Glycol ethers and acetates

Uses and Sources

The compounds in this classification that were reviewed are 2-methoxy ethanol (methyl cellosolve), 2-methoxyethyl acetate (methyl cellosolve acetate), 2-ethoxy ethanol (cellosolve), 2-ethoxy ethyl acetate (cellosolve acetate) and 2-butoxy ethanol (butyl cellosolve).

These glycol ethers and their acetate derivatives are widely used as solvents in the manufacture of paints, lacquers, enamels, varnishes, stains, metal coatings and epoxy resin coatings. More than half of their production is consumed by these applications. They are also used as solvents for printing inks, leather finishes, textile dyes and pigments (Piacitelli et al., 1990). The HSDB (1990) reports their use in adhesives, nail polishes, perfumes, liquid soaps, cosmetics, dry cleaning compounds, varnish removers and liquid household products.

Table 4.19. Consumer product categories in CTCP database that emitted glycol ethers and acetates.

			umber of Produ	icts	
Product Category	2-Butoxy ethanol	2-Ethoxy ethanol	2-Ethoxy ethyl acetate	2-Methoxy ethanol	2-Methoxy ethyl acetate
Cleaning compounds ^a	35	4			
Spot/Stain removers	4	1	_	_	_
Dry cleaning fluids	_	_	_	_	-
Window/glass cleaners	3	2		_	-
Rug/upholstery cleaners	6	3		_	_
Coatings/Inks ^b	2	10	4		
Coating thinners/strippers	8	6	1	2	_
Caulks and grouts		_	1	2	-
Polishes and Waxes ^c	_	_	_	-	-
Insect sprays ^d	7			-	
Moth control products	<u>.</u>	_	-		_
Herbicides and Fungicides ^d	_	1	_	_	-
Wood preservatives	_	•	-	_	_
Medical/Personal hygiene	2	1			_
Room	_	1	_	_	_
deodorants/disinfectants		_	-		_
Lubricants/Penetrants		_			
Adhesives	1	_	_	-	-
Liquid paper	_	_	_	_	
Miscellaneous products	5		-	-	-
Engine degreasers	3		······		<u> </u>
Carburetor and choke cleaners	3		_	-	-
Car waxes and polishes	_	_	-	-	
Miscellaneous automotive ^e	5	_	_	- '	-

^aIncludes general purpose cleaners as well as drain, oven, tile and bathroom cleaners and other degreasers.

bIncludes paints, varnishes, sealants and other coatings. Inks include marking pens and similar items.

^CIncludes wood, metal and shoe-care products.

dNot all items in this category may be available to consumers. Products that were obviously industrial in nature were not

^eIncludes fuel and oil additives, cleaners products, tire-repair products and gasket removers.

The results of a search of the CTCP (1990) database for these compounds are summarized in Table 4.19. The database lists over 80 products containing 2-butoxy ethanol, the majority of which are cleaning compounds. Ethoxy ethanol is listed as an ingredient in 28 products, over half of which are coatings and inks or stripping agents. Ethoxyethyl acetate and methoxy ethanol are listed as ingredients in only ten and three products, respectively. Methoxy ethyl acetate was not present in any products in the database.

In qualitative headspace analyses, emissions of 2-butoxy ethanol have been detected from liquid wax (Knöppel and Schauenburg, 1989) and silicone caulk (Tichenor and Mason, 1988).

Concentration Data

Data on indoor concentrations of glycol ethers and acetates are very limited. The National VOC (NVOC) database (Shah and Heyerdahl, 1988) contains 14 data points for 2-butoxy ethanol. These data points were obtained with a passive sampler over a four-week period in an office and laboratory complex (C. J. Weschler, Bell Communications Research, Red Bank, NJ, personal communication). The average concentration is 0.214 ppbv; the median is 0.075 ppbv; and the lower and upper quartiles are 0.03 and 0.36 ppbv, respectively.

Sheldon et al. (1988) measured concentrations of VOC in three newly constructed and three older public buildings in the U.S. Ethoxyethyl acetate was present in four of these buildings at concentrations ranging from 1.31 to 9.58 µg/m³ (0.24-1.8 ppbv).

Emissions Data

NASA Database

The results of a search of the NASA database (McDonnell Douglas Corp., 1986) for glycol ethers and acetates are summarized in Table 4.20. These data can only be considered to be qualitative since they were obtained at an elevated temperature using closed containers. Eleven materials emitted 2-butoxy ethanol, 24 emitted 2-ethoxy ethanol, 81 emitted 2-ethoxy ethyl acetate and 13 emitted 2-methoxy ethanol. Adhesives, coatings and pens/inks were the highest emitting categories for all of these compounds. No materials were found to emit 2-methoxyethyl acetate.

Building Materials

Schriever and Marutzky (1990) measured concentrations of 2-methoxy ethanol in a West German schoolroom after refinishing of a parqueted floor with a two-component polyurethane coating. The surface area of the floor was 70 m², and the room volume was 200 m³. The air exchange rate was 0.65 h⁻¹. Ten days after refinishing, the concentration was 0.22 mg/m³ (71 ppbv). After 90 days, the concentration was 0.026 mg/m³ (8.4 ppbv).

Mølhave (1982) detected emissions of ethoxyethyl acetate from one of 42 building materials tested in an environmental chamber. A loading factor of 0.25 m^2 of material per m^3 of chamber volume was used in a 1 m^3 stainless-steel chamber. The average chamber concentration for this unspecified material was 5.9 μ g/m 3 (1.1 ppbv).

Table 4.20. Summary of emissions of glycol ethers and acetates from materials in NASA database.^a

imum 8.3 	12.0 53.0	Median - -	N ^b 1 2	0.1 0.09	2-Ethoxy eth Maximum 200	Median 30	N ^b
- 3.3 -		-	1 2				3
3.3 	53.0	-	2			30	3
_			_	UUM	450	2	1.4
	_	_	0	0.07	450	Z	14
_			Ô	_	_		0
	_	_	Õ	_	0.23	•••	0
_	_	_	Õ	_	0.23	-	1
_		_	Õ	_	-	-	0
80	130.0	37	7	0.1	2000	200	0
_	0.2	_	1	0.1	2000	390	6
•	- - - - 80	250.0	20.0	250.0	250.0	2800	0

_		-Ethoxyethyl	acetate			2-Methoxy ethanol		
Category	Minimum	Maximum	Median	Np	Minimu		Median	Nb
Adhesives	0.1	900	1.1	5	1.2	30	2.1	
Coatings	0.05	1578	4.2	66	-	-	2.1)
Compounds ^c	_			0	_	_	_	0
Cosmetics	_	_		0	_		-	0
Fabrics	0.07	0.7	0.37	3	_	0.33	-	U
Foam/Plastic	0.095	0.7	_	2	_	0.55	_	1
Lubricants		_		0		_	-	0
Pens/Inks	0.49	4.3	2.4	5	1.6	960	- 20	0
Rubber	-	_		Õ	1.0	900	38	7

^aAll measurements reported as µg compound per gram product.

Two studies have measured emissions of 2-butoxy ethanol from paints. Clausen et al. (1990) investigated emissions of VOC from five water-based paints in environmental chambers under controlled conditions over a one-year period. Two of the paints emitted 2-butoxy ethanol. For one paint, the chamber concentration was near 200 mg/m³ (41 ppmv) immediately after application. The concentration decreased to a low and stable value after two days. Plehn (1990) investigated the emissions of VOC from low-emitting paints and varnishes from West Germany. Six of these products contained up to six percent by weight of 2-butoxy ethanol. Measurements made in a 17-m³ test chamber showed that concentrations of 2-butoxy ethanol decreased to less than 10 mg/m³ (2.1 ppmv) within 24 hours of application.

Summary

Data on indoor concentrations of glycol ethers and their acetate derivatives are very limited. Only a few measurements of 2-butoxy ethanol and 2-ethoxyethyl acetate in the U.S. have been reported, and these are for non-residential buildings.

bN=number of materials in category that emitted compound.

^cCaulks, resins, epoxies and misc. products.

A number of products commonly used by consumers contain glycol ethers and their acetate derivatives as solvents. The emissions data for these sources are primarily qualitative with only a few quantitative measurements of emissions from predominantly European products.

It is recommended that the glycol ethers and their acetate derivatives be included in a laboratory study of emissions and exposures resulting from the active use of expendable consumer products. Some product types that contain relatively large percent compositions of these compounds and are, therefore, suitable for investigation include architectural coatings, paint/varnish removers, inks, adhesives, household cleaners and cosmetics. The experiments should be conducted in a room-size environmental chamber using protocols that simulate typical consumer use of the products. The compounds should be given a secondary priority for study because they are in CARB Group III.

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Maleic anhydride

Uses and Sources

Maleic anhydride is used as a preservative for oils and fats. It is also used as a chemical intermediate in the production of polyester resins (HSDB, 1990). Rogozen et al. (1987) state that there are no known consumer product uses for maleic anhydride.

Concentration Data

No data on indoor concentrations of maleic anhydride were found.

Emissions Data

No data on emissions of maleic anhydride from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of maleic anhydride, and no field studies of this compound are in progress in California.

Indoor concentrations of maleic anhydride are likely to be nonexistent or very low. However, this compound is used as a chemical intermediate for polyester resins and could be released from some finished products. This possibility could be determined in a laboratory study of emissions of minor constituents from products and materials. Maleic anhydride should be given a relatively low priority for study because it is in CARB Group III and there are few probable sources.

References

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Phenol

Uses and Sources

Phenol is used as a general disinfectant and as a biocide in germicidal paints and slimicides. Its main use is as a chemical intermediate in the manufacture of a large number of other chemicals, particularly phenolic resins which are widely used in building materials (HSDB, 1990). It is also used in medicinal preparations such as throat lozenges, mouth washes and gargles, toothache drops and medicated shave creams (Syracuse Research Corp., 1989).

Krzymien (1989) investigated emissions of VOC from sprayed in place polyurethane foam insulation. One freshly sprayed and three cured foams were tested at elevated temperatures. Phenol was detected but not quantified in the off-gases of two of the foams.

Rittfeldt et al. (1984) detected phenol in the headspace vapors from vinyl floor tiles used in Sweden.

Phenol is a combustion byproduct that has been measured in mainstream cigarette smoke (Nanni et al., 1990). It is, therefore, expected to be emitted in sidestream smoke possibly at higher rates than in mainstream smoke. Phenol is also emitted by wood-burning appliances and internal-combustion engines.

Concentration Data

Very few measurements of indoor concentrations of phenol have been made. Wang (1975) quantified bioeffluents produced in a college auditorium. Samples of the influent and effluent air were collected from ventilation ducts that only handled air flow to and from the auditorium. Samples were collected on Chromosorb and analyzed by GC. The average concentrations of phenol in the effluent air were 4.6±1.9 ppbv (389 people, 85 percent male) and 4.0±0.5 ppbv (225 people, 80 percent female). The first measurement was made during a lecture, the second during an exam. The concentration of phenol in the unoccupied auditorium was 1.0±0.3 ppbv. This value was similar to that found in the influent air.

Investigators in Yugoslavia measured concentrations of phenol simultaneously inside and outside of six office buildings and, subsequently, in 18 school buildings (Kalinic *et al.*, 1987). Samples were collected over 24-hour periods in wash bottles containing 0.1 M NaOH. Phenol was then colorimetrically determined with a diazotized *p*-nitroaniline solution. For the office buildings, the average indoor concentration of $7.0\pm5.9~\mu g/m^3~(1.8\pm1.5~ppbv)$ was less than the average outdoor concentration of $51\pm43~\mu g/m^3~(13\pm11~ppbv)$. Concentrations in the air conditioned buildings were not correlated with outdoor concentrations. In the naturally ventilated buildings, indoor and outdoor concentrations were correlated, suggesting that a considerable portion of the indoor contamination may have been due to outside sources. In the school buildings, the median summer concentration of phenol was about $5~\mu g/m^3~(1.3~ppbv)$. The range was 3.4 to $77.3~\mu g/m^3~(0.88~to~20~ppbv)$. The median winter concentration was similar; the range was 2.2 to $17~\mu g/m^3~(0.57~to~4.4~ppbv)$.

Emissions Data

NASA Database

Only one material in the NASA database (McDonnell Douglas Corp., 1986), a fabric, was found to emit phenol.

Building Materials

Engström (1990) investigated emissions of VOC from 277 European building materials, including 43 floor coverings, 59 wall and ceiling coverings, 55 insulation materials, 45 textiles, 19 paints and eight other furnishings. The remaining materials were insulation products bonded with adhesive to metal plates. Emissions were measured in a 60-liter environmental chamber at a temperature of 40° C and an air exchange rate of 2 h⁻¹. The materials were at least three months old. Phenol was the second most encountered compound after formaldehyde. Only summary statistics are presented; no data are given for individual materials. Phenol was emitted by 48 of the insulations, textiles and floor and wall coverings. The median emission was $0.086 \,\mu\text{g/h}$ with a range of $0.034 \, \text{to } 2.71 \, \mu\text{g/h}$.

