laboratory record book number.

7.2. The date of extraction, the lot numbers of solvents, identification of spike solutions, matrix spike volumes, and internal standard volumes will be recorded in the LRB. The extraction activities of samples will be also recorded in the LRB. The LRB will be retained until the conclusion of the study and will be held for one year after completion of the study.

8. **Quality Control and Quality Assurance**

8.1. Three types of QC samples (laboratory method blank, duplicate sample aliquot, and matrix spiked sample) will be processed with the field samples. The laboratory method blank is to verify that minimal contamination occurs through sample preparation in the laboratory. The duplicate and matrix spiked samples are used for assessing the overall method precision and the accuracy, respectively.

8.2. Surrogate recovery values of 80-120% in blanks and actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than 80% and or greater than 120%, the data will be flagged.

8.3. If significant target analyte levels (>0.1 µg) are found in the laboratory blanks, the source of contamination must be identified and more laboratory blanks and storage blanks will be analyzed.

Standard Operating Procedure for Determination of Phthalates in Sample Extracts by Gas Chromatography/ Mass Spectrometry

1.0 **Scope and Applicability**

This standard operating procedure (SOP) describes the method for detection and quantification of phthalates and their associated surrogate recovery standard (SRS) by gas chromatography/mass spectrometry using multiple ion detection (GC/MS/MID) for sample extracts.

2.0 **Summary of Method**

This SOP describes the method used for the GC/MS/MID determination of target analytes in sample extracts. The analytical column (ZB-35) is installed in the instrument. The GC parameters and acquisition profile are set. A sequence consisting of calibration standards and sample extracts is run. The calibration curves for each analyte and surrogate recovery standard are obtained using the internal standard method and linear regression. The calibration curves are applied to the detected analytes to determine analyte concentration in the extract. Information is also included to quantitate phthalates at high levels.

3.0 **Definitions**

3.1 Extract: The sample extract that contains native target analytes, surrogate recovery standard, and internal standard.

3.2 Surrogate Recovery Standard (SRS): The compound used for QA/QC purposes to assess the extraction efficiency obtained for individual samples. A known amount of the compound is spiked into the sample prior to extraction. The SRS is quantified at the time of analysis and its recovery indicates the probable extraction and recovery efficiency for native analytes that are structurally similar. The SRS is chosen to be as similar as possible to the native analytes of interest, but it must not interfere in the analysis.

3.3 Internal Standard (IS): The compound added to sample extracts prior to GC/MS analysis. The ratio of the detector signal of the native analyte to the detector signal of the IS is compared to ratios obtained for calibration curve solutions where the IS level remains fixed and the native analyte levels vary. The IS is used to correct for minor run-to-run differences in GC injection, chromatographic behavior, and MS ionization efficiency.

4.0 **Cautions**

4.1 Standard laboratory protective clothing, gloves, and eye covering is required.

4.2 The toxicity and carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references of laboratory safety and MSDS must be available for the information of the analyst.

5.0 **Responsibilities**

5.1 The project staff performing the GC/MS analyses will be responsible for obtaining sample extracts, analyzing the samples, maintaining instrument control and maintenance records, and entering relevant information in the laboratory record books.

5.2 The Battelle Task Order Leader (TOL), the QA Manager, or designees will oversee the sample analysis operations and ensure that SOPs are followed by all project staff.

6.0 **Apparatus and Materials**

6.1 Analytical Column - ZB-35ms (or equivalent), 30 m x 0.25 mm id fused silica, 0.25 µm film thickness.

6.2 Gas Chromatograph Mass Spectrometer System: The instrument should be operated in multiple ion detection (MID) mode, with a minimum of two ions monitored per analyte. The extracts will be analyzed in the MID mode.

6.2.1 GC/MS:Hewlett Packard 6890 GC equipped with a HP5973 mass selective detector and an autosampler or equivalent.

6.2.2 Operating Parameters:

Column Flow Rate:	1 mL/min Helium
Injection Port Temperature:	300 °C
Injection Volume:	2 µL splitless for 0.75 min
Oven Temperature Program:	100 °C for 1 min; 100-130 @ 25 C/min, 130-340 @ 6 C/min; hold 340 for 5 min, 42 min run time
Transfer Line Temperature:	300 °C
MS Zone Temperatures:	MS Quad – 150°C MS Source – 230°C
Ions Monitored:	see Table 1

The first ion listed is the target ion, which is used for quantitation. Subsequent ions are used as qualifier ions to confirm the identification of the analyte.

6.3. Microliter syringe, 10 µL, for injection of liquid standards and sample extracts into GC/MS system.

7.0 **Procedure**

7.1 GC/MS Instrument Set-Up. (NOTE: The set-up procedure may be different for different GC/MS systems).

7.1.1 The column is installed in the GC oven and the column flow is set. The GC column temperature program is set.

7.1.2 The MS is set according to the manufacturer's instructions. Once the entire GC/MS system has been set up, the system is calibrated as described in Section 7.3.

7.1.3 The autosampler, containing a 100-vial tray, is positioned on the injection port of the GC. Settings for the sample volume (1 - 5 µL), number of injections per sample (1 - 4), number of sample pre-washes (0 - 10), and number of solvent post-washes (0 - 10) are selected through data acquisition software.

7.2 GC/MS Tuning and Standardization.

7.2.1 The GC/MS system is tuned, according to the manufacturer's instructions, using the "autotune" function. The instrument is tuned each day a sample sequence is set up.

7.2.2 To tune the GC/MS, FC-43 is introduced directly into the ion source via the molecular leak. The instrumental parameters (i.e., lens voltages, resolution, etc.) are adjusted to give documented, standard relative abundance as well as acceptable resolution (i.e., baseline mass resolution) and Gaussian peak shape. If the instrument fails to tune under autotune conditions, then the ion source will require cleaning as per the manufacturer's instructions, or other corrective issues must be considered and carried out.

7.2.3 After tuning is complete, the autotune report is printed and the hard copy is placed in that instrument's autotune record book in the MS laboratory.

7.3 Calibration of the GC/MS system.

7.3.1 Before analyzing a sample set on a new column, a shortened column, or after the instrument has been vented for cleaning or maintenance, calibration runs are performed with one or more calibration standards, under the same conditions used to analyze the field samples.

7.3.2 All ions (quantification and qualifier) are entered into windows in the acquisition method. For the GC/MS, the identification window for each analyte is set at the RT ± 0.2 min.

7.3.3 A calibration curve for each analyte will be constructed with a minimum of 5 calibration standards that will encompass the calibration range. Reference Pyrethroids in Dust SOP 1.01 for calibration curve information.

7.3.3.3 The internal standard is dibromobiphenyl and is present in samples and standards at a concentration of 100 ng/ml.

7.3.4 The calibration curve will be generated using the theoretical analyte concentration vs the relative area (analyte area/IS area). The calibration curve may be forced through the origin. The correlation coefficient (r^2) of the curves must be ≥0.98. The % relative error (%RE) for recalculation of each calibration standard against the curve must be <25%, except for the lowest level standard, which must have a relative error <30%. If the correlation coefficient of any analyte is less than 0.98, or the %RE exceeds tolerance, then the calibration curve can be fit to a second order equation, the top calibration point can be eliminated (if there are no samples at this level), and/or the GC/MS system is checked to determine the sources for this variation. Corrective actions for the instrument (i.e., clean source) will be taken and the sample set will be reanalyzed.

7.4 Analysis Sequence:

7.4.1 A higher level calibration standard is analyzed first to ensure retention times in the method are correct.
7.4.2 One to three standards are analyzed, followed by up to 5 sample extracts (some of which may be QC sample extracts).
7.4.3 A second calibration standard is analyzed.
7.4.4 Steps 7.4.2 and 7.4.3 are repeated until all samples have been analyzed.

7.5 Data processing involves: (1) generating a calibration curve for each target analyte and SRS compound(s) from the results of the standard analyses, (2) calculating the concentrations of target analytes and SRS(s) in the sample extracts and in standards with calibration curves using HP ChemStation software, and (3) manually reviewing each data file to ensure that the identification and integration of quantified target peaks are correct.

7.6 Analyte ID will be based on the following criteria: correct RT ± 0.02 min, using as a guide the RT of the two standards that bracket the sample in the GC/MS run order; correct ratio of quantification (quant) ion area to first qualifier (qual) ion area ± 20%; and co-maximizing peak shapes for the target ion and first qualifier ion. If the relative intensity of the first qual ion (with respect to the quant ion area) is lower than the acceptable range, then the ID cannot be confirmed; if the relative intensity of the first qual ion is higher than the acceptable range, then the ID may be confirmed using the second qualifier ion.

7.7 Calculations

The instrument software will calculate ng/mL of the analytes and SRSs in the sample based on the calibration curve. A quantitation report will be generated for each sample or standard which will include these concentrations.

Phthalates are sometimes found in samples at high concentrations that may overload the analytical column (indicated by peak fronting) or saturate the detector (indicated by flat-top peaks). Table 2 lists ions for the phthalates, except the diisononyl and diisodecyl phthalates, which have a lower detector response. In the event that column overload or detector saturation is observed, the ions listed in this table can be used to quantitate the high level of phthalate.

8.0 **Records**

8.1 All operations, maintenance, daily mass calibration, ion transmission balance, and multiplier gain are stored in each instrument's logbook.

8.2 All analytical results are logged in specific study folders.

8.3 Hardcopy output of QUAN reports will be generated after the qualified analyst reviews the data. For each analysis set, one file folder will be used to hold/archive the hardcopy output of QUAN reports (samples and standards), the calibration curve, copy of the analytical method, and analytical sequence. The QUAN report lists the file name and sample name together with the calculated concentrations.

8.4 All data files are stored on disks or tapes for permanent record. The disks or tapes are stored permanently in the GC/MS laboratory as part of the GC/MS laboratory records.

8.5 Final calculations of the data are performed and/or recorded in the study database.

8.6 A separate data record will be prepared for each sample analysis as part of the electronic data file submitted to the database. Each record must contain, at a minimum, the following information:

8.6.1 The sample ID code.
8.6.2 The sample analysis date.
8.6.3 A code to indicate whether this is a reanalysis for a diluted sample extracts
8.6.4 A code to indicate the overall acceptability of the analysis result.
8.6.5 A code to indicate the type of sample (SMB, DS1, DS2, etc).
8.6.6 The analysis result for the surrogate standard(s).
8.6.7 The percent recovery result for the surrogate standard.
8.6.8 The analysis result for the target analytes as analyzed in the extract.

9.0 **Quality Control and Quality Assurance**

9.1 The absolute response levels for the internal standard must be recorded for each analysis. If IS areas decrease throughout a sample set or if a difference is observed in the area of the IS in samples and in standards, but the SRS recoveries in samples remain within the acceptance range, then no action will be taken. If IS areas decrease or if a difference is observed in the area of the IS in samples and in standards, and the SRS recoveries in samples do not remain within the acceptance range, then corrective action will be taken. These actions will include: cleaning the GC/MS injector, liner, and/or ion source, and removing the first meter of the column, and reanalyzing the sample set.

9.2 Samples will be re-analyzed when the calibration curve data cannot be fit to either a first or second order equation with fit parameter $r^2>0.98$ or when the recalculation of the standards against the curve does not meet the tolerances set in section 7.3.4. Corrective action, as listed in Section 9.1 will be undertaken before samples are reanalyzed.

9.3 Surrogate recovery values of 70-120% in the actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than the minimum goal the data will be flagged. For recoveries greater than the maximum goal, the concentration of the surrogate spiking solution will be checked against a calibration curve to determine whether inadvertent solvent loss has resulted in higher spike levels.

10.0 **Extract Storage**

Extracts are stored protected from light at -20°C except during analysis. Holding times have not been established for sample extracts.

Table 1. Analyte List

Analyte Group	Analyte	Retention Time, min	Primary Ion	Secondary Ion(s)	Ion Ratios
Analyte	Diethyl phthalate	11.04	149	177	100, 25
	Dibutyl phthalate	16.72	149	223	100, 5
	Butylbenzyl phthalate	23.26	149	206	100, 25
	Diethylhexyl phthalate	24.20	149	279	100, 10
	Diisononyl phthalate[1]	27.03	293	149	100, 700
	Diisodecyl phthalate[1]	28.42	307	149	100, 580
Internal Standard	Dibromobiphenyl	18.09	312	314	100, 50
Surrogate Standard	$^{13}C_4$-Di-N-hexyl phthalate	21.91	153	255	100, 8

[1] Diisononyl phthalate and Diisodecyl phthalate elute over approximately 1 minute. The software assigns the highest point in the integrated area as the retention time.

Table 2. Typical Analytical Information for High Phthalate Levels

Analyte Group	Analyte	Retention Time, min	Primary Ion	Secondary Ion(s)	Ion Ratios
Analyte	Diethyl phthalate	11.04	222	177	100, 1060
	Dibutyl phthalate	16.72	278	223	100, 940
	Butylbenzyl phthalate	23.26	312	206	100, 2750
	Diethylhexyl phthalate	24.20	390	279	100, 3000
Internal Standard	Dibromobiphenyl	18.09	312	314	100, 50
Surrogate Standard	$^{13}C_4$-Di-N-hexyl phthalate	21.91	153	255	100, 8

Standard Operating Procedure for Extracting and Preparing Air Samples for Analysis of BDEs

1.0 Scope and Applicability

This standard operating procedure (SOP) describes the method for extracting air samples for BDEs.

2.0 Summary of Method

This method describes the procedures for extracting air samples by accelerated solvent extraction with 1:1 hexane:dichloromethane. The extract is passed through two cleanup steps (acid silica stir and alumina SPE) prior to analysis.