Combustion Sources

Phenol is formed during incomplete combustion of wood and can be emitted by wood-burning stoves and fireplaces. DeAngelis et al. (1980) measured emissions from different types of wood burned in a fireplace and in two air-tight wood-burning stoves. Volatile organic compounds where collected in the flue gas using a Source Assessment Sampling System (SASS) and a Particulate Organic Matter (POM) sampling train and analyzed by GC/FID. The investigators stated that their combustion variables (e.g., air supply and wood size) were representative of a significant portion of the source population. Fireplace emissions of phenol for seasoned oak were 0.015 g per kilogram of wood burned. Green pine released over twice this amount (0.035 g/kg). In the wood-burning stoves, seasoned oak emitted 0.085 g/kg; seasoned pine emitted 0.093 g/kg; and green pine emitted 0.19 g/kg. Some of these values are the averages of the results from both sample types (SASS and POM) while other values are from a single sample type.

Vehicle exhaust and evaporative emissions of fuel from vehicles may enter the living space of homes with attached garages. Cohen et al. (1988) found a strong correlation between indoor concentrations of six chemicals associated with gasoline and the presence of an attached garage. Phenol has been shown to be a component of vehicle exhaust (Hampton et al., 1983).

Other Sources

The rate of production of phenol by humans was calculated in the study of bioeffluents in a college auditorium discussed above (Wang, 1975). Using a mass-balance model, the average phenol emission values were estimated to be 9.5 ± 1.5 mg/person-day (389 people, 85 percent male); 3.8 ± 1.8 mg/person-day (410 people, 80 percent female); and 8.7 ± 5.3 mg/person-day (225 people, 80 percent female).

Summary

No concentration data for phenol have been reported for U.S. residences, and no field studies of this compound are in progress in California. This lack of data suggests either that investigators have not

attempted to identify phenol or that concentrations are below limits of detection for commonly employed sampling and analytical methods.

The emissions data for building materials are unusable for source modeling because they are entirely for European products and have been presented in summary form only. Emissions from other consumer product sources and environmental tobacco smoke (ETS) have not been investigated. This lack of data makes phenol a good candidate for laboratory studies of source emissions. It should be given a secondary priority ranking in these studies because it is in CARB Group III.

Emissions of phenol from building and interior finish materials could be determined in the laboratory by screening possible sources, such as products containing phenolic resins, for emissions in small-scale experiments. If potentially significant sources are identified, quantitative measurements of emission rates from these sources could be made under standardized conditions using environmental chambers.

It is recommended that phenol also be included in an environmental chamber study of emissions from expendable consumer products. These experiments should be conducted in a room-size chamber using protocols that simulate typical consumer use of products which contain phenol as a major ingredient. The predominant consumer product category which should be investigated is disinfectants.

It is further recommended that phenol be included in a laboratory study of emissions due to ETS since there are no data for phenol from this probable source.

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Propylene oxide

Uses and Sources

Propylene oxide is used as a fumigant for sterilization of packaged foods and fruit products and as an herbicide, insecticide, fungicide and soil sterilizer. It is added to dichloromethane as a stabilizer and is a component of brake fluids (HSDB, 1990). It is also used as a stabilizer in coatings (Rogozen *et al.*, 1987).

Sack and Steele (1989) re-analyzed the data from a U.S. EPA sponsored survey of 1,153 brand-name products (Westat, Inc. and Midwest Research Institute, 1987). Originally, the products were analyzed for six chlorinated solvents using a purge and trap technique with GC/MS detection. The stored chromatograms were later searched for additional compounds. The categories in which one or more products contained propylene oxide are shown in Table 4.21 with the number of products tested and the percentage that contained the compound. Table 4.22 lists the product categories which did not contain propylene oxide.

Table 4.21. Consumer product categories that contained propylene oxide (from Sack and Steele, 1989).

	No.	No. Pos./Totala
Product Category	Products	%
Spray shoe polish	13	15
Water repellent	41	2
Paint remover	124	12
Spray paint	169	9
Primer and special primer	54	4
Wood finishes	64	16
Silicone lubricant	25	4
Adhesive	62	15
Miscellaneous non-automotive	16	6
Gasket cleaners/Removers	11	27
Belt lubricants/Dressings	11	9
Tire cleaner/Tire paint	13	38

^aPercent of products in category that contained propylene oxide.

Concentration Data

The only known study of indoor concentrations of propylene oxide produced negative results. Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. Samples for very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished canisters and were analyzed by GC/MS. None of these houses had concentrations of propylene oxide in excess of the 0.13 ppbv detection limit.

Table 4.22. Consumer product categories that did not contain propylene oxide (from Sack and Steele, 1989).

B 1	No.		No.
Product Category	Products	Product Category	Products
Suede protector	8	Spray cleaner/degreaser	9
Fabric finisher	6	Electric shaver cleaner	11
Spot remover	19	Correction fluid	10
Stain remover	2	Record cleaner	18
Furniture polish	16	Record player cleaner	5
Floor Wax	12	Tape recorder cleaner	10
Wax stripper	1	VCR cleaner	8
Wood Cleaner	16	TV/computer screen cleaner	4
Deodorizer/disinfectant	7	Adhesive removers	8
Oven cleaner	8	Carburetor and choke cleaner	30
Laundry presoak	6	Engine cleaner	18
Anti-static spray	2	Automotive undercoat	6
Spray starch	4	Battery cleaners/protectors	10
Rug cleaner	11	Brake quieters/Cleaners	13
Window cleaner	5	Tire puncture sealers	1
Bathroom cleaner	5	Starting fluid spray	1
Dip metal cleaner	6	Windshield de-icer	2
Specialized cleaner	11	Door spray lubricant	3
Paint thinner	. 12	Chrome protector/wax	1
Lubricant	51	Vinyl top spray	1
Rust remover	6	Water pump lubricant	1
All purpose liquid cleaner	12	Transmission cleaner	9
Wallpaper removers/adhesive	2	Automotive sealant	5
Caulking	7	Liquid exterior car cleaner	3
Upholstery cleaner	3	Miscellaneous auto products	9

Emissions Data

Only six consumer products in the NASA database (McDonnell Douglas Corp., 1986) were found to emit propylene oxide. Four were adhesives and two were lubricants. The emissions from the adhesives ranged from 0.5 to 19 μ g propylene oxide per gram of material. The lubricants emitted 13.3 and 28.9 μ g/g. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Summary

The current data on indoor concentrations of propylene oxide are minimal. Propylene oxide is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured

for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

There are no quantitative emissions data for proplyene oxide. Propylene oxide is present in some consumer products that are used indoors. The percent composition of propylene oxide in these products is probably low since the compound is an additive used as a biocide or stabilizer. Therefore, it is recommended that propylene oxide be included in a laboratory study of emissions of minor constituents from products and materials. Because it is in CARB Group II, it should be given high priority for study. The types of products that could be investigated include architectural coatings, adhesives, lubricants and shoe polish. If significant sources are identified by preliminary screening, source emission rates could be measured under standardized conditions using environmental chambers.

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- Rogozen, M. B., Rich, H. E., Guttman, M. A. and Grosjean, D. (1987) Evaluation of potential toxic air contaminants phase I, Final Report. Contract No. 68-02-4252. California Air Resources Board, Sacramento, CA.
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Allyl chloride

Uses and Sources

Allyl chloride is used in thermosetting resins for varnishes and in plastics and adhesives. It is used in the manufacture of insecticides, pharmaceuticals and resins (HSDB, 1990).

Concentration Data

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. A total of 12 homes and eight people were monitored during this study. The homes were purposefully, not randomly, selected. Samples for allyl chloride were collected on Tenax sorbent tubes over 24-hour periods and analyzed by GC/MS. Allyl chloride was detected in 13 percent of the indoor samples. The mean concentration for 12 homes was 0.28±0.10 µg/m³ (0.090±0.032 ppbv).

Emissions Data

No data on emissions of allyl chloride from potential indoor sources were found.

Summary

The current data on indoor concentrations of allyl chloride are minimal. Allyl chloride is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

Allyl chloride is used as a chemical intermediate and may be emitted by some products that are used indoors. This could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Product types which are possible sources of allyl chloride include some varnishes, adhesives and insecticides. Allyl chloride should be given secondary priority for study because it is in CARB Group III.

References

HSDB, Hazardous Substances Database (1990) National Library of Medicine TOXNET service. Bethesda, MD.

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Benzyl chloride

Uses and Sources

Benzyl chloride is used in the manufacture of bactericides, fungicides, flavors, odorants, insecticides, lubricants, plastics, plasticizers and gasoline gum inhibitors (HSDB, 1990). Benzyl chloride is present as a contaminant in butyl benzyl phthalate, a plasticizer used in the manufacture of vinyl floor tiles. Rittfeldt et al. (1984) found benzyl chloride in different brands of butyl benzyl phthalate at concentrations ranging from 0.01 to 0.05 percent.

Concentration Data

Data for indoor concentrations of benzyl chloride are very limited. Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. A total of 12 homes and eight people were monitored during this study. The homes were purposefully, not randomly, selected. Samples for benzyl chloride were collected on Tenax sorbent tubes over 24-hour periods at a low flow rate and analyzed by GC/MS. Concentrations of benzyl chloride were below the unspecified limit of detection in all of the houses. Pleil et al. (1985) used SUMMA-polished canisters to collect air samples in the homes of co-workers. The samples were analyzed using an automated GC/FID-GC/ECD system equipped with a cyrogenic pre-concentrator. The investigators found benzyl chloride in three of the 31 samples analyzed. The average concentration in the positive samples was 6.2 ppbv with a range of 4.9 to 7.2 ppbv.

Emissions Data

Rittfeldt et al. (1984) investigated emissions of benzyl chloride from a new vinyl floor tile. The tile (360 cm²) was placed on the wall of a one-liter cylindrical chamber which was ventilated with charcoal-filtered air. The ventilation rate was varied between 0.1 and 0.7 l/min. Increasing the ventilation rate caused an increase in the emission rate (Table 4.23).

Table 4.23. Emission of benzyl chloride from vinyl floor tile (from Rittfeldt et al., 1984).

Ventilation (l/min)	Concentration $(\mu g/m^3)$	Emission Rate (μg/m ² -h)
0.10	5	0.8
0.40	3	2
0.70	1	2

Summary

The limited data that are available suggest that indoor concentrations of benzyl chloride are typically very low. However, concentrations may be elevated in houses with sources that contain butyl benzyl phthalate as a plasticizer, such as vinyl floor tiles.

Benzyl chloride is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

Emissions data for benzyl chloride are limited to a single study of vinyl floor tiles. Additional data could be obtained by including benzyl chloride in a laboratory study of emissions of minor constituents from products and materials. Products containing butyl benzyl phthalate as a plasticizer should be screened for emissions since benzyl chloride is a contaminant in this compound. Other possible sources of benzyl chloride include various biocides, lubricants and plastics. If significant sources are identified, emission rates could be measured under standardized conditions using environmental chambers. Benzyl chloride should be given secondary priority for study because it is in CARB Group III.

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Chlorobenzene

Uses and Sources

Chlorobenzene is used as a solvent in the manufacture of adhesives, paints, polishes, waxes, pharmaceuticals and natural rubber. It is also used as a tar and grease remover in degreasing operations and is occasionally used as a dry-cleaning solvent (HSDB, 1990). The CTCP (1990) database lists chlorobenzene as an ingredient in only two products: one a coating and the other an herbicide.

Sack and Steele (1989) re-analyzed the data from a U.S. EPA sponsored survey of 1,153 brand-name products (Westat, Inc. and Midwest Research Institute, 1987). Originally, the products were analyzed for six chlorinated solvents using a purge and trap technique with GC/MS detection. The stored chromatograms were later searched for additional compounds. Chlorobenzene was not found in any of these products.

Concentration Data

There are over 2,000 data points for chlorobenzene in the National VOC (NVOC) database (Shah and Heyerdahl, 1988). The average concentration is 0.041 ppbv. The median concentration is zero, indicating that the distribution is highly skewed.

The California TEAM studies were conducted in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of selected VOC in fixed-site indoor and outdoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. Samples were collected on Tenax sorbent tubes for approximately 12 hours. The sorbent tubes were thermally desorbed and analyzed by GC/MS. The fixed-site sampling devices were located in the major living area of the houses during the day and in the kitchen both during the day and at night. The over-night personal air samples were collected at the subjects' bedsides during sleeping hours, and, therefore, provide reasonable measures of VOC concentrations in indoor air. The population size for the Los Angeles study was approximately 350,000. The population size for the Contra Costa County study was approximately 90,000.

Chlorobenzene was only occasionally detected in these studies above the quantifiable limit of 0.4 $\mu g/m^3$ (0.09 ppbv). The range of percent measurable concentrations in air and breath samples was 0-13 percent in Los Angeles in 1984, 0-18 percent for Contra Costa County in 1984, and 0-10 percent in Los Angeles in 1987. Further statistical analysis of the data for chlorobenzene was not undertaken.