3.0 Definitions

3.1 LRB – laboratory record book

4.0 Cautions

4.1 Appropriate laboratory safety equipment such as lab coats, safety glasses, and protective gloves should be worn when performing these procedures.

5.0 Responsibilities

5.1 The project staff who performs the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation laboratory record books, and sending final extracts for analyses.

5.2 The Laboratory Team Leader (LTL), the QA Officer or designee, and Task Order Leader (TOL) will oversee the sample extraction operation and ensure that SOPs are followed by all project staff.

6.0 Materials, Reagents and Equipment

6.1 Materials

6.1.1 Alumina SPE cartridge, 1 g, J. T. Baker or equivalent
6.1.2 Supelco precleaned XAD-2
6.1.3 Glass fiber filters, Pallflex

6.2 Reagents

6.2.1 Sodium sulfate (Na_2SO_4), muffled
6.2.2 Silica (100-200 mesh, 40A, heated in oven to 160 C for 1 hour, stored in desicator)
6.2.3 Acid silica -27 mL concentrated sulfuric acid added to 50g silica and shaken
6.2.4 Dichloromethane (DCM); distilled in glass
6.2.5 Hexane; distilled in glass
6.2.6 Sulfuric acid, concentrated

6.3 Equipment

6.3.1 Accelerated Solvent Extractor (Dionex, ASE 200)
6.3.2 ASE cell, 22-mL
6.3.3 ASE filter, cellulose
6.3.4 Balance, capable of weighing to 0.00 g
6.3.5 ASE collection vial, 60mL
6.3.6 Syringes or pipettes, for spiking
6.3.7 Funnel with large neck
6.3.8 Funnel with small neck
6.3.9 Glass wool, DCM rinsed and muffled
6.3.10 Erlenmeyer flask, 125-mL
6.3.11 Stir plate
6.3.12 Teflon coated stir bar, 1.5 inch
6.3.13 TurboVap tube, 200-mL
6.3.14 TurboVap, large volume
6.3.15 Pasture pipet
6.3.16 Solid phase extraction (SPE) manifold
6.3.17 Vacuum pump, attached to the SPE manifold
6.3.18 Concentrator tube, glass, disposable
6.3.19 Nitrogen evaporator
6.3.20 Oven at 160 C for Silica preparation
6.3.21 Aluminum foil, muffled

7.0 Procedure

An extraction set will contain 8-10 samples including QC.

7.1 Sample Extraction

7.1.1 Transfer XAD and filter from sample cartridge to ASE cell containing a cellulose filter using large neck funnel and placing the filter on top.
7.1.2 Spike 5 µL of the BDE surrogate recovery spike (SRS, 1 µg/mL, see SOP 6.501 for preparation) solution onto the filter. The spike level may be adjusted and the exact spiked amounts will be recorded in the LRB.
7.1.3 Place the ASE cells and the 60mL collection vials on the ASE unit.

Pressure: 2000 psi
Temperature: 100 °C
Solvent: 1:1 Hexane:DCM
Static: 20 minute
Flush: 60% flush
Purge: 120 second purge
Cycles: 3

7.2 Sample Drying

7.2.1 Place a small plug of glass wool in the neck of the small neck funnel.
7.2.2 Add Na_2SO_4 to the funnel to fill about ¾ full.
7.2.3 Decant the extract through the drying column, collecting the sample in a 125 mL Erlenmeyer flask
7.2.4 Rinse the ASE collection vial with two 5 mL aliquots of hexane.
7.2.5 Add the rinses to the flask
7.2.6 Rinse the Na_2SO_4 in the drying column with 10 mL of hexane. Add the rinses to the flask.

7.3 Acid stir

7.3.1 Add the stir bar to the flask.
7.3.2 Place flask on the stir plate and stir just enough to keep the stir bar moving.
7.3.3 Add 5g acid silica, cover with stopper or foil and stir for 2 hours.
7.3.4 Place a large plug of glass wool in the neck of the small neck funnel and rinse with hexane.
7.3.5 Decant the hexane layer through the funnel into a TurboVap tube.
7.3.6 Add 25 mL hexane to the acid silica and stir 10 minutes
7.3.7 Decant hexane through funnel to the TurboVap tube.
7.3.8 Repeat the 25 mL hexane rinse and decant two more times adding to same tube.
7.3.9 Concentrate to 1 mL with TurboVap bath at 42 C rinsing sides several times with hexane.

7.4 Alumina SPE column

7.4.1 Place a 1 g Alumina SPE column in the manifold
7.4.2 Condition the column with 6 mL hexane. Discard eluate.
7.4.3 Place the collection tube under the column.
7.4.4 Apply the sample to the column.
7.4.5 Rinse the TurboVap tube with two 0.5 mL aliquots of hexane. Add the rinses to the column. Allow the liquid level to nearly touch the frit.
7.4.6 Elute the column with 6 mL 1:1 hexane:DCM collecting the eluate in the collection tube.

7.5 Concentration
7.5.1 Concentrate the extract to ~2 mL under a gentle stream of nitrogen using a sand bath at ~30 C.
7.5.2 Rinse down the sides with ~1 mL hexane.
7.5.3 Concentrate to just dry.
7.5.4 Add 190 µL of hexane to rinse the sides.
7.5.5 Spike with 10 µL of the internal standard solution (2 µg/mL dibromobiphenyl, see SOP 6.501 for preparation).

7.6 Mix on a vortex mixer. Transfer to an autosampler vial with 300 µl insert.
7.7 Store the samples at ~-15 C until analyzed.

8.0 Records

8.1 The field samples will be identified in the LRB by field sample ID. The QC samples generated in the laboratory will be assigned a laboratory analysis number.

8.2 The date of extraction, the lot numbers of solvents, surrogate recovery values, matrix spike standard values, and internal standard values will be recorded in the LRB. The extraction activities of samples will be also recorded in the LRB that is kept in the extraction laboratory. This LRB will contain the field sample ID, the assigned laboratory analysis number (see above), the date of extraction, and the lot number of solvent used for extraction. The LRB will be retained in the laboratory where these operations are performed until the conclusion of the study and will be archived in a secure room for three years after completion of the study.

9.0 Quality Control and Quality Assurance

9.1 Four types of QC samples will be processed together with the field samples. The QC samples are laboratory method blank and matrix spiked sample aliquot. The laboratory method blank is to verify that minimal contamination occurs through sample preparation

in the laboratory. The matrix spiked sample is used for assessing the overall method precision and the accuracy, respectively.

9.2 Surrogate recovery values of 70-120% in blanks and actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than 70% and or greater than 120%, the data will be flagged.

9.3 If significant target analyte levels (>0.1 µg) are found in the field blanks and or laboratory blanks, the source of contamination must be identified and more laboratory blanks and storage blanks will be analyzed.

Standard Operating Procedure for Determination of Brominated Diphenyl Ethers in Sample Extracts by Negative Chemical Ionization (NCI) Gas Chromatography/ Mass Spectrometry

1.0 **Scope and Applicability**

This standard operating procedure (SOP) describes the method for detection and quantification of brominated diphenyl ethers (BDEs) and their associated surrogate recovery standard by gas chromatography/negative chemical ionization mass spectrometry using multiple ion detection (GC/MS-NCI/MID) for sample extracts.

2.0 **Summary of Method**

This SOP describes the method used for the GC/MS-NCI/MID determination of target analytes in sample extracts.

3.0 **Definitions**

3.1 Extract: The sample extract that contains native target analytes, surrogate recovery standard, and internal standard.

3.2 Brominated diphenyl ethers (BDEs): Byproducts of brominated flame retardant degradation

3.3 Surrogate Recovery Standard (SRS): The compound used for QA/QC purposes to assess the extraction efficiency obtained for individual samples. A known amount of the compound is spiked into the sample prior to extraction. The SRS is quantified at the time of analysis and its recovery indicates the probable extraction and recovery efficiency for native analytes that are structurally similar. The SRS is chosen to be as similar as possible to the native analytes of interest, but it must not interfere in the analysis.

3.4 Internal Standard (IS): The compound added to sample extracts prior to GC/MS analysis. The ratio of the detector signal of the native analyte to the detector signal of the corresponding IS is compared to ratios obtained for calibration curve solutions where the IS level remains fixed and the native analyte levels vary. The IS is used to correct for minor run-to-run differences in GC injection, chromatographic behavior, and MS ionization efficiency.

3.5 Chemical Ionization (CI): The mode of detection used for these analyses. CI requires a specific detector, source, and methane.

4.0 **Cautions**

4.1 Standard laboratory protective clothing, gloves, and eye covering is required.

4.2 The toxicity and carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references of laboratory safety and MSDS must be available for the information of the analyst.

5.0 **Responsibilities**

5.1 The project staff who perform the GC/MS analyses will be responsible for obtaining sample extracts from the sample coordinator, analyzing the samples, maintaining instrument control and maintenance records, and entering relevant information in the laboratory record books.

5.2 The Battelle Pesticide Laboratory coordinator, the QA Manager, and Task Order Leader (TOL) will oversee the sample extraction and analysis operations and ensure that SOPs are followed by all project staff.

6.0 **Apparatus and Materials**

6.1 Analytical Column - DB-5ms (or equivalent), 15 m x 0.25 mm id fused silica, 0.1 µm film thickness.

6.2 Gas Chromatograph Mass Spectrometer System: The instrument should be operated in multiple ion detection (MID) mode, with a minimum of two ions monitored per analyte. The extracts will be analyzed in the MID mode.

6.3 GC/MS:Hewlett Packard 6890 GC equipped with a HP5973 mass selective detector with chemical ionization capability, pulsed splitless injector, and an autosampler or equivalent.

6.4 Methane, for CI

6.5 Microliter syringe, 10 µL, for injection of liquid standards and sample extracts into GC/MS system.

7.0 **Procedure**

7.1 GC/MS Instrument Set-Up. (NOTE: The set-up procedure may be different for different GC/MS systems).

7.1.1 The column is installed in the GC oven and the column flow is set. The GC column temperature program is set.

7.1.2 The MS is set according to the manufacturer's instructions. Once the entire GC/MS system has been set up, the system is calibrated as described in Section 7.3.

7.1.3 The autosampler, containing a 100-vial tray, is positioned on the injection port of the GC. Settings for the sample volume (1 - 5 µL), number of injections per sample (1 - 4), number of sample pre-washes (0 - 10), and number of solvent post-washes (0 - 10) are selected through data acquisition software.

7.2 Operating Parameters:

Column Flow Rate:	1 mL/min Helium
Injection Port Temperature:	250 C
Injection Mode:	Pulsed Splitless
Pulse Pressure:	20 psi
Pulse Time:	0.5 min
Purge Flow:	50 mL/min
Injection Volume:	2 µL splitless for 0.75 min
Oven Temperature Program:	100 °C for 1 min; 100-300 @ 30°C/min; hold 300 for 20 min, 27.7 min run time
Transfer Line Temperature:	280 °C
MS Zone Temperatures:	

MS Quad: 150°C
MS Source: 230°C
Emission Current: 225
Electron Energy: 200
Percent Methane in Source: 52
Solvent Delay: 3 min

Ions Monitored: see Table 1

7.3 GC/MS Tuning and Standardization.

7.2.1 The GC/MS system is tuned, according to the manufacturer's instructions, Complete CI tuning instructions are included in the instrument manual. At a minimum, the instrument is tuned in the negative CI mode each day a sample sequence is set up.

7.3.2 The instrument is tuned in the positive CI mode with the methane set at 20.

7.2.2 The instrument is then tuned in the negative mode with the methane set at 40.

7.2.3 During tuning, the instrumental parameters (i.e., lens voltages, resolution, etc.) are adjusted to give documented, standard relative abundance as well as acceptable resolution (i.e., baseline mass resolution) and Gaussian peak shape.

7.2.4 Following the negative CI tune, the percent methane is increased to 52%, the emission current is set to 225, and the electron energy is set to 200.

7.2.5 If the instrument fails to tune under autotune conditions, then the ion source will require cleaning as per the manufacturer's instructions, or other corrective issues must be considered and carried out.

7.2.6 After tuning is complete, the autotune reports are printed and the hard copies are placed in that instrument's autotune record book in the MS laboratory.

7.3 Calibration of the GC/MS system.

7.3.1 Before analyzing a sample set on a new column, a shortened column, or after the instrument has been vented for cleaning or maintenance, calibration runs are performed with one or more Calibration Standards, under the same conditions used to analyze the field samples.

7.3.2 All ions (quantification and qualifier) are entered into windows in the acquisition method. For the GC/MS, the identification window for each analyte is set at the RT ± 0.2 min.

7.3.3 A calibration curve for each analyte will be constructed with a minimum of 5 calibration standards that will encompass the calibration range. Reference SOP-6.501(BDE Solutions) for calibration curve information.

7.3.3.3 The internal standard is dibromobiphenyl and is present in samples and standards at a concentration of 100 ng/ml.

7.3.4 The calibration curve will be generated using the theoretical analyte concentration vs the relative area (analyte area/IS area). The calibration curve may be forced through the origin. The correlation coefficient (r^2) of the curves should be ≥0.98. The % relative error (%RE) for recalculation of each calibration standard against the curve must be <25%, except for the lowest level standard, which must have a relative error <30%. If the correlation coefficient of any analyte is less than 0.98, or the %RE exceeds tolerance, then the calibration curve can be fit to a second order equation, the top calibration point can be eliminated (if there are no samples at this level), and/or the GC/MS system is

checked to determine the sources for this variation. Corrective actions for the instrument (i.e., clean source) will be taken and the sample set will be reanalyzed.

7.4 Analysis Sequence:

7.4.1 A solvent blank is analyzed first to verify that the GC/MS system is clean of carry-over or artifacts. The acceptance criterion is an analyte quantification ion area that is 2X lower than the area of the lowest level standard in the previous set.

7.4.2 One to three standards are analyzed, followed by up to 5 sample extracts (some of which may be QC sample extracts).

7.4.3 A second calibration standard is analyzed.

7.4.4 Steps 7.4.2 and 7.4.3 are repeated until all samples have been analyzed.

7.5 Data processing involves: (1) generating a calibration curve for each target analyte and SRS from the results of the standard analyses, (2) calculating the concentrations of target analytes in the sample extracts and in standards with calibration curves using HP ChemStation software, and (3) manually reviewing each data file to ensure that the identification and integration of quantified target peaks are correct.

7.6 Analyte ID will be based on the following criteria: correct RT ± 0.02 min, using as a guide the RT of the two standards that bracket the sample in the GC/MS run order; correct ratio of quantification (quant) ion area to first qualifier (qual) ion area ± 20%; and co-maximizing peak shapes for the target ion and first qualifier ion. If the relative intensity of the first qual ion (with respect to the quant ion area) is lower than the acceptable range, then the ID cannot be confirmed; if the relative intensity of the first qual ion is higher than the acceptable range, then the ID may be confirmed using the second qualifier ion.

7.7 Calculations

The instrument software will calculate ng/mL of the analytes and SRS in the sample based on the appropriate calibration curve. A quantitation report will be generated for each sample or standard which will include these concentrations.

8.0 **Records**

8.1 All operations, maintenance, and daily tune are stored in each instrument's logbook.

8.2 All analytical results are logged in specific study folders.

8.3 Hardcopy output of QUAN reports will be generated after the qualified analyst reviews the data. For each analysis set, one file folder will be used to hold/archive the hardcopy output of QUAN reports (samples and standards), the calibration curve, copy of the analytical method, and analytical sequence. The QUAN report lists the file name and sample name together with the calculated concentrations.

8.4 All data files are stored on disks or tapes for permanent record. The disks or tapes are stored permanently in the GC/MS laboratory as part of the GC/MS laboratory records.

8.5 Final calculations of the data are performed and/or recorded in the study database.

8.6 A separate data record will be prepared for each sample analysis as part of the electronic data file submitted to the database. Each record must contain, at a minimum, the following information:

8.6.1 The sample ID code.
8.6.2 The sample analysis date.
8.6.3 A code to indicate whether this is a reanalysis for a diluted sample extract.
8.6.4 A code to indicate the overall acceptability of the analysis result.
8.6.5 A code to indicate the type of sample (sample, LRB, LFB, etc).
8.6.6 The analysis result for the surrogate standard(s).
8.6.7 The percent recovery result for the surrogate standard.
8.6.8 The analysis result for the target analytes as analyzed in the extract.

9.0 **Quality Control and Quality Assurance**

9.1 The absolute response levels for the internal standard must be recorded for each analysis. If IS areas decrease throughout a sample set, or if a difference is observed in the area of the IS in samples and in standards, but the SRS recoveries in samples remain within the acceptance range, then no action will be taken. If IS areas decrease or if a difference is observed in the area of the IS in samples and in standards, and the SRS recoveries in samples do not remain within the acceptance range, then corrective action will be taken. These actions will include: cleaning the GC/MS injector, liner, and/or ion source, and removing the first meter of the column, and reanalyzing the sample set.

9.2 Samples will be re-analyzed when the calibration curve data cannot be fit to either a first or second order equation with fit parameter r^2>0.98 or when the recalculation of the standards against the curve does not meet the tolerances set in section 7.3.5. Corrective action, as listed in Section 9.1 will be undertaken before samples are reanalyzed.

9.3 Surrogate recovery values of 70 - 130% in the actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than the minimum goal the data will be flagged. For recoveries greater than the maximum goal, the concentration of the surrogate spiking solution will be checked against a calibration curve to determine whether inadvertent solvent loss has resulted in higher spike levels.

10.0 **Extract Storage**

Extracts are stored protected from light at -20°C except during analysis. Holding times have not been established for sample extracts.

Table 1. Analyte List

Analyte Group	Analyte	Retention Time, min	Primary Ion	Secondary Ion	Ion Ratios
BDEs	BDE-47	6.16	79	81	100, 97
	BDE-100	6.68	79	81	100, 97
	BDE-99	6.81	79	81	100, 100
	BDE-154	7.21	79	81	100, 100
	BDE-153	7.40	79	81	100, 100
	BDE-183	7.99	79	81	100, 100
	BDE-181	8.38	79	81	100, 100
	BDE-190	8.43	79	81	100, 100
	BDE-209	14.32	484.6	486.6	100, 100
Internal Standard	Dibromobiphenyl	4.69	79	81	100, 100
Surrogate Standards	$^{13}C_{12}$-BDE-126	7.11	79	81	100, 100
	$^{13}C_{12}$-BDE-209	14.34	494.6	496.6	100, 50

The first ion listed is the target ion, which is used for quantitation. The secondary ion is used as the qualifier ion to confirm the identification of the analyte.

Extraction, Cleaning, and Method Performance Procedures for PBDEs in Dust

Number: MDAB-081.0

1.0 Method Summary

This method describes procedures for the extraction and cleanup of polybrominated diphenyl ethers (PBDEs) in house dust and also includes instructions for evaluating the method performance. House dust samples are extracted using Accelerated Solvent Extraction (ASE). The extraction solvent is a 80:20 mixture of hexane:methylene chloriden. The extracts are then concentrated under a nitrogen flow and cleaned up using solid phase extraction (SPE). The extraction uses two modified silica SPEs in tandem. The cleaned-up extracts are concentrated down to 1ml, to which is added 100 µl of internal standard. Method performance is evaluated by the use of a surrogate dust which is spiked with known concentrations of BDEs and taken through the extraction and cleanup steps. The samples are analyzed by gas chromatography-mass spectrometry (GC/MS) in the negative chemical ionization (NCI) mode.

2.0 Scope and Application

This method is to be used for PBDEs in house dust only. The major sources of BDEs which become incorporated in house dust are thought to be consumer electronics, textiles, carpets, and furniture. It is assumed that the dust sample has been sieved to an appropriate size. The BDE congeners that are included for analysis in this SOP are shown in Table 1. PBDEs found in house dust have been implicated as a cause of various human health outcomes, including neurotoxicity and endocrine disruption.

3.0 Personnel qualifications

The person should have training in the use of basic research laboratory techniques and tools. The person should have minimum of a BS degree in chemistry with at least one course in analytical chemistry. This method assumes that the user is experienced with GC/MS/NCI. The user should also have experience with the necessary sample preparation tools, including:

a. analytical balances,
b. Accelerated Solvent Extractor (ASE) system,
c. TurboVap system,
d. VAC ELUT SPS 24 systems.

All pertinent activities must be recorded in a laboratory notebook.
All users must read the entire SOP before beginning any of the procedures and ask questions if any of the instructions are unclear.

4.0 Health and Safety

Before working in the laboratory, the person must complete EPA health and safety training. Standard laboratory protective clothing, including laboratory coats, safety glasses and/or safety shields, and gloves is required to be worn at all times during chemical operations in accordance with the laboratory Health and Safety Research Protocol. Consult the EPA Chemical Hygiene Plan located on the Safety, Health and Environmental Management (SHEM) website for details on the required protective equipment.

TABLE 1. Name and Congener number for BDEs covered by this SOP. The two surrogates are also shown.

BDE name	BDE number
2,2',4,4'-Tetrabromodiphenyl ether	BDE 47
2,2',4,4',6-Pentabromodiphenyl ether	BDE 100
2,2',4,4',5-Pentabromodiphenyl ether	BDE 99
2,3',4,4',5-Pentabromodiphenyl ether	BDE 118
2,2',4,4',5,6'-Pentabromodiphenyl ether	BDE 154
2,2',4,4',5,5'-Pentabromodiphenyl ether	BDE 153
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE 183
2,3,3',4,4',5,6-Heptabromodiphenyl ether	BDE 190
2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	BDE 197
2,2',3,4,4',5,5',6-Octabromodiphenyl ether	BDE 203
2,3,3',4,4',5,5',6-Octabromodiphenyl ether	BDE 205
2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether	BDE 206
2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl ether	BDE 207
Decabromodiphenyl ether	BDE 209
2,2',3,4,5-Pentachloro[$^{13}C_{12}$]diphenyl ether	MCDE 86L [1]
2,2',3,4',4',5,6-Heptabromodiphenyl ether	BDE 181 [2]

[1]Surrogate for BDEs 47, 100, 99, 118, 154, 153, and 183.
[2]Surrogate for BDEs 190, 197, 203, 205, 207, 206, and 209.

See SOP MDAB-079.0 for the source, purity and other pertinent facts on these chemicals.

5.0 Definitions, Acronyms, and Abbreviations

100 % recovery standard – The reference matrix is taken through the complete extraction and cleanup process , after which the internal standard, surrogate recovery standard and a known amount of a BDE standard solution are added prior to analysis.

ASE – Accelerated Solvent Extraction. Trade name for Pressurized Fluid Extraction

ChemStation© -- data processing software inherent to the GC/MS system.

DE – Diatomaceous Earth

Detection limit—the minimum level at which an analyte can be reliably detected based on the analysis of calibration standards prepared in pure solvent

GC − gas chromatography

Internal standard – Compounds added after cleanup and before GC injection for quantitation purposes.

MS − mass spectrometry

NCI− negative chemical ionization

.

PBDE (or BDE) – Polybrominated diphenyl ethers

Quantitation limit − The lowest concentration of an analyte in a sample that can be determined with

acceptable precision and accuracy under the stated operational conditions of the methods.

R^2 value—residual sum of squares

Reference matrix (Blank matrix) – material free of BDEs used to simulate the presence of dust.

Stock standard − the BDE standards that come from the supplier and are used to prepare calibration standards.

SPE – Solid Phase Extraction

Surrogate recovery standard (SRS) − Compounds added to the sample or blank before the extraction and cleanup process to monitor the recovery efficiency.

6.0 Equipment and Materials

- House dust
- Digital microbalance, readable to 0.1 mg.
- Disposable aluminum weighing dish, 50 ml capacity, or equivalent weighing container
- Stainless steel spatula
- Ottawa sand, 20-30 mesh
- Aluminum foil
- Dionex® ASE 200 system
- ASE 11 ml extraction cells
- ASE 60 mL amber collection vials
- Paper filter for ASE cell, purchased from Dionnex
- Vacuum oven operated at room temp, Precision® Model 19.
- Solid phase extraction (SPE) cartridges (Supelco, Supleclean® LC-Si, 3ml, or equivalent)
- Alumina, (Sigma® type WN-3, or equivalent)
- Acid silica column, prepared by adding 50%(v/v) sulfuric acid to a 3 ml silica SPE
- Pyrex® glass wool fiber
- Culture tubes 16 x 100, 13 x 100 and 12 x 75 mm
- Centrifuge tubes with pennyhead stopper- 5 mL (13 x 117 mm)
- TurboVap LV system (modified, see Appendix A)
- VAC ELUT SPS 24 SPE cleanup system
- Agilent GC/ MS system, Model 6890
- Hexane, 99.97%, OmniSolv®
- Methylene Chloride (MeCl), 99.9+ %, Burdick & Jackson®,
- Laboratory notebook
- Ink pen
- Florinated-bromodiphenyl ether (F-BDE) internal standards (5000ng/mL), F-BDE 69, F-BDE 160, F-BDE 208. F-BDE stock solutions, ≥ 98% purity, 50 µg/ml in isooctane, Cambridge Isotope Laboratories.
- Recovery internal standard (5000ng/mL) – MCDE 86L, BDE 181. MCDE 86L stock solution, ≥ 98 % purity, 50 µg/ml in nonane, Wellington Laboratories. BDE 181 stock solution, ≥ 98 % purity, 50 µg/ml in nonane, Cambridge Isotope Laboratories.
- Sulfuric acid, 95-98%, Aldrich Chemicals.
- Diatomaceous earth, acid washed, Sigma® D-5384 (DE) or equivalent
- Polybrominated diphenyl ether standards (see Table 1)
- Certified BDE standard (S-17190)-specially prepared BDE standard from a chemical supplier. The Certificate of analysis in contained in Appendix A
- SRM 2585—NIST standard reference material, Organic Contaminants in House Dust, containing select BDEs.

- N-EVAP 111 – analytical evaporator using heat and nitrogen for concentrating samples
- Conical centrifuge tube with a volume of 15 millimeters graduated in units of 0.1 millimeters.

7.0 Procedure

7.1. For this procedure, diatomaceous earth is selected as the **reference (blank) matrix**.

7.2. **Extraction**

7.2.1. Diatomaceous earth (DE) blank matrix

7.2.1.1 Line up on the work area an appropriate number of ASE 11 ml extraction cells, based on the number of blanks to be run.

7.2.1.2. Place paper filter in bottom of each ASE cell. Fill each ASE cell about 1/3 full with Ottawa sand. Add the 0.5 gram of diatomaceous earth atop the sand, such that a conical pile of DE is created. (See figure 1.) Carefully add 100 µl recovery internal standard (SRS) to the DE ensuring that the standard is absorbed into the pile and not the sand. The sand serves as a dispersing agent to improve the penetration of the dust by the solvent and as a filling agent. The sample should be absorbed into the DE to better simulate the presence of BDEs in dust.