Data for indoor concentrations of chlorobenzene in the U.S. are available from two other studies. Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. A total of 12 homes and 8 people were monitored during this study. The homes were purposefully, not randomly, selected. Samples for chlorobenzene were collected on Tenax sorbent tubes over 24-hour periods at a low flow rate and analyzed by GC/MS. Concentrations of chlorobenzene were below the limit of detection (LOD) of 0.3 µg/m³ (0.065 ppbv) in all of the homes. Cohen et al. (1988) conducted a survey of 35 homes in the Kanawha Valley, WV. The homes were selected

based on their proximity to heavy industry. Therefore, the sample population was not representative of the entire population in the area. Passive samplers were placed both inside and outside the homes for a three-week period. Sixty-three percent of the houses had indoor concentrations of chlorobenzene above the LOD of $4.3 \, \mu g/m^3$ (0.94 ppbv). None of the outdoor samples were above the LOD. The mean indoor concentration was $16.5\pm21.9 \, \mu g/m^3$ (3.60±4.77 ppbv). The median was $5.62 \, \mu g/m^3$ (1.23 ppbv) and the maximum was $72.2 \, \mu g/m^3$ (15.7 ppbv). These concentrations are substantially higher than the concentrations in the NVOC database and those in the California studies. It is possible that the difference was due to the proximity of industry to the homes in West Virginia. However, outdoor concentrations were low, suggesting the presence of indoor sources.

Lebret et al. (1986) measured VOC concentrations in a survey of over 300 Dutch homes grouped into three age categories. Measurements were taken in 134 post World War II homes in Ede and in 89 prewar homes in Rotterdam during the winter of 1981-82. The following winter, 96 homes in Ede, less than six-years old, were sampled. The homes were selected at random from the housing registers of each city. Samples were collected on charcoal tubes over a period of 5 to 7 days. The samples were desorbed with carbon disulfide and analyzed by GC/FID. For all three groups, the median concentration of chlorobenzene was less than 0.4 μg/m³ (0.087 ppbv). The maximum concentration of 27 μg/m³ (5.9 ppbv) occurred among the group of less than 6-year old homes in Ede.

Emissions Data

NASA Database

The NASA database (McDonnell Douglas Corp., 1986) contains records for 16 materials or products that emit chlorobenzene, 14 of which are foams and plastics. The median emission of chlorobenzene for the foams and plastics was $2.2 \mu g/g$. One coating material emitted 1450 $\mu g/g$ and one rubber product emitted $2 \mu g/g$. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Building Materials

Sheldon et al. (1988) measured emission rates of VOC from materials used in the construction of a new office building in Fairfax, VA. Thirty-two materials were initially screened for emissions using a dynamic headspace technique. Some of the materials were selected for further testing in a small (12-liter) environmental chamber under controlled conditions. Most, if not all, of these materials are likely to be used in residential construction. In the headspace experiments, the emission of chlorobenzene was only detected from polystyrene foam insulation. The emission rate was $0.46 \,\mu\text{g/m}^2$ -h. The other materials did not emit detectable levels of chlorobenzene. However, when tested in the environmental chamber, two of these materials were also found to emit chlorobenzene. A vinyl cove molding had an emission rate of $1.8 \,\mu\text{g/m}^2$ -h and a black rubber molding had an emission rate of $0.31 \,\mu\text{g/m}^2$ -h. The emission rate of chlorobenzene from the polystyrene foam insulation during the chamber studies was $0.38 \,\mu\text{g/m}^2$ -h which is in good agreement with the headspace measurement.

Krzymien (1989) investigated emissions of VOC from sprayed in place polyurethane foam insulation. One freshly sprayed and three cured foams were tested. Using 4-6 gram samples, dynamic-

headspace measurements were made at 80° C with both dry and humidified air and at 40° C with humidified air. The author states that the results are only semi-quantitative, primarily because the breakthrough volumes of the analytes on the Tenax samplers were not determined. The average headspace concentration of chlorobenzene for the four samples at 80° C in dry air was 27 ± 7 mg/m³ (5.9 ±1.5 ppmv). At 80° C and 90 percent relative humidity, the emission of chlorobenzene was greater with an average concentration of 84 ± 23 μ g/m³ (18 ± 5.0 ppmv) for the four samples. The emission was significantly lower at 40° C with the concentration ranging from 0.1-2 mg/m³ (0.022-0.44 ppmv) for the four samples.

Hartwell (1986) also measured emissions of VOC from polyurethane foam insulation. Two board stock and three spray insulation samples were tested using a dynamic-headspace technique at 80° C with dry nitrogen as the carrier gas. Analysis was by GC/MS. The results for two of the spray samples and both of the board stock samples are only semi-quantitative. The emission rate of chlorobenzene from the foam samples was 0.02 and 0.01 $\mu g/cm^2$ -h, respectively. Chlorobenzene emissions from the board stock samples were 0.02 and 0.03, $\mu g/cm^2$ -h, respectively. More accurate data were generated for the third foam sample by determining the percent collection and desorption efficiencies for seven selected compounds, including chlorobenzene. For this case, the emission rate was lower, 0.0018 $\mu g/cm^2$ -h. The collection/desorption efficiency was 90 percent.

Combustion Sources

Small amounts of chlorobenzene were detected in air collected through an inverted funnel above the top burners of two of the three gas cooking ranges tested by Moschandreas et al. (1983). The concentrations of chlorobenzene in the exhaust air were less than 0.22 ppbv.

Other Sources

Volatile organic compounds can enter the substructures of houses built on contaminated soil or near leaking underground fuel tanks. However, it can be difficult to establish relationships between soilgas pollutants and indoor pollutants. Kliest *et al.* (1989) measured VOC concentrations in 97 houses in the Netherlands, 77 of which were constructed on contaminated soil. The remaining 20 houses served as references. Of the 77, only nine percent had crawl spaces that were clearly contaminated. The concentration data are assumed to be reported as $\mu g/m^3$. Chlorobenzene concentrations in the contaminated houses averaged 16.4 $\mu g/m^3$ (3.58 ppbv) in the crawl spaces and 0.2 $\mu g/m^3$ (0.044 ppbv) in the living rooms. The mean concentration in both the crawl spaces and the living rooms of the reference houses was less than 0.1 $\mu g/m^3$ (0.022 ppbv).

Summary

Data for indoor concentrations of chlorobenzene are available from field studies in the U.S. and California which used probability-based samples of homes. In general, chlorobenzene was only occasionally detected, and concentrations were very low with an average value of less than 0.05 ppbv from the NVOC database.

Chlorobenzene is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). Indoor concentrations and personal exposure will be measured

for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

The data in the NVOC database suggest that the distribution of indoor concentrations of chlorobenzene is highly skewed, perhaps because there are only a few important indoor sources of this compound. For example, chlorobenzene was not detected in over 1,000 consumer products that were surveyed for chlorinated solvents.

There are some data available on emission rates of chlorobenzene from building materials. However, the studies were too limited in scope to be of much use in models for estimating indoor concentrations. Additional data for chlorobenzene could be obtained by including it in both a laboratory study of emissions of minor constituents from products and materials and in an environmental chamber study of emissions resulting from the use of expendable consumer products. Chlorobenzene should be given secondary priority for these studies because it is in CARB Group III. Building materials including plastic moldings and polystyrene and polyurethane insulation could be screened for emissions of chlorobenzene. Emission rates for any significant sources that are identified by screening could be measured under standardized conditions using environmental chambers. If chlorobenzene is found to be a major ingredient of some consumer products, such as paints, waxes, adhesives and pharmaceuticals, then use of these products indoors is likely to result in relatively high exposure to this compound. Such exposure could be investigated by the application of representative products in a room-size environmental chamber.

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Chloroprene

Uses and Sources

The chloroprene monomer is primarily used (both alone and with comonomers) in the manufacture of neoprene rubber. Neoprene rubber is a component of a number of domestic products. The extent to which any unreacted monomer would be released from finished products is unknown. Chloroprene is also used as a component of adhesives that are used in food packaging (HSDB, 1990).

Concentration Data

No data on indoor concentrations of chloroprene were found.

Emissions Data

No data on emissions of chloroprene from potential indoor sources were found.

Summary

Chloroprene is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. Only qualitative data will be obtained for chloroprene.

Unreacted chloroprene may be released from household products containing neoprene rubber. The potential for this release could be determined in a laboratory study of emissions of minor constituents from products and materials. Chloroprene should be given secondary priority for study because it is in CARB Group III.

References

HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.

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p-Dichlorobenzene

Uses and Sources

Para-dichlorobenzene (DCB) is primarily used as a room deodorizer and for moth control. It is also used in pesticides, other agricultural chemicals, abrasives, floor waxes and floor finishes and for dye synthesis (HSDB, 1990; Life Systems, Inc., 1989). The CTCP (1990) database lists over 100 products containing DCB that are marketed as deodorants, moth repellants, or both. Most of them contain 97-100 percent DCB by weight. A few animal repellants, bacteriocides, mildewcides and fumigants are additionally listed. These also contain up to 100 percent DCB by weight.

In qualitative dynamic headspace analyses, emissions of DCB have been detected from hardwood plywood and carpeting (Montieth, et al. 1984).

The NASA database (McDonnell Douglas Corp., 1986) does not differentiate between isomers of DCB. Low-level emissions of unspecified DCB were detected from a few fabric products and one adhesive. No room deodorizers appear to have been tested.

Concentration Data

The major sources of data for indoor concentrations of DCB are the National VOC (NVOC) database, Krause et al. (1987) and the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies. All three studies are summarized in Table 4.24.

There are over 2,000 data points for DCB in the NVOC database (Shah and Heyerdahl, 1988). The average concentration is 4 ppbv, and the median concentration is 0.3 ppbv.

Krause et al. (1987) made measurements of VOC in 230 West German homes, selected at random. Passive charcoal samplers were exposed for two-week periods between June, 1985 and April, 1986. The compounds were desorbed with carbon disulfide and analyzed by GC/FID and GC/ECD. The average concentration of DCB was 22 μ g/m³ (3.7 ppbv), and the median concentration was 4.7 μ g/m³ (0.8 ppbv). These concentrations generally agree with the data from the NVOC database and the California TEAM studies.

The California TEAM studies were conducted in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of selected VOC in fixed-site indoor and outdoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. Samples were collected on Tenax sorbent tubes for approximately 12 hours. The sorbent tubes were thermally desorbed and analyzed by GC/MS. The fixed-site sampling devices were located in the major living area of the houses during the day and in the kitchen both during the day and at night. The over-night personal air samples were collected at the subjects' bedsides during sleeping hours, and, therefore, provide reasonable measures of VOC concentrations in indoor air. The population size for the Los Angeles study was approximately 350,000. The population size for the Contra Costa County study was approximately 90,000.

The concentrations of DCB were similar in both locations in the summer of 1984 with median concentrations near 0.1 ppbv. In Los Angeles, concentrations were higher in the winter than in the summer for both years. This difference was particularly noticeable in the 95th percentile concentrations, which ranged up to 47 ppbv in the winter of 1987. Generally higher concentrations in the winter could have resulted from decreased ventilation rates and greater use of room deodorizers or moth crystals.

Table 4.24. Summary statistics for concentrations of p-dichlorobenzene in ppbv (from Shah and Heyerdahl, 1988; Krause et al., 1987; Pellizzari et al., 1987; Wallace et al., 1989a).^a

				P	ercentil	es		
Study	N	Average	25	50	75	90	95	Range
NVOC	2121	4.0	0.05	0.28	0.93		-	_
Krause et al. (1987)	230	3.7	b	0.78		2.8	_	<0.17-212
<u>TEAM</u> b,c								
L.AWinter '84 Overnight Personal	112	3.4	0.21	0.43	1.22	9.02	16.7	0.005-71.8
L.ASummer '84 Overnight Personal	51	2.30	0.07	0.14	0.45	3.84	18.4	0.01-41.8
C.CSummer '84 Overnight Personal	69	1.21	0.04	0.09	0.50	1.39	6.68	0.01-25.2
L.AWinter '87								
Overnight Kitchen	42	6.05	0.23	0.39	3.09	26.6	47.1	0.05-53.4
Daytime Kitchen	46	3.92	0.11	0.23	1.02	11.4	39.2	0.01-55.3
Daytime Living Area	45	4.44	0.17	0.27	1.55	15.3	38.7	0.05-45.6
L.ASummer '87								
Overnight Personal	39	2.82	0.07	0.24	1.20	3.82	34.7	0.01-45.4
Overnight Kitchen	34	0.67	0.05	0.12	0.56	2.37	3.74	0.01-5.71
Daytime Kitchen	36	1.08	0.05	0.10	0.62	1.31	5.56	0.01-26.2
Daytime Living area	39	1.20	0.07	0.16	0.59	1.75	7.98	0.01-25.6

^aStatistic not presented in reference.

Emissions Data

Consumer Products

Wallace et al. (1989b) conducted a study of the influence of personal activities on exposure to VOC. Seven study subjects were asked to perform specific activities suspected of increasing exposure to 17 target VOC. Each subject was monitored for nine sequential time periods over three days using a personal sampling pump and Tenax sorbent tubes. The investigators associated increased exposure to DCB with the

bConverted from mass/volume units.

^cm- and p- isomers reported together.

use of solid and liquid room deodorizers. Use of a toilet-bowl deodorizer resulted in a large increase in the air concentrations and personal exposures for DCB as shown in Table 4.25.

Table 4.25. Effect of a toilet-bowl deodorizer on indoor air concentrations of, and personal exposures to, p-dichlorobenzene (from Wallace et al., 1989b).^a

			Persona	l Exposure
Time Period	Averaging Time (h)	Air Concentration (ppbv)	Person 1 (ppbv).	Person 2 (ppbv)
1	3.7	0.17	0.17	0.17
2	8.2	0.33	0.33	0.50
3b	11.6	11	1.3	7.2
4	4.0	42	40	42
5	12.0	20	50	55
6	8.6	32	37	c
7	3.5	72	71	57
8	11.5	75	78	68
9	8.5	105	75	84

^aData converted from mass/volume units.