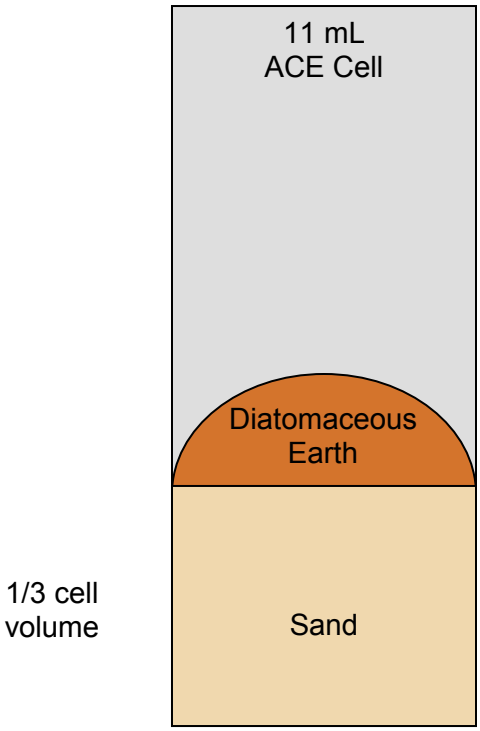


FIGURE 1. **Loading the ASE cell**

7.2.2. House dust sample

7.2.2.1. Select the dust sample for analysis. Weigh out approximately 1.0 gram of dust to three significant figures in a weight boat. Record the exact amount in the laboratory notebook.

7.2.2.2 Place paper filter in bottom of each ASE cell. Fill each ASE cell about 1/3 full with Ottawa sand. Add the 1.0 gram house dust atop the sand. Carefully add the recovery internal standard to the house dust ensuring that the standard is absorbed into the pile and not the sand.

7.2.3. Place the ASE cell containing the sample (diatomaceous earth from step 7.2.1 or house dust from step 7.2.2) in the vacuum oven and let it dry until all the hexane solvent has evaporated. Typically, about 1 hour is necessary.

7.2.4. After the sample is dry, thoroughly mix the sample and the dried dust by stirring with a small spatula. Add additional sand to completely fill the ASE cell.

7.2.5. Place end cap on the cell and hand tighten in preparation for ASE analysis.

Note: For instruction on how to use the ASE 200 system and its cells parts please refer to the ASE 200 owner manual or ASE 200 SOP (MDAB-052.0). See Figure 2 for a photograph of the ASE system.

Figure 2. ASE 200 System

7.2.6. The essential parameters for the ASE extraction are shown below.

ASE Operation

Solvent	80% hexane, 20% methylene chloride
Pressure	1500 psi
Temperature	75 °C
Heat time	5 min.
Static time	5 min
Flush volume	50%
Purge time	60 sec.
Static cycles	2

7.2.7. Extract the sample with 80/20 hexane:methylene chloride. Collect 2 extractions from each sample into ASE 60 ml amber vials.

7.2.8. Remove extracts from ASE system.

7.2.9. Combine the two extractions of the same sample into one of the vials. Rinse the empty vial three times with hexane:methylene chloride (~ 2mL), adding each rinse to the sample vial. Place the sample vials into the appropriate slots on the TurboVap LV. (See Figure 3.)

Figure 3. Turbo Vap LV with a custom made tray to hold 60 ml vials prepared by the EPA machine shop.

7.2.10. Evaporate the total sample down to approximately 2 mL of solution using the TurboVap LV (See Figure 4). Specific operation parameters include a bath temperature of 27˚ Centigrade and a nitrogen flow adjusted so that the surface of the liquid shows slight movement. The loss of some of the lower molecular weight BDEs could occur is the temperature is too high or the nitrogen flow is too great.

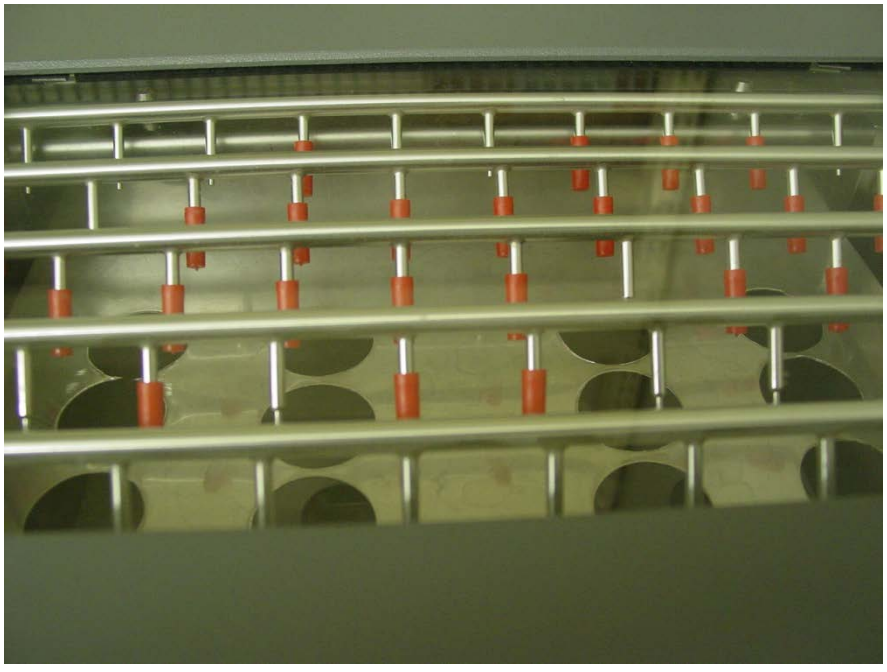


Figure 4. Turbo Vap Evaporation Nozzles.

7.3. **Clean up**

7.3.1. Two different silica SPE cartridges are used for each analysis. Modify the first silica SPE cartridges as follows: add 1 g alumina and 0.5 g Na_2SO_4, respectively, atop the silica. Add clean glass wool atop the Na_2SO_4 to hold the material in place and to trap any large particles that might be in the extract.

7.3.2. A second silica SPE is modified as follows: add 500 µl sulfuric acid solution (50:50 sulfuric acid:water) to a 3 ml silica SPE. Store covered until used so that SPE does not dry out.

7.3.3 The SPEs from 7.3.1 and 7.3.2 above are used in tandem, with the acid silica SPE being the second in the series.

7.3.4. Add the SPEs (in tandem) to the appropriate inserts on the VAC ELUT SPS 24 system. (See Figure 5.)

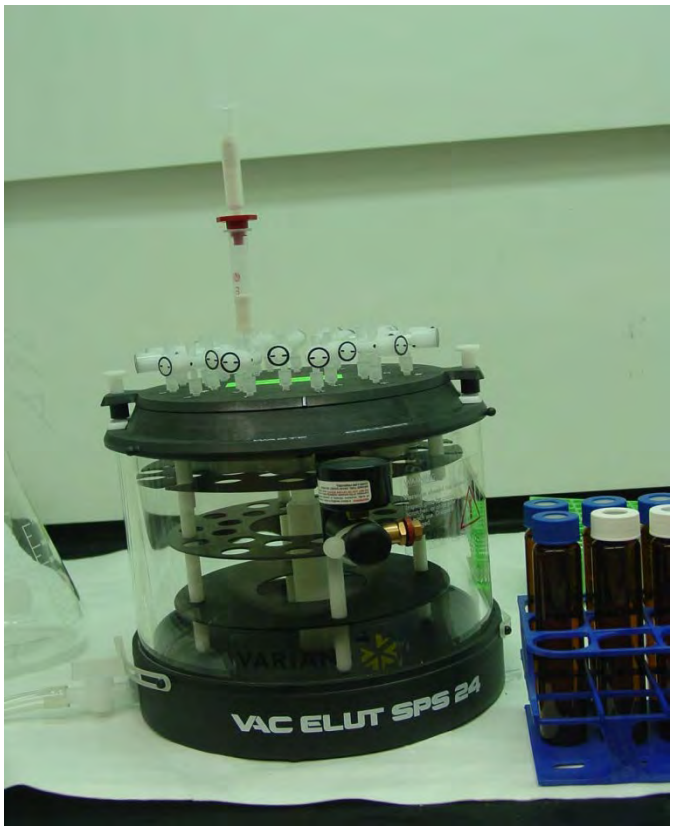


Figure 5. Vac Elut SPS 24.

7.3.5. Rinse the SPEs with a total of 6 ml hexane:methylene chloride (80:20). Incremental amounts of the hexane:methylene chloride solution passed through the SPE until all 6 ml has been used. This goes to waste.

7.3.6. The VacElut is switched to the collect position.

7.3.7. Using a disposable pipette, add the sample from the 60 ml vial (from step 7.2.10) to the SPE. Stop the flow through the SPEs before all the sample has passed through so SPEs

do not dry out.

7.3.8. Add 6 ml hexane:methylene chloride (80:20) to the 60 ml vial to recovery any residual sample. Vortex briefly. Add this to the SPE, in increments as the solution moves through the SPE. Repeat for each sample.

7.3.9. Collect the fractions from the SPE cleanup in a clean 15 ml conical centrifuge tube.

7.3.10. Repeat for each sample.

Note: For instruction on how to use the VAC ELUT SPS 24 system, please refer to the VAC ELUT SPS 24 system owner's manual.

7.4 Concentration

7.4.1. Transfer the conical centrifuge tube containing the samples (from step 7.3.9) to N EVAP 111.

7.4.2. Evaporate cleanup extractions to 1.0 ml. Avoid evaporation to dryness. Add hexane-methylene chloride mix to bring the volume to 1 ml, if necessary.

7.4.3. Add 100 µL of the 5000ng/mL Fluorinated-BDE internal standard to the 15 ml concentration vial and vortex. Transfer the sample to a GC autosampler vial before GC/MS analysis.

7.5 Method Performance Check

7.5.1. Calibration and retention time

7.5.1.1. Refer to the Owner's Manual for the GC/MS system and the SOPs, MDAB-050.0, MDAB-051.1, and MDAB-036 for general operation and maintenance of the GC/MS system.

7.5.1.2. Refer to the MDAB-079.0, Standard Operating Procedure for the Analysis of Polybrominated Diphenyl Ethers by GC/MS/NCI for more specific details of the analysis

7.5.1.3. Identification of BDEs used in this SOP.

The identification and retention time of the each compounds used in this procedure were established by analysis of a diluted sample of the individual certified materials supplied by the manufacturer. The compounds and their retention times are shown in Table 1. The retention time, target ion, and qualifier ions determined for identifying each congener are shown in Table 2.

TABLE 2. BDE Analysis Criteria

Congener	Retention time	Retention time window	Target ion	Qualifier ion	Qualifier ion #2	DL ng/ml	QL ng/ml
BDE 47	8.834	8.734-8.934	81	79	161	4	29
BDE 100	9.564	9.464-9.664	81	79	161	5	50
BDE 99	9.806	9.706-9.906	81	79	161	4	26
BDE 118	10.005	9.905-10.105	81	79	161	4	7
BDE 154	10.374	10.274-10.474	81	79	562	6	6
BDE 153	10.689	10.589-10.789	81	79	562	5	8
BDE 183	11.509	11.409-11.609	81	79	562	6	13
BDE 190	12.177	12.077-12.277	81	79	562	8	28
BDE 197	12.889	12.739-13.039	408.70	79	81	8	31
BDE 203	13.209	13.059-13.359	81	79	561.70	8	11
BDE 205	13.771	13.621-13.921	81	79	561.70	9	8
BDE 207	15.888	15.738-16.038	486.60	488.60		4	81
BDE 206	16.833	16.683-16.983	486.60	488.60	641.60	18	111
BDE 209	19.289	19.139-19.439	488.60	486.60		17	364
FBDE 69	8.398	8.298-8.498	81	79	161		
FBDE 160	10.862	10.762-10.962	81	79	502		
FBDE 208	15.435	15.285-15.585	486.60	488.60			
MCDE 86L	7.897	7.797-7.997	318	354			
BDE 181	12.049	11.949-12.149	81	79	562		
BDE 209L	19.281	19.131-19.431	494.60	496.60			

he GC/MS system is calibrated using the concentrations in Table 3.

7.5.1.4.1. Prepare the appropriate dilutions of the BDE congeners from the manufacturer's stock solution, nominally 50µg/ml. See MDAB-079.0, Standard Operating Procedure for the Analysis of Polybrominated Diphenyl Ethers by GC/MS/NCI, for details on sample preparation.

7.5.1.4.2. The ranges in Table 3 for the calibration standards were selected so as to be above and below the expected range of linearity, based on preliminary runs of the BDEs and information from the literature.

TABLE 3. Calibrations levels used for determining DL.

	Calibration levels (CL) ng/ml										
Compound	**CL 1**	**CL 2**	**CL 3**	**CL 4**	**CL 5**	**CL 6**	**CL7**	**CL8**	**CL9**	**CL10**	**CL11**
BDE 47	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 99	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 100	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 118	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 153	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 154	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 183	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 190	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 203	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 205	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 206	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 207	.008	.04	0.2	1	5	10	25	50	250	500	1000
BDE 209	.016	.08	0.4	2	10	20	50	100	500	1000	2000
Surrogates											
MCDE 86L	200	200	200	200	200	200	200	200	200	200	200
BDE 181	200	200	200	200	200	200	200	200	200	200	200
Internal standards											
FBDE 69	500	500	500	500	500	500	500	500	500	500	500
FBDE 160	500	500	500	500	500	500	500	500	500	500	500
FBDE 208	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000

7.5.1.4.3. Determination of detection limits.

The detection limit is determined using the formula below. (See Reference 3)

$$DL = \frac{3.3\,\sigma'}{S}$$

Where

S = slope of the calibration curve

σ' = standard deviation of the y-intercept

Run the standards. Transfer the analysis results to an Excel file. Create two columns. One column contains the concentrations from Table 3 ("X" values) and the second contains the instrument response in area counts ("y" values). The four lowest standards that produced an instrument response are used for the DL determination. Use the LINEST function of Excel to derive values of S and σ'. Determine the DL.