Table 4.26 presents emissions measurements made by Tichenor et al. (1990) for moth repellant cakes. The tests were conducted in a 166-liter stainless-steel chamber. The emission rates of DCB increased with increasing chamber ventilation rate and temperature. After two of the tests, the chamber walls were carefully washed with methanol. The volume of solvent was measured and an aliquot analyzed by GC/ECD. About 160 mg of DCB were recovered after test 8 and about 23 mg were recovered after test 9. The final concentrations in the chamber for these tests were 5,300 and 1,170 mg/m³ (885 and 195 ppmv), respectively. These results demonstrated that there were significant wall losses of DCB that were related to concentrations in the chamber.

Table 4.26. Emissions of p-dichlorobenzene from moth crystal cakes (from Tichenor et al., 1990).

Test Number	Temperature (°C)	Relative Humidity (%)	Air Exchange Rate (h-1)	Emission Rate (mg/cm ² -hr)
1	23	20	0.25	1 1
2	23	20	0.50	1.1 1.4
3	23	20	1.0	1.6
4	23	50	0.25	1.2
5	23	50	1.0	1.5
6	23	50	2.0	1.8
7	35	20	0.25	4.2
8	35	50	0.25	4.0
9	35	20	1.0	5.0
10	35	50	2.0	5.9
11	35	50	0.5	4.3

bDeodorant placed in toilet bowl during this period.

^CSample lost.

Tichenor et al. (1990) developed an indoor air quality model to estimate the effects of a number of parameters on the concentrations of pollutants in indoor air. Model predictions of concentrations of DCB resulting from use of moth repellent cakes were in close agreement with actual concentrations measured in a test house when appropriate values for source emission rates, air exchange rate, in-house air movement and losses to sinks were provided. Table 4.27 shows predicted and measured concentrations of DCB in the various rooms of the test house.

Table 4.27. Comparison of measured concentrations of p-dichlorobenzene with model predictions (from Tichenor et al., 1990).

Room	Measured Concentration (ppbv) ^a	Predicted Concentration (ppbv) ^a
Closet	12	12
Corner bedroom	0.85	0.95
Master bedroom	0.65	0.67
Den	0.62	0.67

^aData converted from mass/volume units.

Building Materials

Sheldon et al. (1988) measured emission rates of VOC from 32 materials used in the construction of a new office building in Fairfax, VA. The materials were initially screened for emissions using a dynamic headspace technique. Some of the materials were selected for further testing in a small (12-liter) environmental chamber under controlled conditions. Most, if not all, of these materials are likely to be used in residential construction. The results are summarized in Table 4.28. Emissions of DCB from these materials were relatively low. No emission rate exceeded $1 \mu g/m^3$ -h.

Net specific source strengths were also estimated for the building using a simple mass-balance model and measurements of ventilation rate and indoor and outdoor concentrations of DCB (Sheldon et al., 1988). Immediately after construction, the mean specific source strength of DCB was $0.076 \,\mu g/m^3$ -h with a maximum of $0.15 \,\mu g/m^3$ -h. The building was sampled again four months after construction when it was fully occupied. At that time, the mean specific source strength was $0.8 \,\mu g/m^3$ -h, with a maximum of $1.4 \,\mu g/m^3$ -h. The increase indicated that sources were imported with the building's occupants.

Wallace et al. (1987) measured emission rates of DCB from painted sheetrock (twenty-two 1.98×1.22 m surfaces), wallpaper glued to sheetrock (twenty-two 1.98×1.22 m surfaces) and carpet glued to wood panels (twelve 1.98×1.22 m surfaces). All materials were aged for one week before emissions were measured in a 34-m³ environmental chamber. The carpet/wood assembly was the only material that emitted DCB. The emission rate was $2.5 \, \mu g/m^2$ -h. The emission rate for the combined use of cleaning agents and an insecticide on a wood panel was $26 \, \mu g/m^2$ -h.

Hartwell (1986) measured emissions of VOC from polyurethane foam insulation. Two board stock and three spray insulation samples were tested using a dynamic-headspace technique at 80° C with dry nitrogen as the carrier gas. Analysis was by GC/MS. The results were only semi-quantitative. The amount of compound present was estimated by comparing its total-ion-current area to the total-ion-current areas of chlorobenzene or n-decane standards. The emission rate of unspecified dichlorobenzene isomers for

one of the foam samples was 0.003 $\mu g/m^2$ -h. No DCB was detected from the second sample. The emission rate of DCB from one of the board stock samples was 0.004 $\mu g/m^2$ -h. Again, no DCB was detected from the second sample.

Table 4.28. Emission rates of p-dichlorobenzene from building materials in $\mu g/m^2$ -h (from Sheldon et al., 1988).

Sample	Headspace	Chamber
Particle board	0.14	0.18
Carpet adhesive	a	_
Black rubber molding	0.51	0.97
Latex paint	_	_
Linoleum tile	0.08	_
Polystyrene foam insulation	0.71	0.47
Vinyl cove molding	0.18	_
Cove adhesive	NMb	
Carpet	-	_
Vinyl edge molding	0.18	
Small diameter telephone cable	0.58	
Large diameter telephone cable	0.24	
Urethane sealant	-	
Latex paint	_	
Tar paper		
Primer/adhesive		
Latex caulk	_	
PVC pipe		
Water repellant mineral board	_	
Cement block	_	
Treated metal roofing	_	
Fiberglass insulation	_	
Duct insulation		
Exterior mineral board	_	
Interior mineral board	_	
Ceiling tile		
Red clay brick	_	
Plastic laminate		
Plastic outlet cover		
Joint compound		
Linoleum tile cement	_	

^aNo detectable emissions.

bNot measured, sample overloaded.

Combustion Sources

Small amounts of unspecified DCB were detected in air collected through an inverted funnel above the top burners of one of the three cooking ranges tested by Moschandreas *et al.* (1983). The fuel was municipal gas. The concentrations of DCB in the exhaust air were less than 0.17 ppbv.

Summary

Data for indoor concentrations of DCB in California are available. These data have been used to construct frequency distributions for indoor concentrations and personal exposures for two communities with populations of approximately 90,000 and 350,000 individuals. Median concentrations were estimated to range between 0.1 and 0.4 ppbv. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

The most significant indoor source of DCB is cakes, crystals, or pellets of nearly pure compound used as a deodorant or moth repellant. Emissions from moth crystal cakes have been well characterized in chamber studies. The measured emission rates have been used in an indoor air quality model which takes into account losses to surfaces. The ability of the model to predict concentrations of DCB was validated in a test house. If the important parameters are known, this model can be used to predict concentrations of DCB in other environments.

Because both indoor concentration and source emission data exist for DCB, further investigation of this compound should probably be given low priority.

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Epichlorohydrin

Uses and Sources

Epichlorohydrin is used as a solvent for paints, varnishes, lacquers, nail enamels and natural and synthetic resins. It is also used as an insect fumigant and sporicide (HSDB, 1990). Epichlorohydrin is manufactured primarily for use as a chemical intermediate in the production of epoxy resins and elastomers. The elastomers are used to make automotive parts, adhesives and rubber coating for fabrics. These products may contain epichlorohydrin as a trace contaminant (Rogozen et al., 1987).

Concentration Data

No data on indoor concentrations of epichlorohydrin were found.

Emissions Data

The NASA database (McDonnell Douglas Corp., 1986) provides the only data on emissions of epichlorohydrin. The emissions of epichlorohydrin from three adhesives ranged from 0.6 to 13 ng per gram of material. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Summary

There are no data on indoor concentrations of epichlorohydrin, and no field studies of this compound are in progress in California.

Data on emissions of epichlorohydrin could be obtained by including it in both a laboratory study of emissions of minor constituents from products and materials and in an environmental chamber study of emissions from expendable consumer products. It should be given a relatively low priority for these studies because it has not yet been classified as a candidate toxic air contaminant by the CARB. Product types which could be screened for possible low-level release of epichlorohydrin include adhesives and rubberized fabric coatings. Epichlorohydrin is a solvent in some architectural coatings. Use of these products indoors could result in relatively high exposure to this compound. Such exposure could be investigated by the application of representative products in a room-size environmental chamber.

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Hexachlorobenzene

Uses and Sources

Hexachlorobenzene is used in the production of synthetic rubber and as a plasticizer for polyvinyl chloride (PVC). The extent to which hexachlorobenzene is released from finished products is unknown. It is also used as a fungicide for commercial crops (HSDB, 1990).

Concentration Data

The Nonoccupational Pesticide Exposure Study (NOPES) was conducted by the U.S. EPA in the Summer of 1986 in Jacksonville, FL, and in the Spring of 1987 and the Winter of 1988 in Jacksonville and Springfield, MA (Immerman and Schaum, 1990). Measurements of selected pesticides in fixed-site indoor and outdoor air, personal air, and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. The population size for the Jacksonville study area was approximately 290,000. The population size for the Springfield study area was approximately 135,000. Samples were collected on polyurethane foam plugs using small sampling pumps. The compounds were Soxhlet extracted and concentrated. Quantitative analysis was performed by GC/ECD, and GC/MS was used for confirmation. Only six to 45 percent of the samples had detectable concentrations of hexachlorobenzene. Weighted mean concentrations for all three seasons are shown in Table 4.29. Median concentrations were reported as zero for both study areas in all seasons.

Table 4.29. Weighted mean concentrations of hexachlorobenzene in indoor and personal air (from Immerman and Schaum, 1990). All concentrations are in parts per trillion by volume and have been converted from mass/volume units. Numbers of samples are shown in parentheses.

Summer	Spring	Winter
0.11 (62)	0.03 (72)	0.03 (71)
0.08 (63)	0.03 (71)	0.03 (71)
a	0.00 (49)	0.01 (51)
	0.00 (48)	0.00 (52)
	0.11 (62) 0.08 (63)	0.11 (62) 0.03 (72) 0.08 (63) 0.03 (71) a 0.00 (49)

^aMeasurement not made during this season.

Emissions Data

No data on emissions of hexachlorobenzene from potential indoor sources were found.

Summary

The data for two U.S. communities demonstrate that indoor concentrations and personal exposure for hexachlorobenzene are very low (considerably less than a part per trillion).

Hexachlorobenzene is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990) For the second phase of the study, combined vapor- and particle-phase concentrations will be measured in a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

Hexachlorobenzene partitions between vapor and particle phases in air due to its low vapor pressure at room temperature. In general, it is difficult to measure emissions of semivolatile compounds in chamber experiments because losses to chamber surfaces and sampling lines are substantial. If additional data are needed for hexachlorobenzene, they would best be obtained by a field study.

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Methyl bromide

Uses and Sources

Methyl bromide, or bromomethane, is widely used as a biocide. It has a number of indoor applications as an insecticide, herbicide and fungicide. In the food industry, methyl bromide is used for pest control on fruits, vegetables, dairy products, nuts and grains (HSDB, 1990).

Concentration Data

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA to measure indoor concentrations and personal exposures for toxic air contaminants. Samples of very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished cannisters and were analyzed by GC/MS. None of these houses had concentrations of methyl bromide in excess of the detection limit of $0.26~\mu g/m^3~(0.067~ppbv)$

Emissions Data

No data on emissions of methyl bromide from potential indoor sources were found.

Summary

Methyl bromide is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

It is possible that a field study will not produce data that are adequate for assessing indoor exposure to methyl bromide since this exposure is expected to be directly related to the episodic use of certain biocides. Therefore, it is recommended that methyl bromide be included in an environmental chamber study of emissions from consumer products. Exposure resulting from the use of biocides could be directly determined by applying the products in a typical manner in a room-size chamber. Methyl bromide should be given a secondary priority for study because it is in CARB Group III.

References

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Methyl chloroform

Uses and Sources

Methyl chloroform, or 1,1,1-trichloroethane (TCE), is widely used as a solvent for natural and synthetic resins, oils, waxes, adhesives, coatings and inks. It is used as a dry cleaning solvent and in many general purpose cleaners. It is also found in aerosol sprays, in which it acts as a vapor-pressure depressant and as a solvent/carrier for the active ingredient (HSDB, 1990).

Table 4.30. Percent weight composition of 1,1,1-trichloroethane in consumer product categories (from Westat, Inc. and Midwest Research Institute, 1987).