Example. DL calculation for BDE 47

X	Y
1 ng/ml	1249 counts
5 ng/ml	4317 counts
25 ng/ml	20625 counts
50 ng/ml	37366 counts

From LINEST, S= 741 and σ'= 1004

DL = 3.3*1004/741 = 4 ng/ml

See Table 2 for the detection limits calculated for each BDE.

7.5.1.5. Determination of range and linearity

The detection limit is selected as the lower limit of the range. The upper limit of the range is selected such that the R^2 value is 0.98 or greater. For all congeners the upper limit is 500 ng/ml.

7.5.1.6 Determination of Quantitation limit (QL)

Using the procedure, starting in Section 7.4, prepare 8 cells with diatomaceous earth. Cells are spiked with the BDE concentrations, Blank, 1, 5, 10, 25, 50, 250, and 500 ng/ml. Process each sample (cell) through the extraction, cleanup, concentration, and method performance steps covered previously in this SOP. The analysis results are transferred to an Excel file. One column contains the concentrations from above ("X" values) and the second contains the instrument response in ng/ml counts ("y" values). The ng/ml responses are blank and surrogate corrected. The five lowest responses that produced an instrument response are used for the QL determination. Use the LINEST function of Excel to derive values of S and σ'. Determine the QL.

.

$$QL = \frac{10\,\sigma'}{S}$$

Where

S = slope of the calibration curve

σ' = standard deviation of the y-intercept

Example. QL calculation for BDE 47

X	Y
1 ng/ml	6ng/ml
5 ng/ml	9 ng/ml
10 ng/ml	11 ng/ml
25 ng/ml	38 ng/ml

X = concentration spike onto the DE
Y = concentration found after analysis, after blank and surrogate correction
X and Y are the inputs to LINEST

From LINEST, S= 1.375 and Ơ= 3.929

QL = 10*3.929/1.375 = 29 ng/ml

Calculate the QL for each congener using its calibration curve.
See Table 2 for the quantitation limits calculated for each BDE.

.

7.5.1.6. Determination of range and linearity.
The determination is based upon the analysis of triplicate samples at the concentrations in section 7.5.1.6. For each congener, the respective QL was set as the lower range. The upper range for each was set at 500 ng/ml. Linearity was considered acceptable if the R^2 was 0.99 or greater. For all congeners, R^2 exceeded 0.99. In addition, recovery must also be considered. Recoveries for all congeners was between 70 and 125 %.

7.5.2. Sample determination

7.5.2.1 Select the dust samples to be run.

7.5.2.2. Process per procedure in starting in section 7.2.

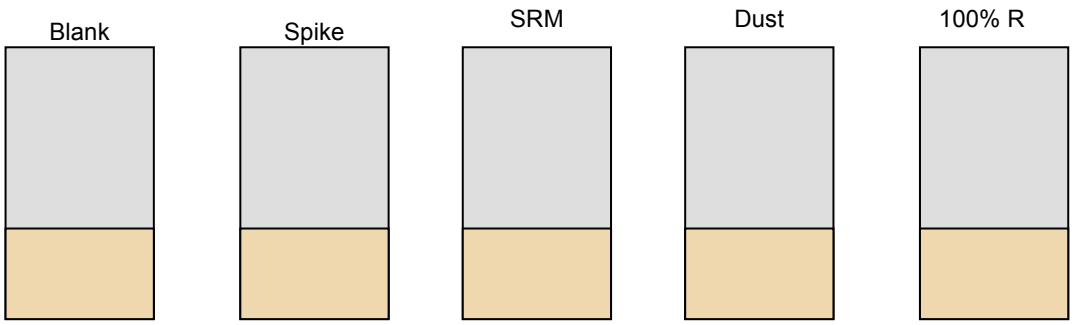
7.5.2.3. Each sample run will consist of a method blank, a method spike, and a 100% recovery spike. In addition, field QA/QC sample(s) will be run with the sample run, as appropriate. Also, as a further check, SRM 2585 will be included in the analysis, for each 25-30 samples (See Figure 6).

7.5.2.4. Label autosampler vials as appropriate.

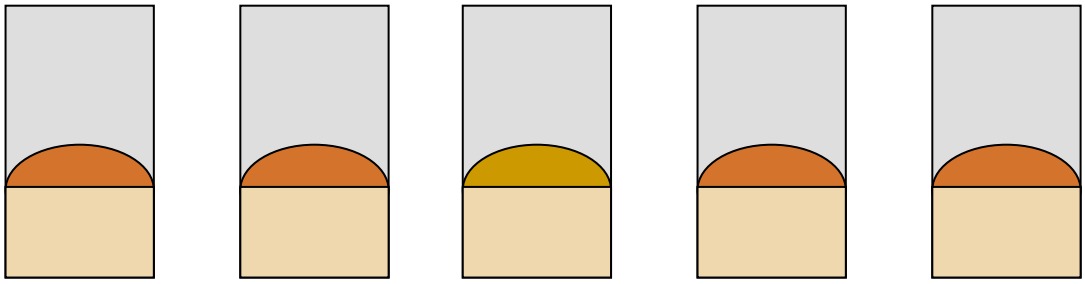
7.5.2.5. Inject 1µl sample using the splitless mode.

7.5.2.6. Process samples using the ChemStation software.

Step 1 Add Ottawa Sand to cell. Fill to 1/3



Step 2 0.5 g DE 0.5g DE 1 g SRM 1g Dust



Step 3 100 µL SRS 100 µL SRS 100 µL SRS 100 µL SRS
150 µL BDE
Spiking solution

Step 4 Dry in oven, room temperature, house vacuum.

Step 5 Mix dried media (dust or DE) thoroughly with sand.

Step 6 Add more sand. Fill cell to ~ ¾ full. Thoroughly mix with sand.

Step 7 Completely fill cell with sand.

Step 8 Cap cell.

Step 9 After extraction, cleanup, and concentration to 1 mL add 100 µL IS (FBDE). Only for the 100% R: add an additional 100 µL SRS and 150 µL BDE spiking solution.

Figure 6. Analysis

8.0 Data and records management

Maintain all the records and data generated through the procedure in a laboratory book. Laboratory books must be appropriately signed and dated daily to document all laboratory work. All analytical spectra are saved in the instrument data system. The location of the data and spectra are recorded in the laboratory notebook.

9.0 Quality Control and Quality Assurance

House dust is a complex matrix with the potential for analytical interference from a variety of dust components. The method must successfully remove potential contaminant to a low level while quantitatively retaining the analytes, especially where they are present at low levels. Analysis of method blanks are required to demonstrate that the extraction and cleanup Process removes contaminants and interferences

.

Stock standards.

. The analyst must note the Lot numbers and any expiration dates of the materials and chemicals used in the extraction and cleanup process.

Working standards.

Working solutions are prepared and used in sets of three, the BDE standards solution, the surrogate recovery standard and the internal standard. Newly prepared working solutions are calibrated against the Certified BDE Standard. This is accomplished as follows. Calibrate the GC/MS using the BDE standard. Add 100 µl each of the surrogate recovery standard and the internal standard to 1 ml of hexane. Add 5 µl of the Certified BDE Standard. Analyze this sample. The results should agree to within 15% of the certified values. Repeat this process bi-weekly. Working solutions will be discarded when they no longer meet this criteria.

10.0 Waste management

Waste chemicals and solvents should be disposed of using procedures covered in EPA's chemical hygiene plan. In accordance with EPA's commitment to reduce the the generation of waste solvents, procedures will be reviewed to see where solvent consumption can be reduced..

11.0 References

Standard Operating Procedure for the Analysis of Polybrominated Diphenyl Ethers by GC/MS/NCI, MDAB-079.0. Chemical Hygiene Plan, Office of Research and Development, USEPA, May 2005.

ICH Topic Q 2 B, Validation of Analytical Procedures:Methodology, 6 November 1996.

Analytical Detection Limit Guidance and Laboratory Guide for Determining Method Detection Limits, Wisconsin Department of Natural Resources Laboratory Certification Program, April 1996.

Accelerated Solvent Extractor Operator's Manual, Revision 3, 1997, Dionex Corporation.

AutoASE Software User's Guide, Revision 01, 1997, Dionex Corporation.

Operation and Maintenance of the Dionex Accelerated Solvent Extractor 200 (MDAB-052.0)

VAC Elut SPS 24 User's Guide, Revision 11092004, Varian Corporation, Lake Forest, CA.

Standard Operating Procedure for Analysis of Polybrominated Diphenyl Ethers by GC/MS/NCI

Prepared by Maribel Colon, U.S. EPA.

1.0 Method Summary

This SOP describes procedures to ensure the proper analysis of polybrominated diphenyl ethers (PBDEs) by gas chromatography/mass spectrometry (GC/MS) with a negative chemical ionization (NCI) source. This procedure will be used to analyze the concentration of PBDEs from polyurethane foam (PUF), surface wipes, and dust samples collected in the field. The GC/MS system consists of four principal components: (1) the injector system, (2) a capillary column, (3) the MS detector with a NCI source, and (4) the data acquisition system. Each component is selected to provide the optimum separation, selectivity, and sensitivity for the compounds under study.

In this procedure, extracted samples from different studies are introduced into the GC column by means of an auto injector system. After injection, the sample components travel through the column at a rate primarily determined by their physical properties, temperature and composition of the column, and thus elute into the detector in increasing molecular weight. As a component elutes from the column, it will undergo a negative chemical ionization, where it will achieve a soft ionization by colliding with methane ions, resulting in ions that contain the intact molecular species of the component. The abundance is recorded by the data acquisition system and is plotted against time to produce a chromatogram and an individual spectrum for each compound.

In this procedure, deactivated fused silica tubing (guard column) is attached to the front of a Durabond-5 mass spectrometer (DB-5MS) column. Guard columns are used when samples contain non-volatile residues that may contaminate a column. The non-volatile residues deposit in the guard column and not in the column. Also, guard columns are used to improve peak shapes for some types of samples, column and GC conditions. Approximately 1.0 meter of guard column was used in order to optimized the separation and detection of PBDEs, especially the highly brominated compounds like decabromodiphenyl ether (BDE-209).

2.0 Scope and Application

This method is to be used only for the anlysis of PBDEs by Agilent 6890N gas chromatography attached to a 5973 inert mass specrometer with a NCI source. Negative chemical ionization is the source of choice in detecting PBDE since it provides enhanced analyte detection in complicated matrices.

3.0 Personnel Qualifications

Personnel must have general knowledge, training, and experience in GC/MS operation. They should understand and be familiar with the instrument reference and operation manuals. The operator must know how to operate an Agilent GC/MS system and the ChemStation software. They must also have knowledge of general laboratory safety practices, including appropriate cylinder and chemical handling procedures. It is important for all users to read the entire SOP before beginning any of the procedure, and to ask questions if any of the instructions are unclear. It is assumed that the user has experience keeping a detailed laboratory notebook

4.0 Health and Safety

Standard laboratory protective clothing must be worn at all times during chemical operations in accordance with the laboratory Health and Safety Research Protocol. Safety glasses or face shields

must be worn to prevent possible eye injury from flying particles while handling samples, cutting glass, or capillary columns. Capillary columns should also be handled with caution to prevent puncture wounds. Material Safety Data Sheets (MSDS) should be reviewed for all chemicals and gases to be used with the instrument. Extreme caution is required when handling gas cylinders according to health and safety protocols. Fume hoods must be used every time when handling chemicals.

5.0. Acronyms

- GC/MS - gas chromatography/mass spectrometer
- PBDE- Polybrominated Diphenyl ether
- PUF- Polyurethane Foam
- NCI- Negative Chemical Ionization
- MSDS - Material Safety Data Sheets
- SIM - Selected Ion Monitoring
- EI - Electron Ionization
- PCI- Positive Chemical Ionization
- CI- Chemical Ionization
- MSD - Mass spectrometer detector
- IS - Internal Standard Solution
- SOP- Standard Operating Procedure
- EMAB - Exposure Measurements and Analysis Branch
- MDAB- Methods Development and Applications Branch

Table 1 Solutions:

Abbreviation	Name
Stock Spiking Solution	
BDE-47	2,2',4,4'-Tetrabromodiphenyl ether a
BDE-100	2,2',4,4',6-Pentabromodiphenyl ether a
BDE-99	2,2',4,4',5-Pentabromodiphenyl ether a
BDE-118	2,3',4,4',5-Pentabromodiphenyl ether a
BDE-154	2,2',4,4',5,6'-Hexabromodiphenyl ether a
BDE-153	2,2',4,4',5,5'-Hexabromodiphenyl ether a
BDE-183	2,2',3,4,4',5',6-Heptabromodiphenyl ether a
BDE-190	2,3,3',4,4',5,6-Heptabromodiphenyl ether a
BDE-197	2,2',3,3',4,4',6,6'-Octabromodiphenyl ether a
BDE-203	2,2',3,4,4',5,5',6-0ctabromodiphenyl ether a
BDE-205	2,3,3',4,4,,5,5',6-0ctabromodiphenyl ether a
BDE-207	2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl ether a
BDE-206	2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether a
BDE-209	Decabromodiphenyl ether a
Internal Standard Solution	
F-BDE-69	4'-fluoro-2,3',4,6-tetrabromodiphenyl ether b
F-BDE-160	4'-fluoro-2,3,3',4,5,6-hexabromodiphenyl ether b
F-BDE-208	4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether b
Standard Recovery Solution	
MCDE-86L	2,2',3,4,5-Pentachloro[$^{13}C_{12}$]Diphenyl ether c
BDE-181	2,2',3,4,4',5,6-Heptabromodiphenyl ether a
BDE-209L	Decabromodiphenyl ether ($^{13}C_{12}$, 99%) a

a Cambridge Isotope Laboratories or Accustandard (each 1 ml at 50 g/ml)
b Chiron AS (each 1 ml at 50/mL)
c Wellington Laboratories (each 1 ml at 50 g/ml)

6.0 Equipment and Materials

Eppendorf repeater pipette
Agilent Technologies 6890N Gas Chromatography/5973 inert Mass Spectrometer
Agilent Technologies 7683B Series Injector
Agilent Negative Chemical Ionization (NCI) source
Methane gas cylinder- National Welders, Grade 5.0: 99.999% pure or equivalent Helium gas cylinder- National Welders, 99.9999% research grade or equivalent Hexane- OmniSolv high purity solvent or equivalent
Vortexer
Laboratory notebook
Ink pen
Standards (Stock, Recovery and Internal)
IBM compatible computer system with Agilent ChemStation software
Printer- HP LaserJet 2300 or equivalent, double-sided capability
J&W Scientific DB-5MS column (15m x 0.25 mmiD x 0.1 µm) and guard column or equivalent
Agilent 4 mL wash vials or equivalent
Agilent 1.5 mL Amber autosampler vials or equivalent
Volumetric flasks (10, 25 and 50 mL)

7.0Procedure

7.1 Calibration

NOTE: It is important for all users to read the entire SOP before beginning any of the procedure, and to ask questions if any of the instructions are unclear.