Product Category	Brands Tested	Positive/Total ^a	Composition Range % (w/w)
Non-automotive Products			
Drain cleaners	1	100	97.8
Specialized aerosol cleaners	12	50	0.2-83.8
Spot removers	18	50	10.5-110.8
General purpose spray cleaners	9	44	0.1-71.4
General purpose liquid cleaners	12	33	72.7-126.7
Wood cleaners	13	15	12.3-20.4
Oven cleaners	8	13	97
VCR cleaners	7	14	97.8
Tape recorder cleaners	15	33	0.2-101.5
Electric shaver cleaners	12	17	2.5-20.3
Adhesive removers	9	22	0.1-95.0
Paint removers/strippers	109	6	0.1-25.7
Primers/special Primers	61	3	1.2-61.8
Wood stains/varnishes/finishes	63	9	0.1-21.4
Suede protectors	8	88	4.8-118.5
Water repellents	32	50	0.2-116.2
Spray shoe polishes	11	45	11.4-62.3
Fabric finishes	5	40	77.9-85.1
Silicone lubricants	28	54	0.2-91.1
Lubricants	53	32	0.1-104.5
Adhesives	66	26	0.2-121.1
Typewriter correction fluids	9	89	16.0-110.1
Miscellaneous products	17	24	12.5-67.5
Automotive Products			
Brake quieters/cleaners	12	75	0.4-75.6
Belt lubricants/dressings	10	60	11.4-72.0
Door spray lubricants	2	50	95.6
Ignition wire driers	7	43	93.0 24.3-43.6
Tire cleaners/paints	14	42	0.1-90.3
Transmission cleaners/lubricants	7	14	113.0
Battery terminal protectors/cleaners	10	10	
2	10	10	37.1

^aPercent of products in category that contained 1,1,1-trichloroethane.

A U.S. EPA sponsored survey of 1,153 brand-name products for the presence of six chlorocarbon solvents provides extensive data on the TCE composition of consumer products (Westat, Inc. and Midwest Research Institute, 1987). Each material was analyzed by a purge and trap GC/MS method and the results reported as percent TCE by weight. Table 4.30 lists all the product categories with products that contained more than one percent TCE by weight. Table 4.31 lists the categories with products that contained less than one percent TCE by weight. The survey did not include all possible consumer sources of TCE. Insecticides and health and beauty aids, for example, were not tested.

Table 4.31. Consumer-product categories that contained less than one percent 1,1,1-trichloroethane by weight (from Westat, Inc. and Midwest Research Institute, 1987).

Product Category	Brands Tested
Non-automotive Products	
Aerosol furniture polish/wax/cleaner	10
Aerosol spray paints	155
Air deodorizers/disinfectants	7
Anti-static sprays	1
Bathroom/kitchen cleaners	6
Caulking products	7
Dip dye metal cleaners	6
Floor wax	11
Laundry presoaks/pre-cleaners	6
Non-aerosol furn polish/wax/cleaner	5
Paint thinners	11
Record cleaners	19
Rug/upholstery cleaners	12
Spray starches	4
Stain removers	2
Stereo/record player cleaners	6
TV/computer screen cleaners	5
Video disk cleaners	3
Wallpaper removers/adhesives	2
Wax stripper	1
Window/glass cleaners	6
Automotive Products	
Automotive sealants	5
Automotive undercoats	6
Bumper/chrome waxes	i
Carburetor cleaners	29
Engine degreasers	20
Gasket removers/adhesives	12
Liquid exterior car cleaners	3
Rust removers	7
Starting fluid sprays	1
Tire puncture sealers	1
Upholstery cleaner sprays	3
Vinyl top sprays	1
Water pump lubricants	1
Windshield de-icers	2
Miscellaneous automotive	8

Wallace et al. (1989b) conducted a study of the influence of personal activities on exposure to VOC. Seven study subjects were asked to perform specific activities suspected of increasing exposure to 17 target VOC. Each subject was monitored for nine sequential time periods over three days using a personal sampling pump and Tenax sorbent tubes. One subject visited a dry-cleaning establishment for ten minutes; the resultant personal exposure to TCE, averaged over an 11-hour period, was 1,000 µg/m³ (183 ppbv). Contact with dry-cleaned clothes may also have resulted in increased exposure of another subject to TCE.

Concentration Data

The major sources of indoor concentration data for TCE are the National VOC (NVOC) database, Krause et al. (1987) and the EPA's Total Exposure Assessment Methodology (TEAM) studies (Table 4.32).

Table 4.32. Summary statistics for concentrations of 1,1,1-trichloroethane in ppbv (from Shah and Heyerdahl, 1988; Krause et al., 1987; Pellizzari et al., 1987; Wallace et al., 1989a).

			· · · · · · · · · · · · · · · · · · ·	I	Percenti	les		
Study	N	Average	25	50	75	90	95	Range
NVOC	2120	48.9	0.55	1.84	5.51	b	_	_
Krause et al. (1987) ^a	230	1.46	-	0.80	_	2.41		<0.19-48.8
<u>TEAM</u> ^a								
L.AWinter '84 Overnight Personal	112	7.49	3.52	4.81	9.25	15.5	24.1	0.01-44.4
L.ASummer '84 Overnight Personal	51	2.50	1.13	1.33	2.04	3.15	4.44	0.35-66.6
C.C Summer '84 Overnight Personal	69	1.17	0.43	0.80	1.63	2.22	2.96	0.06-7.40
L.AWinter '87								
Overnight Kitchen	42	4.48	1.50	3.55	6.51	9.32	12.5	0.24-16.7
Daytime Kitchen	47	2.59	1.21	1.77	3.44	5.64	8.08	0.42-10.5
Daytime Living Area	45	2.76	1.14	2.33	3.18	6.09	8.44	0.67-11.1
L.ASummer '87								
Overnight Personal	40	1.91	0.96	1.44	2.20	3.79	6.14	0.34-9.77
Overnight Kitchen	37	2.42	1.02	1.68	2.68	4.42	11.7	0.06-12.7
Daytime Kitchen	38	3.42	0.89	1.96	2.35	4.48	10.8	0.28-55.7
Daytime Living area	40	2.72	0.96	1.67	2.78	5.00	13.0	0.32-22.0

^aConverted from mass/volume units.

There are over 2,000 data points for TCE in the NVOC database (Shah and Heyerdahl, 1988). The average concentration is 49 ppbv while the median concentration is only 1.8 ppbv. This indicates that the data are highly skewed.

^bStatistic not presented in reference.

Krause et al. (1987) made measurements of VOC in 230 West German homes, selected at random. Passive charcoal samplers were exposed for two-week periods between June 1985 and April 1986. The compounds were desorbed with carbon disulfide and analyzed by GC/FID and GC/ECD. The average concentration is 7.9 μ g/m³ (1.5 ppbv), and the median is 4.3 μ g/m³ (0.80 ppbv). These concentrations are somewhat lower than concentrations measured in the U.S.

The California TEAM studies were conducted in 1984 and 1987 in and around Los Angeles (two seasons each year) and in 1984 in Contra Costa County (one season). Measurements of selected VOC in fixed-site indoor and outdoor air, personal air, breath and drinking water samples were made for stratified random samples of residents in both areas. The results were weighted to represent the entire populations of the study areas. Samples were collected on Tenax sorbent tubes for approximately 12 hours. The sorbent tubes were thermally desorbed and analyzed by GC/MS. The fixed-site sampling devices were located in the major living area of the houses during the day and in the kitchen both during the day and at night. The over-night personal air samples were collected at the subjects' bedsides during sleeping hours, and, therefore, provide reasonable measures of VOC concentrations in indoor air. The population size for the Los Angeles study was approximately 350,000. The population size for the Contra Costa County study was approximately 90,000.

The results for the two locations in the summer of 1984 are similar with somewhat higher concentrations of TCE for the Los Angeles population. In Los Angeles, relatively high concentrations occurred during the winter of 1984, perhaps due to decreased ventilation rates. Differences between the two seasons were less pronounced in 1987.

Emissions Data

NASA Database

The NASA database (McDonnell Douglas Corp., 1986) contains records for 73 materials or products that emitted TCE (Table 4.33). The median emissions were relatively low. Adhesives had the highest emissions with a median of 1.2 μ g TCE released per gram of material and a maximum value of 1500 μ g/g. These data can only be considered to be qualitative since emissions were measured at an elevated temperature in closed containers.

Table 4.33. Summary of emissions of 1,1,1-trichloroethane from materials in NASA database.^a

Category	Minimum	Maximum	Median	Nb
Adhesives	0.01	1500	1.2	14
Coatings	0.1	11.7	0.36	9
Compounds		0.07	-	1
Cosmetics	0.005	0.2	_	2
Fabrics	0.002	0.5	0.03	13
Foam/Plastic	0.01	92.9	0.15	14
Lubricants	0.8	1	1	3
Pens/Inks	0.04	0.2	0.1	5
Rubber	0.02	10.7	0.2	12

^aAll measurements reported as µg TCE per gram product.

bN=number of materials in category that emitted TCE.

Consumer Products

Many aerosol spray products contain TCE as a solvent. Otson et al. (1984) investigated the effects of two aerosol fabric protectors (FP1, FP2) on indoor levels of TCE and petroleum distillates. Approximately 450 grams of each product were applied to two square meters of fabric in a house in separate experiments. Both integrated and grab samples were collected using passive and active samplers at various times during the eight hours after the products were applied. Both products were tested with all exterior doors and windows closed (unventilated). Product FP1 was also tested with two exterior doors and a second-floor window open (ventilated). Air exchange rates were not measured. Exposure concentrations for the person who applied the products are shown in Table 4.34. The subject remained in the house for eight hours after product application.

Table 4.34. Personal exposures to 1,1,1-trichloroethane in ppmv from use of fabric protectors (after Otson et al., 1984).^a

Test Conditions	Averaging Time (min)	Passive Sampler	Active Sampler
FP1-Unventilated	0-15 ^a	660	b
	15-30	642	_
	0-480	61 ^c	73
FP2-Unventilated	0-15	816	_
	15-30	889	_
	0-480	65 ^c	64
FP1-Ventilated	0-15	400	_
	15-30	430	_
	0-480	15 ^c	15

^aConverted from mass/volume units.

Otson et al. (1984) also conducted experiments in a closed 28-m³ test chamber. Application of 225 g of fabric protector resulted in a maximum concentration of TCE of 10,300 mg/m³ (1,910 ppbv). The initial concentrations were highest near the floor, where small children might be at risk. When the room was opened, concentrations dropped rapidly.

Building Materials

Sheldon et al. (1988) measured emission rates of VOC from 32 materials used in the construction of a new office building in Fairfax, VA. The materials were initially screened for emissions using a dynamic headspace technique. Some of the materials were selected for further testing in a small (12-liter) environmental chamber under controlled conditions. Most, if not all, of these materials are likely to be used in residential construction. The results are summarized in Table 4.35. The material with the highest emission rate is a latex caulk.

Net specific source strengths were also estimated for the building using a simple mass-balance model and measurements of ventilation rate and indoor and outdoor concentrations of TCE (Sheldon et al., 1988). Immediately after construction, the mean specific source strength of TCE was 7.6 µg/m³-h with a

bMeasurement not made for this time period.

^cDuplicate measurement, precision <±10%.

Table 4.35. Emission rates of 1,1,1-trichloroethane from building materials in $\mu g/m^2$ -h (from Sheldon et al., 1988).

Sample	Headspace	Chamber
Particle board	a	
Carpet adhesive	_	_
Black rubber molding	0.12	0.11
Latex paint	_	_
Linoleum tile	0.06	
Polystyrene foam insul.		_
Vinyl cove molding	0.17	0.30
Cove adhesive	NMb	-
Carpet	_	_
Vinyl edge molding	0.20	
Small dia. phone cable	-	
Large dia. phone cable	0.21	
Urethane sealant	_	
Latex paint	_	
Tar paper	_	
Primer/adhesive	_	
Latex caulk	4.9 ^c	
PVC pipe		
Water rep. mineral board	_	
Cement block	_	
Treated metal roofing		
Fiberglass insulation	_	
Duct insulation	_	
Exterior mineral board	-	
Interior mineral board	-	
Ceiling tile		
Red clay brick		
Plastic laminate	_	
Plastic outlet cover	_	
Joint compound	_	
Linoleum tile cement	_	

^aNo detectable emissions.

bNot measured, sampler overloaded.

^CMinimum value. Compound saturated detector during analysis.

maximum of 48 μ g/m³-h. The building was sampled again four months after construction when it was fully occupied. At that time, the mean specific source strength was 12 μ g/m³-h with a maximum of 40 μ g/m³-h. The lack of decrease in source strength with time suggests that occupant activities may have contributed to emissions of TCE.

Wallace et al. (1987) measured the emission rates of TCE from painted sheetrock (twenty-two 1.98×1.22 m surfaces), wallpaper glued to sheetrock (twenty-two 1.98×1.22 m surfaces) and carpet glued to wood panels (twelve 1.98×1.22 m surfaces). All materials were aged for one week before emissions were measured in a 34-m³ environmental chamber. In addition, cleaning agents were applied to the surfaces of a wood panel placed in the chamber. An insecticide was sprayed onto a portion of the same panel after the cleaning was completed. The emission rates of TCE for the painted sheetrock, wallpaper/sheetrock assembly and carpet/wood assembly were 1.9, 5.0 and $16 \,\mu\text{g/m}^3$ -h, respectively. The emission rate from the combined use of cleaners and insecticide was $2,200 \,\mu\text{g/m}^3$ -h.

Combustion Sources

Small amounts of TCE were detected in the air collected through an inverted funnel above the top burners of three gas cooking ranges tested by Moschandreas *et al.* (1983). The concentrations of TCE in the exhaust air were $4.3 \pm 5.5 \,\mu\text{g/m}^3$ ($0.8 \pm 1.0 \,\text{ppbv}$).