7.1.1 Stock Spiking Solution- using individual compounds PBDE standards, combine 2.0 mL of each standard in a 50 mL volumetric flask to make up a concentration of2000 ng/mL mix. (Use 4.0 mL ofBDE-209 into the 50 mL volumetric to make up a concentration of 4000 ng/mL). Dilute in hexane.

Example: Vl*C1=V2*C2,

(2.0 mL BDE-47) (50000 ng/mL BDE-47) =(50 mL in Hexane)
(X ng/mL BDE-47) X = 2000 ng/mL BDE-47 in Hexane

7.1.2 Internal Standard Solution- three internal fluorinated-BDEs were selected: F-BDE-69, F-BDE-160 and F-BDE-208. Combine 1.0 mL of F-BDE-69, F-BDE-160 and 2.0 mL ofF-BDE-208 in a 10 mL volumetric flask to make up a concentration of 5000110 k ng/mL mix. Dilute in hexane.

7.1.3 Standard Recovery Solution- three recovery standards were selected: MCDE-86L, BDE-181 and BDE-209L. Combine 1.0 mL of each 50 µg/mL standard in a 25 mL volumetric flask to make up a concentration of 2000 ng/mL mix. Dilute in hexane.

7.1.4 From the stock spiking solution, prepare the following concentrations that will be used for system calibration: 1000, 500, 250, 100, 50 and 25 ng/mL (for BDE-209 the concentration will be double). Pipette the required amount and transfer to an amber GC vial. **NOTE:** See the Laboratory notebook for the different amounts needed to pipette from the stock spiking solution to make up the different concentrations.

7.1.5 Using a repeated pipette, add to each stock spiking solution concentration (prepared on 7.1.5) 100 µL of the internal standard solution and 100 µL of the standard recovery solution. Bring the volume up to 1.0 mL with hexane (see table below). Vortex for 10 seconds and place the vial at the GC rack for analysis.

Table 2 Calibration Standards

Concentration (ng/ml)	1000	500	250	100	50	25
	µl	µl	µl	µl	µl	µl
Stock Solution	500	250	100	50	25	125
Recovery Solution	100	100	100	100	100	100
Hexane	300	550	700	750	775	787.5
IS Solution	100	100	100	100	100	100
Total (ml)	1.0	1.0	1.0	1.0	1.0	1.0

7.1.6 Refer to the laboratory notebook for the corresponding method to be used for GC/MS analysis (see 7.3.1 for Operating Conditions). Select method according to the matrix (PUF, surface wipes, or dust) to be analyzed.

7.1.7 Place1.0 mL of hexane in an empty vial; use this as a system blank to wash away anything from the system before running any sample or calibration standards.

7.1.8 Open methane gas cylinder, select gas A on MS panel and turn knob to 40 for NCI. At the computer ChemStation select Tune system, select CI. Tune NCI once a week. (Refer to system manual for CI tuning information).

7.1.9 At the computer ChemStation, select Sequence from Instrument Control and fill in the appropriate information on sample type, vial position, sample identification, method used, etc. Save the Sequence according to the date (ex.080624.S- 08 for the year, 06 for the month and 24 for the day).

7.1.10 Use the same system for saving the data under project file you are working on (ex. BFR CI or SUPERB).

7.1.11 Run the sequence and update the calibration table. (Refer to system manual for calibration information)

7.2 Sample Collection

7.2.1 After receiving each sample collected in the field, follow appropriate SOP for extraction and cleanup procedure before analysis. (Extraction and Cleaning Procedures for Polybrominated Diphenyl Ether in Dust (in preparation), Standard Operating Procedures for Extraction of Selected Pesticides and Brominated Flame Retardants from Polyurethane Foam Disk (EMAB-SOP-020), and Standard Operating Procedure for Preparation of Cotton Surface Wipes for Pyrethroid, Organophosphate, Bisphenol A, and Brominated Flame Retardant Analysis (EMAB-115.0).

7.2.2 The final concentrated sample should be transferred to an amber vial and labeled accordingly to matrix, sample ID, personnel initials, and dates. Record this information in the laboratory notebook.

7.3 Sample Analysis

The GC/MS/NCI is used to quantify compounds and verify the formation of individual ions products according to the following procedure.

7.3.1 Operating Conditions

Refer to the operator's manual on how to set these conditions. Set the GC operating conditions as follows:

Initial oven temp: 95°C
Initial oven temp hold: 2 min
Oven temp program 1: 20 °C/min
Final oven temp 1: 280°C
Oven temp hold 1: 6 min
Oven temp program 2: 35°C/min
Final oven temp 2: 310°C
Final oven temp hold: 5 min

Set the MS conditions as follows:

Negative Chemical Ionization (NCI) operating in SIM mode
Electron Multiplier Voltage: Tune 200 V Transfer
Line: 285℃
MS Source: 150℃
MS Quad: 150℃

Set the NCI conditions as follows:
Select Reagent A for methane gas and set the flow control knob to 40.

7.3.2 Sample Analysis

7.3.2.1 Before sample analysis, verify that the MSD performs well in EI mode before changing to CI. Make sure CI ion source and GC/MSD interface tip seal are installed. And make sure the reagent gas plumbing has no air leaks. This is determined in PCI mode, checking for m/z 32 after the methane pre-tune. (Please refer to the operator manual for more information).

7.3.2.2 If ready for sample analysis, then open methane gas cylinder. Select reagent A from MS panel for methane gas (when selecting methane always use the highest purity). Make sure the flow controller readout correspond to the negative chemical ionization source set it to 40.

7.3.2.3 Tune the system (For NCI once a week).

7.3.2.4 Place 1.0 mL of hexane in an empty vial, inject into the column to wash away anything from the system before running any sample or calibration standards.

7.3.2.5 After cleaning up the system, place the calibration standards to be used and the samples. For better results, alternate a calibration level with a sample until all the standards are run.

7.3.2.6 Load method to be used for analysis. Select method according to the matrix to be analyzed.

7.3.2.7 Select Sequence from Instrument Control and fill in the appropriate information on sample type, vial position, sample identification, method used, etc. Save the Sequence according to the date (ex. 080624.S-08 for the year, 06 for the month and 24 for the day).

7.3.2.8 Use the same system for saving the data under project file you are working on (ex. BFR CI or SUPERB).

7.3.2.9 Run the sequence and update the calibration table.

7.3.3 Troubleshooting

See the troubleshooting and Maintenance sections of the Agilent 6890N GC/5973 inert MS Reference Manual.

7.3.4 System Maintenance

7.3.4.1 Change gas cylinder when the pressure gauge reads 400-500 psi.

7.3.4.2 See the operation and reference manuals for other aspects of the system maintenance, including the following:

- Column connections
- Leak checking
- MS and auto sampling system operation and maintenance
- Electronics troubleshooting and servicing
- Chromatographic troubleshooting
- Preventive maintenance
- Performance verification
- Component diagrams and parts replacements
- EI/PCI/NCI source exchange and cleaning

8.0 Data and Records Management

Maintain all the records and data generated through the procedure in a laboratory book. Keep all the NCI tune files in the Agilent maintenance record book.

Paper copies of results and spectra will be kept in folders identified by their matrix and day of analysis. EMAB staff will keep copies concerning the BDE results from PUF and surface wipes. MDAB BFR team will keep the results from dust samples. Electronic quantitative results will be stored in a stick drive or sent by email to EMAB staff so the information can be added to a database for statistical analysis.

9.0 Quality Control and Quality Assurance

Quality assurance and control issues are discussed throughout the procedure. Section 7.0, Procedure, discusses the preparation of the standard to be used for the samples and calibrations. Preparation of these standards will be documented in laboratory notebooks at EPA. Also refer to the Extraction and Cleaning Procedures for Polybrominated Diphenyl Ether in Dust (in preparation), Standard Operating Procedures for Extraction of Selected Pesticides and Brominated Flame Retardants from Polyurethane Foam Disk (EMAB-SOP-020), and Standard Operating Procedure for Preparation of Cotton Surface Wipes for Pyrethroid, Organophosphate, Bisphenol A, and Brominated Flame Retardant Analysis (EMAB-115.0) for specifics on QA/QC for the different matrixes.

10.0 Waste Management

All laboratory personnel will keep up to date and follow the recommendations by the Safety, Health and Environmental Management (SHEM) training in order to avoid exposure to lab particles and chemicals. Proper laboratory personnel protective equipment (goggles, lab coat, gloves) will be used at all time. All waste generated will be labeled and dated as waste container. Maintain an inventory of all the chemicals being disposed; a log book is located next to the fume hood. Always keep the waste on secondary containment. Keep container closed. After container is full, complete form 435e and either email to WastePickup@epa.gov, waste will be pickup by Chemical Services.

For more information on Waste Management refer to the SHEM website: http://intranet.epa.gov/nerlintrlshem/

10.0 References

- Extraction and Cleaning Procedures for Polybrominated Diphenyl Ether in Dust (in preparation)
- Standard Operating Procedures for Extraction of Selected Pesticides and Brominated Flame Retardants from Polyurethane Foam Disk (EMAB-SOP-020)
- Standard Operating Procedure for Preparation of Cotton Surface Wipes for Pyrethroid, Organophosphate, Bisphenol A, and Brominated Flame Retardant Analysis (EMAB-115.0)
- Agilent GC/MS Operator's Manual
- The 5975 inert MSD- Benefits of Enhancements in Chemical Ionization Operation, Technical Note; Sandy, Chris; et. al. Agilent Technologies.
- Safety, Health and Environmental Management (SHEM) Website: http://intranet.epa.gov/nerlintr/shemlindex.html

Standard Operating Procedure for Extracting and Preparing Air Samples for Analysis of Perfluorinated Acids

1. Scope and Applicability

This standard operating procedure (SOP) describes the method for extracting air samples for perfluorinated acids for subsequent analysis by ion chromatography tandem mass spectrometry (IC-MS/MS). This group of chemicals include perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and perfluorononanoic acid (PFNA).

2. Summary of Method

This method describes the procedures for extracting air samples for perfluorinated acids in which a quartz fiber filter (that was used to collect the air sample) is extracted. The extract is cleaned up using a solid phase extraction (SPE) cartridge and concentrated to produce 2 x 1mL aliquots. One of the aliquots is spiked with a solution containing the perfluorinated acids. Both sample aliquots are subsequently analyzed by IC-MS/MS.

3. Definitions

3.1. LRB – laboratory record book
3.2. SPE – Solid phase extraction

4. Cautions

Appropriate laboratory safety equipment such as lab coats, safety glasses, and protective gloves should be worn when performing these procedures.

5. Responsibilities

5.1. The project staff performing the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation LRB, and sending final extracts for analyses.

5.2. The Laboratory Team Leader (LTL), the Quality Assurance(QA) Officer or designee, and Task Order Leader (TOL) will oversee the sample extraction operation and ensure that standard operating procedures (SOPs) are followed by all project staff.

6. Reagents and Equipment

6.1. Reagents

6.1.1. Methanol (MeOH); distilled-in-glass
6.1.2. Ethyl acetate; distilled-in-glass
6.1.3. MilliQ water
6.1.4. Hydrochloric acid (HCl), analytical grade
6.1.5. pH 2 MilliQ water (adjusted with concentrated HCl)
6.1.6. C18 SPE cartridges (0.5 g)

6.2. Equipment

6.2.1. Serological pipettes, 10-mL
6.2.2. Pipette bulb

6.2.3. Centrifuge tubes, 15 mL capacity
6.2.4. Syringes or pipettes for spiking samples and extracts
6.2.5. Centrifuge, equipped with a rotor for the centrifuge tubes
6.2.6. Sonication bath
6.2.7. TurboVap, small volume
6.2.8. TurboVap tubes, 15-mL
6.2.9. Vortex Mixer
6.2.10. SPE vacuum manifold, equipped with vacuum pump
6.2.11. Concentrator tubes, glass, disposable
6.2.12. Nitrogen Evaporator (N-Evap)
6.2.13. Analysis vials and caps

7. Procedure

An extraction set will consist of 10-16 samples including 3 QC samples.

7.1. Extraction of Quartz Fiber Filters for Air Samples

7.1.1. Place each filter sample into a 15 mL centrifuge tube.
7.1.2. For the matrix spike samples, add 50 µL of the PF acids spiking mix (1 µg/ml mix); allow it to equilibrate for approximately 1 minute (see SOP 6.601).
7.1.3. For the solvent method blank, add 12 mL of ethyl acetate to an empty centrifuge tube.
7.1.4. Sonicate each tube in an ultrasonic bath for 15 minutes
7.1.5. Centrifuge at 2000-3000 rpm for 10 minutes.