Summary

Extensive data for indoor concentrations of TCE that are specific to California are available. These data have been used to construct frequency distributions for indoor concentrations and personal exposure for two communities with populations of approximately 90,000 and 350,000 individuals. Median concentrations were estimated to range between 0.8 and 4.8 ppbv. Additional data for another California community are being obtained by the Woodland field study being conducted by the CARB (Sheldon, 1990).

A large number of consumer products contain TCE as a solvent. For example, of the 1,153 brandname products tested in a shelf survey, 16 percent were found to contain TCE. In addition, some building materials emit TCE. As a result, indoor concentrations of TCE are expected to be almost always elevated with respect to outdoor concentrations.

Because adequate indoor concentration data exist for TCE, further investigation of this compound should probably be given low priority.

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Pentachlorophenol

Uses and Sources

Pentachlorophenol (PCP) is an effective, general purpose biocide that is primarily used as a wood preservative. All non-wood applications of PCP were banned by the U.S. EPA in 1987 (EPA, 1987) and indoor use has now been banned by the U.S. EPA (EPA Region IX, personal communication). Products containing PCP are now only available to licensed applicators. Indoor sources should, therefore, be limited to historically treated building materials, with the possible exception of imported products such as rope and wicker baskets.

Concentration Data

Levin and Hahn (1986) measured concentrations of PCP in an office building in Southern California. The building's structural beams, which were exposed in the interior, had been pressure treated with PCP. Measurements were made before and after the beams were sealed to reduce the vaporization of PCP. Concentrations of PCP in pre-remedial air samples averaged 30.7 μ g/m³ (2.8 ppbv, 6 samples) with no ventilation and 27.2 μ g/m³ (2.5 ppbv, 7 samples) with low ventilation. After the beams were sealed and ventilation system defects were corrected, concentrations of PCP ranged from 0.9 to 9.9 μ g/m³ (0.08-0.9 ppbv) at various ventilation rates.

Saur et al. (1982) measured concentrations of PCP in 11 different buildings in the U.S. that had been designed for widely varying uses. The results are summarized in Table 4.36. The concentrations are for single measurements. The highest concentration, 3.5 ppbv, occurred in an unventilated basement. Most of the concentrations of PCP were considerably less than 1 ppbv.

Krause et al. (1989) measured concentrations of PCP in 104 homes in West Germany. Indoor air concentrations ranged from 2 to 25 μ g/m³ (0.19-2.3 ppbv). The median was 5 μ g/m³ (0.46 ppbv). An average of 40 liters of wood preservative, containing approximately 2 kg of PCP, had been used on about 130 m² of wood in each of the homes within the nine years prior to the measurements. Dust samples were collected from a subset of 65 of the homes. The median concentration of PCP in these samples was 13.3 μ g per gram of dust (ppm). Control dust samples were collected from 41 homes that had not been treated with PCP. The median concentration of PCP in these samples was only 0.008 μ g/g (ppm).

Barbieri et al. (1990) measured concentrations of PCP in house-dust samples collected in homes in Northern Italy. Five of these homes did not have any prior use of PCP and five had wood surfaces that had been previously treated with PCP. The range of concentrations of PCP in dust from the treated homes was 20-166 ppm. The range of concentrations in dust from the control houses was 2-11 ppm. The study additionally found a significant correlation between PCP concentrations in dust and urine which suggests that PCP exposure may be attributable to house dust.

Table 4.36. Air concentrations of pentachlorophenol in eleven buildings (from Saur et al., 1982).

Building Type	Building Age	Vent. Rate	PCP carrier ^a	Wood Loading (m ² /100m ³) ^b	Temperature (°C)	PCP Conc. (ppbv) ^c
Office/Lab-basement	4	Low	A	72.1	21	3.5
Office/Lab-main floor	4	Medium	Α	0.0	21	0.8
Warehouse	6	Medium	Α	8.8	11	0.3
Research barn		Medium	Α	6.2	16	0.05
Pole barn (enclosed)	5	High	Α	16.8	17-27	0.004
Pole barn (enclosed)	5	Medium	Α	56.3	17	0.08
House-basement	1	Low	В	0.3	21-27	0.09
House	3	Low	С	22.6	23	0.03
Natatorium-pool room	2	Medium	D	12.8	28	0.03
Natatorium-mech. room	2	Medium	D	10.5	28	0.01
Log home	1	Medium	С	36.0	18-29	0.01
Warehouse	9	High	A	24.6	15-24	0.009
Greenhouse	11	High	A	15.7	18-28	0.009
Log home	1	Medium	С	40.3	18-28	0.008

^aA = P9 Type A; B = Woodtreat TC gel; C = Mineral spirits; D = Dichloromethane.

Emissions

Building Materials

Ingram et al. (1983) used a small chamber to measure emissions from wood specimens treated with PCP. One set of samples consisted of southern yellow pine boards $(28 \times 7.6 \times 1.9 \text{ cm})$ that were dip treated in a commercial wood preservative formulation containing about five percent PCP in mineral spirits. A second set of samples was made up of similar-sized wood blocks cut from logs that had been commercially dip treated in the same formulation. Chamber concentrations from the first set of samples averaged 140 μ g/m³ (13 ppbv) at 31° C. Emissions from the log sections were much lower, with chamber concentrations averaging 20.4 μ g/m³ (1.9 ppbv). Wood blocks were also pressure treated with PCP in dichloromethane. Emissions from these samples were relatively high, with chamber concentrations averaging 175 μ g/m³ (16 ppbv). Samples treated with PCP in an oil-based carrier had even higher emissions. A variety of sealant coatings were applied to all of the treated samples, most of which reduced emissions of PCP by 80-90 percent.

Combustion Sources

Traynor et al. (1990) detected PCP in the emissions of unvented kerosene space heaters. An average of 5.4 ng of PCP were released per kilojoule of fuel consumed during tests of five properly tuned radiant heaters. Two mal-tuned convective heaters emitted 130 ng/kJ. The kerosene fuel was tested for chlorinated compounds, but the concentrations were below the detection limits of 10 ppm. The PCP may have been formed via free-radical chemistry. Dichloromethane used outside of the test chamber before and after the experiments was a possible source of the chlorine, as was airborne sea salt.

^bSurface area of treated wood to volume of building airspace.

^cData converted from mass/volume units.

Summary

Data on indoor concentrations of PCP in U.S. residences are minimal. Because PCP has a relatively low vapor pressure, it partitions between vapor- and particle-phases in air. European field studies suggest that exposure to PCP may be primarily due to contact with dust, either dermally or through inhalation. The low vapor pressure of PCP also results in persistent vapor-phase concentrations that are measurable for years after products containing PCP have been used.

Since the indoor use of PCP has been banned by the U.S. EPA, population exposure to this compound is primarily limited to occupants of historically treated homes and is expected to decrease slowly with time.

Pentachlorophenol is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, combined vapor- and particle-phase concentrations will be measured in a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

Pentachlorophenol is not well-suited for a laboratory study of emissions because losses to chamber surfaces and sampling lines are expected to be substantial due to its low vapor pressure. If additional data are needed for PCP, they would best be obtained by a field study.

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Tri- and tetrachlorophenols

Uses and Sources

The trichlorophenol isomer, 2,4,5-trichlorophenol, is used as a preservative for adhesives, synthetic textiles, rubber, wood and paints. It is also used around swimming pools and in bathrooms and hospital rooms as a bactericide and fungicide. Other tri- and tetrachlorophenols are used as intermediates in the manufacture of phenolic resins and dyes. Some are used directly as flea repellants, mold inhibitors, antiseptics, disinfectants and anti-gumming agents in gasoline (HSDB, 1990).

All tri- and tetrachlorophenols are found as contaminants in commercial grade solutions of pentachlorophenol (Crosby, 1981).

Concentration Data

No data on indoor concentrations of tri- and tetrachlorophenols were found.

Emissions Data

No data on emissions of tri- and tetrachlorophenols from potential indoor sources were found.

Summary

Like pentachlorophenol, these compounds have low vapor pressures and will partition between vapor- and particle-phases in air. Contact with dust, either dermally or through inhalation, may be the most important route of exposure.

Both 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol are included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, combined vaporand particle-phase concentrations will be measured in a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

These compounds are not well-suited for a laboratory study of emissions because losses to chamber surfaces and sampling lines are expected to be substantial due to their relatively low vapor pressures at room temperature. If additional data are needed, they would best be obtained by a field study.

- Crosby, D. G. (1981) Environmental chemistry of pentachlorophenol. *Pure and Appl. Chem.* 53, 1051-1080.
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Vinylidene chloride

Uses and Sources

Vinylidene chloride is primarily used as a monomeric intermediate in the production of plastics, particularly Saran-type polymers. It is also used in adhesives (HSDB, 1990). The extent to which any monomer is released from finished products is unknown.

Concentration Data

The major sources of data for indoor concentrations of vinylidene chloride are the National VOC (NVOC) database (Shah and Heyerdahl, 1988) and some of the U.S. EPA's Total Exposure Assessment Methodology (TEAM) studies which are incorporated into the NVOC database. There are no data for vinylidene chloride from the California TEAM studies.

There are 2,120 data points for vinylidene chloride in the NVOC database. The mean indoor concentration is 19.7 ppbv. However, the data are highly skewed since the 25th, 50th and 75th percentile concentrations are all zero. The limit of detection for the TEAM studies was 2.6 ppbv. The compound was detected in only a few samples as indicated by the low percent measurable values.

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for air toxics. Samples for very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished cannisters and were analyzed by GC/MS. None of these houses had concentrations of vinylidene chloride in excess of the detection limit of 0.79 µg/m³ (0.2 ppbv).

Emissions Data

Finkel et al. (1979) attempted to measure the release of vinylidene chloride monomer from six polymeric materials, three carpets and three fibers. Both dynamic-headspace experiments, conducted at 50° C and 50 percent humidity and direct insertion mass spectral analysis failed to detect the monomer in any of the samples. The limit of detection of vinylidene chloride was approximately 0.04 ppm in a 10-g sample of the material.

Summary

Data for indoor concentrations of vinylidene chloride are not available for California. However, the data for other parts of the U.S. are extensive. These data indicate that the distribution of indoor concentrations is highly skewed and that concentrations rarely exceed typical limits of detection of several parts per billion.

Vinylidene chloride is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

Vinylidene chloride is primarily used as a monomer in the manufacture of Saran-type plastics. The potential release of unreacted monomer from finished products could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Vinylidene chloride should be given a secondary priority for study because it is in CARB Group III.

- Finkel, J.M., James, R.H. and Miller, H.C. (1979) Residual monomers in acrylic and modacrylic fibers and fabrics. Contract No. 68-01-4746. U.S. EPA, Washington, D.C.
- HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.
- Shah, J. J. and Heyerdahl, E. K. (1988) National ambient volatile organic compounds (VOCs) database update. Report No. EPA 600/3-88-010(a). U.S. EPA, Washington, D.C.
- Sheldon, L. S. (1990) Indoor pollutant concentrations and exposures, Revised interim report. Contract No. A833-156. California Air Resources Board, Sacramento, CA.
- Sheldon, L. S. and Jenkins, P. (1990) Indoor pollutant concentrations and exposures for air toxics -- a pilot study. *Precedings of the 5th Int. Conference on Indoor Air Quality and Climate*, Toronto, Canada, July 29-August 3. Vol. 2, 759-764.

Acrylamide

Uses and Sources

Acrylamide is used in adhesives, permanent-press fabrics, paper and textile sizes and soil conditioners (HSDB, 1990). Its primary use is in the production of polyacrylamides used as flocculants for water treatment (Suta, 1979).

Concentration Data

No data on indoor concentrations of acrylamide were found.

Emissions Data

No data on emissions of acrylamide from potential indoor sources were found.

Summary

Acrylamide is a semivolatile compound which will partition between vapor and particle phases in air. Indoor concentrations of this compound have not been measured but are expected to be quite low because there are few probable indoor sources. Acrylamide is not included in an ongoing California field study.

In general, it is difficult to measure emission rates of semivolatile compounds using environmental chambers because losses to chamber surfaces and sampling lines are substantial. Data for this compound would best be obtained by including it in a field study that measured both vapor- and particle-phase concentrations. Acrylamide is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.

Suta, B. E. (1979) Assessment of human exposure to acrylonitrile. EPA Contract No. 68-02-2835. U.S. EPA, Washington, D.C.

Acrylonitrile

Uses and Sources

Acrylonitrile is used as a comonomer in the production of many types of elastomers, resins and polymers, including acrylic fibers. It is often used in varying proportions with styrene and butadiene to produce ABS plastics which have a wide variety of applications. It is also used as fumigant and in insecticides (HSDB, 1990). More than 60 percent of the acrylic fibers produced are used for the manufacture of apparel. Carpeting is the second largest use. Acrylic fibers are also incorporated into numerous home furnishings (Suta, 1979). The extent to which unreacted acrylonitrile monomer would be released from finished products is unknown.

Concentration Data

Sheldon and Jenkins (1990) conducted a pilot study in Woodland, CA, to measure indoor concentrations and personal exposures for toxic air contaminants. Samples for very volatile organic compounds were collected in four houses using 6-liter SUMMA-polished canisters and were analyzed by GC/MS. One house had concentrations in excess of the 0.89 μ g/m³ (0.41 ppbv) detection limit. The mean concentration for the four houses was 0.61 μ g/m³ (0.28 ppbv).