7.2. Concentration

7.2.1. Aliquot 10 mL of liquid from centrifuge tube.
7.2.2. Concentrate to near dryness in TurboVap at 60 °C.
7.2.3. Add 1 mL methanol.
7.2.4. Vortex to resuspend extract.
7.2.5. Add 10 mL of pH 2 MilliQ water and vortex to mix.

7.3. Solid Phase Extraction and Concentration

7.3.1. Condition a 0.5 g C18 SPE cartridge with 6 mL methanol and 6 mL pH 2 MilliQ water.
7.3.2. Add the sample extract and let it run through without collecting the extract.
7.3.3. Rinse sample tube with 6 mL MilliQ water (pH ~ 7) and add to SPE cartridge.
7.3.4. Dry for 1 hour under vacuum ~ 5 psi.
7.3.5. Elute cartridge with 6 mL methanol.
7.3.6. Concentrate to just dryness and reconstitute with 2 mL of MeOH. (Use N-Evap or equivalent apparatus).
7.3.7. Divide sample equally; transferring each 1 mL aliquot to a sample vial.
7.3.8. Spike one of the aliquots with 50 µl of 1 µg/mL PF acid analyte mix and vortex (see SOP 6.601).

7.4. Store at ~ -10^{o}C or below until analyzed.

8. Records

8.1. The samples will be assigned an LRB number; the field sample ID (if applicable) will be documented with the LRB number. The QC samples generated in the laboratory will be assigned a laboratory record book number. The standard addition aliquots of each sample will have the same assigned LRB number as the un-spiked aliquot with the addition of “PS” for post

spike.

8.2. The date of extraction, the lot numbers of solvents, identification of spike solutions, and matrix spike volumes will be recorded in the LRB. The extraction activities of samples will be also recorded in the LRB. The LRB will be retained until the conclusion of the study and will be held for one year after completion of the study.

9. **Quality Control and Quality Assurance**

9.1. Three types of QC samples will be processed with the field samples. The QC samples are laboratory method blank, duplicate sample aliquot, and matrix spiked sample aliquot. The laboratory method blank is to verify that minimal contamination occurs through sample preparation in the laboratory. The duplicate and matrix spiked samples are used for assessing the overall method precision and the accuracy, respectively.

9.2. If significant target analyte levels (>0.5 ng/mL) are found in the laboratory blanks, the source of contamination must be identified and more laboratory blanks and storage blanks will be analyzed.

Standard Operating Procedure for Determination of Perfluorinated Acids in Sample Extracts by Ion Chromatography Tandem Mass Spectrometry

1.0 Scope and Applicability

This standard operating procedure (SOP) describes the method for analyzing the perfluorinated acids using an ion chromatography tandem mass spectrometry (IC/MS/MS) method.

2.0 Summary of Method

The method for analyzing sample extracts for determining perfluorinated acids using IC/MS/MS is summarized in this SOP. It covers the procedures for IC/MS/MS calibration, operation, and data reduction.

3.0 Definition

3.1 Ion Chromatography (IC): is the means by which the analytes in the liquid sample are separated over time. Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate molecular ions based on their interaction with the resin of the analytical column. The analyte is eluted by the mobile phase (10% 100 mM KOH/ 90% MeOH) and passed through a suppressor. The suppressor carries out a neutralization reaction and a selective desalting process across a cation exchange membrane with the use of a regenerate (50 mM H_2SO_4). The resulting chromatogram is a collection of time-resolved peaks with minimal baseline noise and reduced matrix effects.

3.2 Tandem Mass Spectrometry (MS/MS): is the creation and detection of specific ions. In IC-MS/MS, the eluent enters the mass spectrometer and is ionized by a voltage applied to the inlet capillary. These ions are focused through the high vacuum of the spectrometer into a quadrupole mass filter for the precursor ion. The precursor ions are then bombarded with an inert gas (nitrogen or argon) to fragment the ions into product ions. They are filtered through a second quadrupole mass filter. The transmission of these ions to the detector depends on the specific combination of RF and DC voltage applied to the quadrupole rods, with only the product ions reaching the detector. The detector counts the ions and sends the information to the data processing computer.

3.3 Matrix Spike Standard (MSS): The compounds that are used for QA/QC purposes to assess the recovery efficiency obtained for the individual samples. Known amounts of the analytes are spiked into the sample prior to extraction. The matrix spikes (MSs) are quantified at the time of analysis and their recoveries indicate the probable extraction and recovery efficiencies.

3.4 Continuing Calibration Blank (CCB): a blank sample used to assess the extent of carryover

3.5 Qualifying Standard (QS): the lowest standard in which response for the quantitation ion must be at least 3/1 signal-to-noise (S/N).

4.0 Cautions

4.1 Standard laboratory protective clothing, gloves, and safety glasses are required.

4.2 The toxicity and carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references of laboratory safety and MSDS must be available for the information of the analyst.

5.0 Responsibilities

5.1 The project staff who perform the sample analysis will be responsible for obtaining sample extracts from the sample coordinator, entering relevant information in the acquisition sequence, calibrating and operating the instrument, recapping the sample vials after analysis and storing the sample extracts in the designated freezer in the laboratory.

5.2 The Battelle Task Order Leader (TOL), the QA Manager, or designees will oversee the sample analysis operations and ensure that SOPs are followed by all project staff.

6.0 Apparatus and Materials

6.1 Micromass (Waters) Quattro LC mass spectrometer

6.2 Waters 2695 Separations module

6.3 MassLynx v. 4.0 (or higher) software

6.4 Dionex AS11-HC (High capacity) analytical column (or equivalent) 9 □m packing, 2 250 mm, Catalog #: 052961

6.5 Dionex AS11-HC guard column 13 □m packing, 2 x 50

6.6 Dionex ASRS MS 2 mm Supressor, Catalog #: 063008

6.7 Sulfuric Acid (H_2SO_4)

6.8 Fixanol 0.1 M ampoule of Potassium hydroxide (KOH), Reidal-deHaen Catalog #: 38070

6.9 Deionized water (DI)

6.10 Acetonitrile (ACN), HPLC grade

6.11 Matrix Spiking Standard Solution in methanol

6.12 Polyethylene glycol solution (PEG) used for mass tuning of mass spectrometer

7.0 Procedure

7.1 IC/MS/MS Instrument Set-Up.

7.1.1 The analyst will record base analyzer gas pressures, nebulizer and desolvation gas flows, chiller temperature, etc. in the Micromass Quattro LC Operations

Logbook. Analyst will also document any routine/ non-routine maintenance in the appropriate logbook.

7.1.2 The HPLC column will be installed on the HPLC pump. The HPLC pump should be primed daily (wet-prime). The column should also be equilibrated prior to sample analysis. The equilibration time will depend upon the use of the column, with the duration decreasing with the frequency of usage.

7.2 Daily IC/MS/MS Tuning and Standardization.

7.2.1 The mass calibration of the MS/MS system will be performed daily, following the manufacturer's guidelines, to verify that acceptable performance criteria are achieved. Maximum standard deviation of matched peaks should be no greater than 0.20 Da.

7.2.2 To tune the MS/MS, a reference solution of PEG is introduced into the ESI inlet using a syringe drive. The analyst should verify that the instrumental parameters (e.g., capillary voltage, resolution, etc.) are optimal for observing PEG fragments. If the instrument fails to tune under autotune conditions (which matches the observed peaks to those of a stored PEG reference file), then the analyst must take the appropriate corrective action.

7.2.3 After tuning is complete, the analyst will save the new calibration with the date (e.g., “26JAN04.cal”) and place the output of the Instrument Calibration Report in the Micromass Quattro Calibration logbook in the LC/MS laboratory.

7.3 External Standard Calibration of the LC/MS System.

7.3.1 The standards will be analyzed in the multiple reaction monitoring (MRM) mode. An acquisition method is established and will be used for all samples and standard solutions. Two ions are monitored for each analyte. Quantification will be performed using the peak area of the most abundant ion, with the other ion used for confirmation.

7.3.2 Typically, 7-point calibration curves will be constructed with calibration standards at 150, 100, 50, 10, 2, 0.5, and 0.2 ng/ml. These calibration curves will be generated for each sample set. The calibration standards will be interspersed throughout the sequence to capture the change of sensitivity of the MS system over the course of the sequence. The analyst may edit these calibration curves to best fit the data.

7.3.3 Following the calibration standards, a CCB will be immediately analyzed to determine extent of carryover. The CCB should be less than 0.5 ng/ml.

7.3.4 After data acquisition, analyst will manually check all peak integration prior to importing data to Excel for additional calculations.

7.4 Sample Extract Analysis

7.4.1 Separation of the analytes in achieved by injecting 50 µl of sample extract on the analytical column (Dionex AS11-HC) equilibrated at 30 ^{o}C. The eluent, or mobile phase, is 10% 100 mM KOH in deionized water / 90% MeOH (HPLC grade purity), flowing isocratically at 0.4 L/ min for 6 minutes. A Dionex AS11-HC guard column is used to preserve the life of the analytical column. Columns should be

changed or cleaned when the analyst notices non-optimal peak shapes, increased back pressure, etc.

7.4.2 The eluent is passed through a Dionex ASRS MS 2 mm Supressor using a 50 mM H_2SO_4 regenerate flowing between 5 – 10 mL/min.

7.4.3 The mass spectrometer settings necessary for the for ionization and detection of these analytes are given in Table 1 and Table 2, the general settings and the monitored mass to charge ratios respectively.

7.4.4 If the analyst finds that the response for the Qualifying Standard (0.5 ng/mL) is less than 3/1 signal-to-noise (S/N), the analyst must take the appropriate corrective action (e.g., cleaning ion source, remaking standard solution, remaking mobile phase).

7.5 Data processing involves: (1) generating a calibration curve for each target analyte from the results of the calibration standard analyses, (2) calculating the concentrations of target analytes in the sample extracts and in standards with calibration curves using MassLynx software, and (3) manually reviewing each peak integration to ensure that the identified and quantified target peak areas are properly integrated.

7.6 Calculation

7.6.1 The analyte concentration in sample is determined using a linearly regressed curve. The curve is weighted to a 1/X fitting to reduce the relative error of the lower concentration points. The point of origin will be forced through the origin.

7.6.2 The MassLynx software will process these calculations and generate a compound output report.

7.6.3 The analyst will import the electronic data from MassLynx into Excel for further calculations.

7.6.4 At the end of the extraction process 2 x 1 mL aliquots of samples extracts are aliquoted into analysis vials. One is post spiked with 50 µL of 1 µg/mL analyte mix. Below is the calculation used to quantify the estimated true concentration (ng/mL) of the non-spiked sample extract.

$$estimated\ true\ conc = \frac{spike\ addition\ conc, ng/mL \times measured\ unspiked\ conc, ng/mL}{measured\ spiked\ conc, ng/mL - measured\ unspiked\ conc, ng/mL}$$

8.0 Records

8.1 All operations, maintenance, and performance calibration data are stored in each instrument's logbook.

8.2 All analytical results are logged in specific study folders.

8.3 Hardcopy output and electronic copy of sample output reports will be generated after the data are reviewed by the qualified analyst. For each analysis set, one file folder will be used to hold/archive the hardcopy output of sample output reports (samples and standards), and the calibration curve. The sample output report lists the file name and sample name together with the calculated concentration. These hardcopy files are kept in the individual study folder for reference and comparison of instrument performance until the end of the program.

8.4 All data files are stored on ZIP disks or compact disc (CD) for permanent record. The disks are stored permanently in the LC/MS laboratory as part of the LC/MS laboratory records.

8.5 Final calculations of the data are performed in Excel spreadsheets and stored on removable disks for the study.

8.6 A separate data record will be prepared for each sample analysis as part of the electronic data file submitted to the database. Each record must contain, at a minimum, the following information:

8.6.1 The sample ID code.
8.6.2 The sample analysis date.
8.6.3 A code to indicate whether this is a reanalysis for a diluted sample extracts
8.6.4 A code to indicate the overall acceptability of the analysis result.
8.6.5 A code to indicate the type of sample (SMB, DS1, DS2, etc).
8.6.8 The analysis result for the target analytes as analyzed in the extract.

9.0 Quality Control and Quality Assurance

9.1 A laboratory method blank will be extracted together with the field samples. The laboratory method blank analyses are performed to verify that minimal contamination occurs through sample preparation.

9.2 Recoveries of the matrix spike sample of 50-150% will be deemed acceptable. For recoveries less than 50% or greater than 150%, the reported data will be flagged.

9.3 Percent relative difference of duplicate aliquots of samples within 20% will be deemed acceptable.

9.4 Samples will be re-analyzed when the calibration curve data cannot be fit to a first order equation with fit parameter r^2>0.95. Corrective action, as listed in Section 7.4.4 will be undertaken before samples are reanalyzed

9.5 If significant target analyte levels (> 0.5 ng/mL) are found in the laboratory blanks, the source of contamination must be identified and corrected.

10.0 Extract Storage

Extracts are stored protected from light at -20°C except during analysis. Holding times have not been established for sample extracts.