Emissions Data

Finkel et al. (1979) attempted to measure the release of acrylonitrile monomer from six polymeric materials, three carpets and three fibers. Both dynamic-headspace experiments, conducted at 50° C and 50 percent humidity and direct insertion mass spectral analysis failed to detect the monomer in any of the samples. The limit of detection of acrylonitrile was approximately 0.02 ppm in a 10-g sample of material.

Summary

Acrylonitrile is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

The primary use of acrylonitrile is in the manufacture of acrylic fibers for fabric and carpeting. One study showed that the release of the monomer from these highly processed materials is low. This result could be corroborated by a laboratory screening study of emissions of minor constituents from products and materials. Acrylonitrile should be given a high priority for study because it is in CARB

Group II. However, since the emission rates are expected to be low, the study of other Group II compounds could take precedence.

- Finkel, J.M., James, R.H. and Miller, H.C. (1979) Residual monomers in acrylic and modacrylic fibers and fabrics. Contract No. 68-01-4746. U.S. EPA, Washington, D.C.
- HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.
- Sheldon, L. S. (1990) *Indoor pollutant concentrations and exposures, Revised interim report.* Contract No. A833-156. California Air Resources Board, Sacramento, CA.
- Sheldon, L. S. and Jenkins, P. (1990) Indoor pollutant concentrations and exposures for air toxics -- a pilot study. *Precedings of the 5th Int. Conference on Indoor Air Quality and Climate*, Toronto, Canada, July 29-August 3. Vol. 2, 759-764.
- Suta, B. E. (1979) Assessment of human exposure to acrylonitrile. EPA Contract No. 68-02-2835. U.S. EPA, Washington, D.C.

1,1-Dimethylhydrazine

Uses and Sources

Dimethylhydrazine has varied uses as a chemical intermediate, a component of jet and rocket fuel, a stabilizer for organic peroxide fuel additives and a control agent for plant growth. It is also used in photography (HSDB, 1990).

Concentration Data

No data on indoor concentrations of dimethylhydrazine were found.

Emissions Data

No data on emissions of dimethylhydrazine from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of dimethylhydrazine, and this compound is not included in an ongoing California field study.

Indoor concentrations of dimethylhydrazine are expected to be quite low because there are few probable indoor sources. It is possible, however, that dimethylhydrazine could be released from some finished products. This could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Dimethylhydrazine is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.

Hydrazine

Uses and Sources

Hydrazine is used as a rocket fuel and as a corrosion inhibitor in the boiler water at power plants and in the heating water of district water systems. It is also used as a chemical intermediate in the production of pesticides and pharmaceuticals (Kauppinen et al., 1989). Hydrazine is found as a contaminant in maleic anhydride, a widely used growth inhibitor for tobacco suckers. Tobacco smoke is probably the predominant indoor source of hydrazine (Liu et al., 1974).

Concentration Data

No data on indoor, non-occupational, concentrations of hydrazine were found.

Emissions Data

Liu et al. (1974) trapped hydrazine emitted from cigarettes by reaction with pentafluorobenzaldehyde to form decafluorobenzaldehyde azine (DFBA) which prevents loss by reaction with other smoke constituents. The DFBA was then enriched by chromatography and analyzed by GC/FID and GC/ECD. The average emission of hydrazine in the sidestream smoke of commercial cigarettes was 94 ng per cigarette.

Summary

There are no data on indoor concentrations of hydrazine, and this compound is not included in an ongoing California field study.

Environmental tobacco smoke (ETS) is expected to be the major source of hydrazine in indoor air. Since the data on emissions of hydrazine from this source are minimal, it is recommended that the compound be included in a laboratory study of ETS emissions. Methods for analysis of hydrazine in air contaminated with ETS may have to be evaluated as part of this study. Hydrazine should be given a high priority for study because it is in CARB Group II.

References

Kauppinen, T. P., Alho, J. M. and Lindroos, L. O. (1989) Exposure to hydrazine and its control in power plants. *Appl. Ind. Hyg.* 4, 245-250.

Liu, Y. Y., Schmeltz, I. and Hoffmann, D. (1974) Chemical studies on tobacco smoke: Quantitative analysis of hydrazine in tobacco and cigarette smoke. *Anal. Chem.* 46, 885-889.

4,4'-Methylenedianiline

Uses and Sources

The compound 4,4'-methylenedianiline (MDA) is used as a curing agent for polyurethane elastomers and polyurethane epoxy resins and as a chemical intermediate in the production of polyamide and polyimide resins and fibers. It is also used as a corrosion inhibitor (HSDB, 1990). The extent to which unreacted MDA would be released from finished products is unknown.

Concentration Data

No data on indoor concentrations of MDA were found.

Emissions Data

No data on emissions of MDA from potential indoor sources were found.

Summary

Methylenedianiline is a semivolatile compound which will partition between vapor and particle phases in air. Indoor concentrations of this compound have not been measured but are expected to be quite low because there are few probable indoor sources. Methylenedianiline is not included in an ongoing California field study.

In general, it is difficult to measure emission rates of semivolatile compounds using environmental chambers because losses to chamber surfaces and sampling lines are substantial. Data for this compound would best be obtained by including it in a field study that measured both vapor- and particle-phase concentrations in indoor air. Methylenedianiline is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.

Nitrobenzene

Uses and Sources

Nitrobenzene is used in soaps; in shoe, metal and floor polishes; as a preservative in spray paints; and as a substitute for almond essence. It is used as a chemical intermediate in the manufacture of pesticides, rubber chemicals, pharmaceuticals and isocyanates (HSDB, 1990). Small amounts of unreacted nitrobenzene may be present as a contaminant in this second group of products.

Concentration Data

Nitrobenzene was measured in the pilot phase of the Woodland, CA, field study (Sheldon, 1990). Ten of the 25 indoor, outdoor and personal air samples had concentrations in excess of the $0.04 \,\mu g/m^3$ (0.007 ppbv) detection limit. The range of measurable concentrations of nitrobenzene in samples from unspecified locations was 0.04- $0.21 \,\mu g/m^3$ (0.009-0.042 ppbv).

Emissions Data

No data on emissions of nitrobenzene from potential indoor sources were found.

Summary

Nitrobenzene is one of the compounds included in the Woodland, CA, field study being conducted by the CARB (Sheldon, 1990). For the second phase of the study, indoor concentrations and personal exposure will be measured for a probability-based sample of approximately 130 homes. This study design will allow the results to be applied to the general population of the study area.

It is recommended that nitrobenzene be included in a laboratory study of emissions of minor constituents from products and materials. Possible product types for investigation include various polishes, soaps and pesticides. If significant sources are identified by preliminary screening, source emission rates could be measured under standardized conditions using environmental chambers. Nitrobenzene should be given a secondary priority for study because it is in CARB Group III.

References

HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, M.D.

Sheldon, L. S. (1990) Indoor pollutant concentrations and exposures, Revised interim report. Contract No. A833-156. California Air Resources Board, Sacramento, CA.

N-Nitroso compounds

Uses and Sources

N-Nitrosodimethylamine (NDMA) is used as an industrial solvent, antioxidant, plasticizer, rubber accelerator and lubricant additive. N-Nitrosodiethylamine (NDEA) is used as an antioxidant, stabilizer and gasoline and lubricant additive. N-Nitrosomorpholine (NMOR) has no commercial uses in the U.S. (HSDB, 1990).

The primary source of the nitrosamines in indoor air is environmental tobacco smoke (ETS). Other possible sources include rubber products, leather upholstery, cosmetics, beer and scotch, and cooking bacon. For most sources, the nitrosamines are formed either as a by-product of manufacture or during product use (i.e., cooking bacon).

Concentration Data

The results of analyses of nitrosamines must be interpreted cautiously. Artifactual formation of the compounds can occur rapidly if conditions are right. For example, Angeles et al. (1978) found that formation of nitrosamines occurred readily in nonaqueous solutions like dichloromethane if solid nitrites and secondary amines were present.

Cigarette smoke is the predominate source of the nitrosamines in indoor air. Brunnemann and Hoffmann (1978) made measurements in environments where smoking was occurring. These results are summarized in Table 4.37. Details as to the sizes of the spaces, the numbers of smokers and the ventilation rates were not reported. Samples were collected with midget impingers containing ascorbic acid buffered at pH 4.5 as the trapping solution. Analysis was by GC/TEA. Control measurements were made in the homes of non-smokers, where the concentrations of NDMA were less than 1.7 ppbv. Concentrations in smoking environments ranged up to 79 ppbv.

Table 4.37. Concentrations of N-nitrosodimethylamine in indoor air (from Brunnemann and Hoffmann 1978)^a.

Environment	Оссиралсу	Ventilation	Concentration (ppbv)
Train bar car	Primarily smokers	Air conditioned	43
Train bar car	Primarily smokers	Natural	36
Bar	Primarily smokers	Not given	79
Sports Hall	Not given	Not given	30
Betting parlour	Not given	Not given	17
Discotheque	Not given	Not given	30
Bank	Not given	Not given	3.3
Houseb	Not given	Not given	<1.7
Houseb	Not given	Not given	<1.0

^aAll data converted from mass/volume units.

^bControls. No smokers present.

A similar investigation was conducted by Stehlik et al. (1982) for a variety of environments contaminated with ETS. These results are summarized in Table 4.38. For one set of measurements, subjects were asked to smoke as much as possible during sampling. Ventilation in the rooms was low or absent. Another set of measurements were conducted in environments where smoking occurred, but the occupants were unaware that measurements were being made. In the unnaturally high smoking environments, the levels of contamination were elevated and all subjects agreed that they would have left the rooms or opened the windows under normal circumstances. Concentrations of NDMA ranged up to 50 ppbv. Under natural smoking conditions, concentrations of NDMA were generally lower, ranging from less than 3 to 23 ppbv. The cause of the discrepency between these results and the generally higher concentrations obtained by Brunnemann and Hoffmann (1978) is not known.

Table 4.38. Concentrations of N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) in indoor air (after Stehlik et al. 1982).

Environment	Size (m ³)	Occup- ancy	Tobacco products consumed	Sample time (hr)	Venti- lation ^b	NDMA (ppbv) ^c	NDEA (ppbv) ^c
Unnatural conditions ^a							
Conference room	43	11	64 cigarettes	2	None	23	< 2.4
Office	22	3	35 cigarettes	2	None	43	< 2.4
Office	22	3	38 cigarettes	2	None	50	< 2.4
Office	22	3	28 cigarettes	2	Low	26	< 2.4
Office	22	2	12 cigarettes	2	Low	6.6	2.4
Office	46	7	18 cig., 2 pipes	2	Low	26	< 2.4
Conference room	43	10	40 cigarettes	2	Low	7.3	< 2.4
Natural conditions							
Work room	207	7	Continuous smoking	2	Low	7.6	< 2.4
Conference room	301	15	26 cig., 1 pipe, 6 cigarillos	2	Low	10	< 2.4
Office	70	6	27 cigarettes	2	Low	9.9	7.2
Conference room	50	12	37 cig., 4 pipes, 3 cigars	2	None	6.6	4.8
Suburban restaurant	120	20	20-30 cig., 2 pipes	2	?	< 3.3	< 2.4
Restaurant in Vienna	160	23	20 cigarettes	1	?	3.3	< 2.4
Restaurant in Vienna	180	25	25-30 cigarettes	1	?	13	< 2.4
Restaurant in Vienna	160	23	15-20 cigarettes	1	?	17	< 2.4
Dance club	320	30-70	Not determined	4	?	23	48

^aIn unnatural conditions, occupants were asked to smoke as much a possible during the sampling period. In natural conditions, nothing was done to influence the occupants smoking behavior.

^bIn unventilated rooms, the windows and door remained closed over the course of the measurement. In low ventilation rooms, the windows remained closed but the door was opened and closed several times.

^CAll data converted from mass/volume units.

Another source of exposure to N-nitroso compounds is the materials used in automobile interiors. Rounbehler et al. (1980) measured concentrations of N-nitroso compounds in a group of 38 automobiles. All but one were new and tested at dealerships. NDMA was present in all but one of the vehicles at concentrations up to $0.83~\mu g/m^3~(0.27~ppbv)$. The mean concentration was $0.29~\mu g/m^3~(0.096~ppbv)$. NMOR was present in 16 vehicles at concentrations up to $2.5~\mu g/m^3~(0.53~ppbv)$ with a mean concentration of $0.65~\mu g/m^3~(0.14~ppbv)$. NDEA was found at lower concentrations in 17 vehicles. Leather interiors produced the highest levels of NDMA, followed by cloth, then vinyl interiors. Samples collected in the rear seats were consistently higher than samples collected in the front seats of the same vehicle. In at least one vehicle, the spare tire was identified as the primary source of N-nitroso compounds. The concentration of NMOR in the spare-tire well of this vehicle was almost 70 times greater than that measured in the rear seat.

Emissions Data

Combustion Sources

Adams et al. (1987), Brunnemann et al. (1977) and Brunnemann et al. (1980) conducted experiments on emissions of nitrosamines in sidestream and mainstream cigarette smoke. The experimental protocols were similar in all three studies. Weight-selected cigarettes were smoked sequentially by machine and the sidestream smoke was directed through two gas washing bottles containing ascorbic acid buffered at pH 4.5. The trapping solution was extracted with dichloromethane and the organic fraction was analyzed by GC/TEA. Table 4.39 summarizes the results of these studies.