10.0 Reference

10.1 MassLynx NT Users Guide, Version 4.0, June 2004

10.2 Micromass (Waters) Quattro LC User's Guide, Issue 2

10.3 MassLynx NT Guide to Data Acquisition, Version 4.0, June 2004

Table 1 General setting for ionization source and quadrupole

Source

Capillary	3.5
Cone Voltage	See Table 2
Extractor	2
RF Lens	0.02
Source Block Temperature	120 C
Desolvation Temperature	400 C

Quadrupole and Analyzer	
Ion Mode	Negative
LM Resolution 1	15.0
HM Resolution 1	14.0
I Energy 1	0.8
Entrance	1
Collision Energy	See Table 2
Exit	1
LM Resolution 2	14.0
HM Resolution 2	14.0
I Energy 2	8.0
Multiplier	700

Table 2 Settings for Monitored Mass / Charge ratios

Analyte Group	Analyte	Precursor Ion	Cone Voltage	Product Ions	Collision Energy
Perfluorinated acids	Perfluorooctanoic acid (PFOA)	413	15	169	17
				369	10
	Perfluorooctane sulfonic acid (PFOS)	499	45	99	30
				80	40
	Perfluorononanoic acid (PFNA)	463	15	169	18
				219	15

Standard Operating Procedure for Extraction and High Performance Liquid Chromatography/ Mass Spectrometry Analysis of Perfluorinated Acids and Sulfonates from House Dust

1.0 Scope and Applicability

This standard operating procedure (SOP) describes a method for the extraction and high performance liquid chromatography/mass spectrometry (HPLC/MS) analysis of perfluorinated acids and sulfonates isolated from house dust. Note that this SOP assumes a thorough working knowledge of basic laboratory skills, reagents, and instrumentation. This document is designed to guide a competent laboratory worker in the analysis of the target compounds discussed below and it is not intended to instruct individuals on the basic aspects of analytical chemistry.

2.0 Summary of Method

This method involves the solvent extraction of 100 mg of house dust (< 150 μm diameter) via sonication followed by analysis of the resulting extract via HPLC/MS/MS operated in the negative turbo ion spray atmospheric pressure ionization (API) mode.

3.0 Definition

3.1 Extract: The sample extract that contains native target analytes and internal standards.

3.2 Internal Standard (IS): The fixed amount of compound that is added to each dust sample prior to its extraction. The ratio of the detector signal of the native analyte to the detector signal of the IS is compared to ratios obtained from calibration curves where the IS level remains fixed and the native analyte levels vary. The IS is used to correct for minor sample-to-sample differences in extraction, purification, injection volume, chromatographic behavior, and MS ionization efficiency.

3.2 Equipment: Agilent 1100 high pressure liquid chromatography system coupled with a Sciex API 3000 triple quadrupole mass spectrometer.

4.0 Cautions

Standard laboratory protective clothing, gloves, and eye covering is required when extracting the dust samples, aliquoting standard solutions into GC vials for analysis, and recapping standard solutions and sample extracts vials after analysis for storage.

5.0 Responsibilities

5.1 The project staff who perform the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation laboratory record books, and conducting the analysis of the extracts.

5.2 The Laboratory Team Leader (LTL) will oversee the sample extraction, cleanup, and analysis to ensure that this SOP is followed by all project staff.

6.0 Apparatus and Materials

6.1 Materials

Mettler-Toledo AB204-S Balance (Switzerland)
15 mL polypropylene Falcon centrifuge tube, Becton Dickinson, Franklin Lakes, NJ

Sonicator, Fisher Scientific, FS 30
Thermo IEC Centra CL2 centrifuge (Needham Heights, MA).
Phenomenex (Torrance, CA) Luna C18(2), 50 x 3.0 mm, 5 um pore size column
Agilent 1100 high pressure liquid chromatography system with autosampler (Agilent Technologies, Wilmington DE)
PE Sciex API 3000 triple quadrupole mass spectrometer (Applied Biosystems/MDS Sciex, Foster City, CA).

6.2 Reagents

Perfluorobutane sulfonic acid (PFBS) (3M Corporation, Saint Paul, MN)
Perfluorohexane sulfonic acid (PFHxS) (3M Corporation, Saint Paul, MN)
Perfluorooctane sulfonic acid (PFOS) (3M Corporation, Saint Paul, MN)
18O2-Ammonium perfluorooctane sulfonate (sulfonate IS) (Research Triangle Institute, Research Triangle Park, NC)

Perfluorooctanioic acid (PFOA, C8 acid)(Oakwood Products, West Columbia, SC)
1,2-13C2-Perfluorooctanoic acid (acid IS) (Perkin Elmer Life and Analytical Sciences, Boston MA)
Perfluorohexanoic acid (C6 acid) (Oakwood Products, West Columbia, SC)
Perfluoroheptanoic acid (C7 acid) (Oakwood Products, West Columbia, SC)
Perfluorononanoic acid (C9 acid) (Oakwood Products, West Columbia, SC)
Perfluorodecanoic acid (C10 acid) (Oakwood Products, West Columbia, SC)
Perfluroundecanoic acid (C11 acid) (Oakwood Products, West Columbia, SC)
Perfluorododecanoic acid (C12 acid) (Oakwood Products, West Columbia, SC)
Acetonitrile (HPLC grade, Fisher Scientific, Fair Lawn, NJ)

7.0 Procedure

7.1 Extraction

Prior to the removal of sample, the bottle containing the dust is rotated in the x, y, and z planes for 1 minute to assure homogeneous mixing. After rotation, approximately 100 mg of material is removed, the mass recorded to 0.1 mg using a Mettler-Toledo AB204-S balance (or equivalent) and placed in a 15 mL polypropylene centrifuge tube. To each tube 5.0 mL of acteonitrile containing 50 ng of the acid and sulfonate IS is added. Each tube is then sonicated for 30 minutes followed by centrifugation at 3500 rpm for 10 minutes using a Thermo IEC Centra CL2 centrifuge. A 250 µl aliquot of the supernatant is combined with 250 µl of 2 mmolar ammonium acetate in a clean autosampler vial and vortexed for 30 seconds prior to analysis.

7.2 HPLC/MS Analysis

Samples are analyzed using an Agilent 1100 high performance liquid chromatography system coupled with a Sciex API 3000 triple quadrupole mass spectrometer. The HPLC is equipped with a Phenomenex (Torrance, CA) Luna C18(2) 50 x 3.0 mm, 5 um pore size column. Samples are injected (10 µl) onto the column using an isocratic mobile phase consisting of 50:50 mixture of 2 mmolar ammonium acetate and acetonitrile at a flow rate of 200 µl/min. All analytes are separated and eluted over the course of a 8 minute run.

The Sciex API 3000 mass spectrometer is operated in the MS/MS mode using negative-ion TurboIonSpray ionization under the following conditions: curtain gas (N2) 9 arbitrary units (au), nebulizer gas (N2) 8 au, turbo dryer gas (zero air) 8 L/m at 350 °C, and ion spray voltage - 1500 V. Ionization and collision cell parameters are optimized for each individual analyte. The transitions monitored for each analyte are indicated in the table below.

Analyte Transition	Monitored $m/z \rightarrow m/z$
Perfluorobutane sulfonic acid (PFBS)	$299 \rightarrow 80$
Perfluorohexane sulfonic acid (PFHxS)	$399 \rightarrow 80$
Perfluorooctane sulfonic acid (PFOS)	$499 \rightarrow 80$
18O2-Ammonium perfluorooctane sulfonate (sulfonate IS)	$503 \rightarrow 84$
Perfluorooctanioic acid (PFOA, C8 acid)	$413 \rightarrow 369$
1,2-13C2-Perfluorooctanoic acid (acid IS)	$415 \rightarrow 370$
Perfluorohexanoic acid (C6 acid)	$313 \rightarrow 269$
Perfluoroheptanoic acid (C7 acid)	$363 \rightarrow 319$
Perfluorononanoic acid (C9 acid)	$463 \rightarrow 419$
Perfluorodecanoic acid (C10 acid)	$513 \rightarrow 469$
Perfluroundecanoic acid (C11 acid)	$563 \rightarrow 519$
Perfluorododecanoic acid (C12 acid	$613 \rightarrow 569$

Area counts for each analyte are determined automatically using the Analyst software provided with the API 3000. Each chromatogram is reviewed by the operator to insure proper and consistent integration, and manual correction of inappropriate integrations is performed if necessary.

7.3 Standard Curve and Calculations

Blank dust matrix is obtained from samples which have undergone preliminary analysis showing no detectable levels of analytes. A composite blank dust matrix, with physical and chemical properties that broadly represent the entire population of dust samples, is obtained by mixing equal quantities of blank dusts determined in the preliminary analysis. A standard curve is prepared by spiking a series of blank dust composite samples (~ 100 mg) with 0, 10, 25, 50, 100, 250, and 500 ng of each of the analytes. The spiked dust standards are treated exactly as the unknown dust samples discussed above with regard to extraction, concentration, and analysis. Upon analysis a standard curve is created separately for each analyte by plotting the area count ratio of the analyte to the I.S. (y-axis) versus the mass of analyte spiked into the dust (x-axis). The resulting standard curves (r^2 values >0.99) are used for calculation of analyte concentration in the unknown samples. Unknown concentrations are calculated by determining the analyte:IS ratio and calculating the mass of analyte in the sample using the standard curve. The mass of each analyte in the sample (ng) is normalized by dividing by the mass of dust extracted (mg).

7.4 Recovery

The recovery of the analytes from house dust is determined using the above methodology in the following manner. Blank dust samples are spiked with either a high (250 ng, n=5) or low (25 ng, n=5) level of each analytes and the IS. The samples are extracted, purified, and concentrated as noted above, and then the analyte:IS ratio is determined. Another set of blank house dust samples is spiked with the IS and extracted, purified, and concentrated (10 replicates) with the final concentrated extracts receiving either a high (250 ng, n= 5, added as 250 µl of a 1.0 ng/µl standard solution) or low (25 ng, n= 5, added as 250 µl of a 0.1 ng/µl standard solution) level of spiking solution. Spiking Recovery is assessed by comparing the analyte:IS ratio for the house dust spiked before extraction to the analyte:IS ratio of the solution spiked after extraction.

8.0 Records

8.1 Records of the preparation of dust samples, blanks, and matrix spikes will be retained in a LRB that is kept by the individual conducting the analysis. This LRB will record all sample preparation activities and any other data that may be used to interpret results. All samples will be recorded in the LRB by a unique sample ID (this number that combines the LRB number, LRB page number, and sequential item for each page). The date of extraction, the lot number of solvents used for extraction, and the spike level of the spike and internal standards will be recorded in the LRB.

8.2 The LRB will be retained in the laboratory (or office area) where these operations are performed until the conclusion of the study and will be archived in a secure room for three years after completion of the study.

9.0 Quality Control and Quality Assurance

9.1 As a quality control check the 25, 50, 100, and 250 ng/100 mg dust standards are analyzed each time dust extracts are analyzed. This analysis is considered acceptable if the calculated concentration is ± 20% of the expected value.

9.2 Samples (10%) are randomly chosen for duplicate analysis. A coefficient of variation for all non-zero responses of 20% is considered acceptable performance.

9.3 One laboratory method blank consisting of extraction solvent will be analyzed for every 20 samples processed. If significant analyte levels (> S/N 5) are found in the laboratory blanks, the source of contamination must be identified, corrected, and verified as being eliminated before additional analyses of unknown samples can proceed.

10.0 Reference

Not Applicable

Standard Operating Procedure for Analysis of VOC

1.0 Sorbent tubes will be thermally desorbed for analysis by gas chromatography/mass spectrometry (TD-GC/MS) using a thermodesorption auto-sampler (Model TDSA2; Gerstel), a thermodesorption oven (Model TDS3, Gerstel), and a cooled injection system (Model CIS4; Gerstel).

1.1. The cooled injection system is fitted with a Tenax-packed glass liner (P/N 013247-005-00; Gerstel).

1.2. Desorption temperature of 25 ^{o}C with a 0.5-minute delay followed by a 60 ^{o}C ramp to 250 ^{o}C and a 4-minute hold time will be used.

1.3. The cryogenic trap is held at -10 ^{o}C and then heated within 0.2 minutes to 270 ^{o}C at a rate of 12 ^{o}C/s, followed by a 3-minute hold time.

2.0 Analytes will be resolved on a GC (Series 6890Plus; Agilent Technologies) equipped with a 30 meter HP-1701 14% Cyanopropyl Phenyl Methyl column (Model 19091U-233; Agilent Technologies)

2.1. GC will run at an initial temperature of 1 ^{o}C for 0.5 minutes then ramped to 40 ^{o}C at 25 ^{o}C/min, to 115 ^{o}C at 3 ^{o}C/min and finally to 250 ^{o}C at 10 ^{o}C/min, holding for 10 minutes.

3.0 The resolved analytes will be detected using an electron impact MS system (5973; Agilent Technologies).

3.1. The MS will be operated in scan mode.

3.2. All compounds over the detection limit (< 1 to several ng) will be evaluated by library search using the NIST spectral library followed by comparison to reference standards, where available.

3.3. Multipoint calibrations will be prepared from pure standards for common indoor pollutants and used to quantify target compounds.

3.4. All pure standards and analytes will be referenced to an internal standard (~120 ng) of 1-bromo-4-fluorobenzene. Where pure standard is not available or the compound cannot be positively identified, the concentration will be estimated based on the total-ion-current responses using toluene as a surrogate standard.

Standard Operating Procedure for the Quantification of Particle Mass Collected on Teflon Filters

1.0 Each filter used for mass analysis will be weighed on two separate occasions both before deployment and after recovery

1.1. Filters will be weighed using a Sartorius SE- 2F Balance.

1.2. Filters will be weighed twice to confirm accurate weighing and reporting.

2.0 Filters will be equilibrated for a minimum of 24 hours at temperature = 21±3 °C and relative humidity= 30-40% for at least one weighing before and one weighing after sampling.

3.0 A subset of 10 laboratory standard filters will be weighed with each group of sample filters to confirm consistent operation of the balance and to quantify measurement uncertainty of each weighing event.

3.1. Measurement uncertainty of <10 µg per sample has been achieved in past studies at LBNL using 37-mm diameter Fiberfilm filters.