Table 4.39. Sidestream emissions of N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) from cigarettes (from Adams et al., 1987; Brunnemann et al., 1977; Brunnemann et al., 1980).

Study	Cigarette Type	Number Brands Tested	NDMA (ng/cigarette)	NDEA (ng/cigarette)
Adams et al.	U.S. commercial nonfilter	1	735	<u> </u>
(1987)	U.S. commercial filter	2	597, 611	
	U.S. commercial perforated filter	1	685	
Brunnemann et al.	U.S. and foreign commercial nonfilter	3	40±26	2.7±1.6 ^a
(1977)	U.S. and foreign commercial filter	1	5.7	1.3
	Little cigar with filter	1	43	1.1
Brunnemann et al.	Swiss commercial nonfilter	1	359	
(1980)	Swiss commercial filter	11	262±78	
	German commercial filter	6	249±85	
	German commercial nonfilter	4	280±101	

^aOnly two of the three brands tested.

Brunnemann et al. (1977) found that the air velocity around the burning cone of a cigarette between puffs affects the yield of volatile nitrosamines. This is evident from their data for a U.S. brand which showed that increasing the flow rate through the sampling device from 250 ml/min to 500, 1,000 and 1,500 ml/minute increased the emission of NDMA in the sidestream smoke from 90 to 250, 530 and 680 ng per cigarette, respectively. This result is expected, considering the way nitrosamines are formed in cigarette smoke (Neurath, 1972).

Brunnemann and Hoffmann (1978) also detected NDMA in the smoke of burning sticks of incense from Hong Kong, Taiwan and the Peoples Republic of China.

Consumer Products

Spiegelhalder and Preussmann (1984) measured concentrations of N-nitroso compounds in 145 samples of cosmetics and toiletries obtained in retail shops in West Germany. Care was taken to include widely-used products. The N-nitroso compounds were separated from the product matrices by vacuum distillation and were analyzed by GC/TEA. The results for NDMA and NMOR are presented in Table 4.40. A single product was found to contain 15 µg/kg (ppb) NDEA.

Table 4.40. Concentrations of N-nitrosodimethylamine (NDMA) and N-nitrosomorpoline (NMOR) in µg/kg (ppb) for cosmetics and toiletries (from Spiegelhalder and Preussmann, 1984).

		NDMA			NMOR			
		Concentrat				Concentrati		
Product type	N	# pos.a	Max.	Ave.	# pos.a	Max.	Ave.	
Shampoos	45	23	24	6.3	13	640	133	
Color toners	7	1	10	-	_	_	_	
Hair conditioners	16	5	5	3.3	_	-	_	
Foam baths	7	-			_	-	_	
Shower gels	9	3	10	4.3	4	380	145	
Cream and oil baths	8	1	20	_	2	440	_	
Cosmetic bath additives	5		_	-	-	_		
Children's shampoos	5	4	20	6.4	1	230	_	
Children's bath/care prod.	8	3	10	-	6	360	80	
Body lotions and rubs	6	_	_		_	_	_	
Face tonics, cleaners and masks	29	12	3	1.5	-		_	

^aNumber of products in a category found to contain NDMA or NMOR.

Nitrosamines are present in rubber products due to the use of amine-based accelerators during their manufacture. Preussmann and Eisenbrand (1984) summarized some of their results for rubber products. They found up to 200 µg NDMA per kilogram of product (0.2 ppm) and up to 100 µg NDEA per kilogram. (0.1 ppm) They also found nitrosatable compounds in concentrations up to 16 ppm in products made from natural rubber.

Many pesticides and herbicides which contain amine compounds are contaminated with relatively high levels of N-nitroso compounds. Bontoyan et al. (1979) analyzed a number of these products by GC/TEA or HPLC/TEA. They found the highest levels of N-nitrosamines in substituted amine, dinitroaniline and amine salt formulations. Similar results were obtained by Zweig et al. (1980). They

found that most dinitroaniline based pesticides contained levels of nitrosamines ranging from less than 1 to 430 mg/kg (ppm). Analysis of over 60 dimethylamine salt pesticides (e.g., the dimethylamine salt of 2,4-D) showed NDMA contamination at concentrations ranging from 2 to 85 mg/kg (ppm). Four of 28 quaternary salt compounds tested contained morpholine. These were possibly contaminated with NMOR at concentrations up to 15.8 mg/kg (ppm) but the identification of NMOR was not confirmed.

Mixed-bed resin ion-exchange water softeners with anion resins containing amine functional groups can form NDMA if the water being treated contains traces of nitrite (Gough et al., 1977). The extent to which the NDMA would vaporize during water use is unknown.

Other Sources

Beer and scotch whiskey contain trace levels of N-nitroso compounds. Spiegelhalder et al. (1979) analyzed 158 samples of commercially available beer in West Germany. Of these, 111 were found to contain NDMA. The mean concentration of NDMA was 2.7 µg/kg (ppb), with a maximum value of 68 µg/kg (ppb). Two samples contained NDEA at concentrations of 0.5 and 3.0 µg/kg (ppb). Goff and Fine (1979) conducted similar measurements on 18 brands of U.S. domestic and imported beers and on seven brands of scotch whiskey. All eighteen beers contained NDMA at levels ranging from 0.4 to 7.0 µg/liter. Six of the whiskeys also contained NDMA at levels ranging from 0.3 to 2.0 µg/liter. It is not known how much of these contaminants would volatilize into room air.

Cooking bacon may also release NDMA to the air. Lee et al. (1978) measured 46 µg of NDMA in the condensible vapor formed during the frying of one kilogram of bacon. Ten micrograms remained in the cooked meat and the fat. In a similar study, Gough and Walters (1976) found that 90 to 100 percent by weight of the NDMA in bacon components after frying was present in the condensable vapor.

Summary

Concentrations of N-nitroso compounds have not been measured in any statistically-selected sample of residences in California or the U.S. They are also not included in an ongoing California field study. These compounds, however, are expected to be widely present, probably at very low concentrations. The predominate indoor source of nitrosamines is ETS. Emissions of N-nitroso compounds are also expected from interior furnishings, rubber products and cosmetics. Other potential sources include cooking bacon, beer and whiskey, pesticides and domestic water treated with ion-exchange resins.

Data for N-nitroso compounds could be obtained by laboratory studies. It is recommended that they be included both in a study of ETS emissions and in a screening study of emissions of minor constituents from products and materials. The N-nitroso compounds should be given a relatively high priority for these studies because they are in CARB Group II. Since some data are already available for cigarette emissions, the study of ETS should be given lower priority than the study of emissions from products and materials. Possible sources which could be examined in a screening study include plastic and leather upholstery, rubber products, cosmetics, biocides and food products. If significant sources are identified, emission rates can be measured under standardized conditions using environmental chambers.

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Toluene diisocyanates

Uses and Sources

The two isomers of toluene diisocyanate, toluene 2,4-diisocyanate and toluene 2,6-diisocyanate, are generally used as a mixture in the manufacture of polyurethane products. Toluene diisocyanates are, therefore, used in a large number of products with architectural applications. They are a component of polyurethane coatings, paints, varnishes, cement sealers, mastic sealants and adhesives. They are also used in the manufacture of flexible polyurethane foams and of polyurethane elastomers. The former are widely incorporated into furnishings and the latter are used to coat fabrics. Toluene diisocyanates have an additional use as a cross-linking agent for nylon (HSDB, 1990). Polyurethane mastic sealants used in building construction may contain up to 7.6 percent toluene diisocyanates by weight (Jennings et al., 1988).

Concentration Data

No data on non-industrial concentrations of toluene diisocyanates were found.

Emissions Data

No data on emissions of toluene diisocyanates from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of toluene diisocyanates, and they are not included in an ongoing California field study. It is particularly important to obtain data on these compounds. In addition to being suspected human carcinogens, they are potent respiratory irritants and sensitizers, even at very low airborne concentrations (IARC, 1986). Because toluene diisocyanates are in CARB Group II, they should be given a high priority for study.

Toluene diisocyantes are considered to be semivolatile by the definition used in this report. Nevertheless, it is recommended that they be included in a study of emissions of minor constituents from products and materials because it is likely that useful information about indoor sources can be obtained in this manner. Some potential sources which are widely used in buildings are flexible polyurethane foams and polyurethane finishes. Although there are no data, it is suspected that emissions of toluene diisocyanates from these materials may occur under some circumstances. Source categories for a laboratory screening study of emissions should, therefore, include polyurethane carpet pads, foam furniture cushions, varnishes and caulks. It will be necessary to validate an analytical method for these compounds as part of this study.

It is also recommended that toluene diisocyanates be included in a field study conducted in a probability-based sample of homes. Since these compounds are highly reactive, methods for sampling and analysis that are suitable for use in indoor air must be developed and validated before this study can be undertaken.

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Dimethyl sulfate

Uses and Sources

Dimethyl sulfate is used as a solvent in the manufacture of dyes, perfumes and pharmaceuticals and for the separation of mineral oils. It is also used as a sulfating and methylating agent in the production of agrichemicals, fabric softeners, dyes and pharmaceuticals (HSDB, 1990). The extent to which any unreacted dimethyl sulfate is present as a contaminant in these products is unknown.

Concentration Data

No data on indoor concentrations of dimethyl sulfate were found.

Emissions Data

No data on emission of dimethyl sulfate from potential indoor sources were found.

Summary

There are no data on indoor concentrations or source emissions of dimethyl sulfate, and this compound is not included in an ongoing California field study.

Indoor concentrations of dimethyl sulfate are expected to be quite low because there are few probable indoor sources. It is possible, however, that dimethyl sulfate could be released from some finished products. This could be determined in a laboratory screening study of emissions of minor constituents from products and materials. Dimethyl sulfate is in CARB Group II but should be given secondary priority for study due to the lack of probable indoor sources.

References

HSDB, Hazardous Substances Data Bank (1990) National Library of Medicine TOXNET network. Bethesda, MD.

CHAPTER 5

Methods for Measuring Emissions of VOC

Introduction

A variety of methods were used to evaluate the potential emissions of some of the candidate compounds from their sources. These methods ranged in complexity from simple bulk analyses and static-headspace measurements of products to experiments conducted in large-scale environmental chambers. The data produced by the methods ranged from weight compositions and emissions expressed as mass of compound per mass of material to true emission rates. In one case, measured emission rates were used in a model to predict indoor concentrations of VOC.

In this chapter, various methods which have been used to estimate and measure emissions of VOC from materials and products are reviewed. The appropriate uses and the limitations of these methods are assessed. The chapter concludes with discussions of specific aspects of experiments conducted in environmental chambers, including the effects of environmental parameters on emission rates, the importance of sink effects, and methods of data analysis.

Bulk Analysis, Extraction and Headspace Techniques

The potential emissions of VOC from materials and products can sometimes be estimated by bulk analyses of the volatile components. A study was conducted for the U.S. EPA to provide information on the concentrations of six chlorinated solvents in approximately 1,200 common household products (Westat, Inc. and Midwest Research Institute, 1987). Measured aliquots of the products were added to water, and the compounds were analyzed by a purge and trap technique using GC/MS. In a follow-up study, the stored chromatograms were searched for 25 additional VOC (Sack and Steele, 1989). The purpose of these studies was to provide inputs for mathematical models of human lifetime exposures to these compounds. A national usage survey was conducted to provide additional inputs on the frequencies and durations of the uses of the products (Westat, Inc., 1987) For some products, use of composition data for this type of modeling is a valid approach. An example is aerosol sprays, for which the emissions and exposures primarily occur during the actual use of the product and are directly related to product composition (Girman and Hodgson, 1986). However, in other cases, use of bulk analyses for modeling may result in greatly overestimated emissions and exposures. Experiments conducted in a large-scale chamber showed this to be true for emissions of alcohol from liquid detergents (Wooley et al., 1990).

Qualitative and semi-quantitative data on the composition of minor constituents in materials and products can be obtained by various extraction techniques. Thirty building-construction and interior-finish materials were screened for the emissions of VOC and semi-volatile compounds by vacuum extraction (Hodgson *et al.*, 1983). For a number of samples of adhesives which had been dried for one to two weeks, there was good qualitative agreement between the results obtained by vacuum extraction and by a small-chamber (3.8 L) technique. Another method for estimating emissions by direct product analysis is Soxhlet

extraction using various organic solvents. New carpeting was examined for potential emissions of VOC using both Soxhlet extraction with dichloromethane and a dynamic-headspace technique (Pleil and Whiton, 1990). There was relatively good qualitative agreement between the methods for compounds with room-temperature equilibrium vapor pressures from about 0.05 to 25 torr.

Static-headspace measurements have commonly been used to evaluate potential emissions of VOC from materials and products. A major example is the NASA sponsored study of over 5,000 materials, either considered for use in the construction of space-shuttle cabins or likely to be used by crew members of the space shuttles (McDonnell Douglas Corp., 1986). The purpose of this study was to identify and eliminate those materials which might have high emissions and, therefore, pollute the cabin atmosphere. Many of the evaluated materials were specialized assemblies, but a large number were common construction or household items.

Emissions were measured in closed containers with a minimum volume of two liters. Specimens were placed in the containers at an initial pressure of 12 psia (620 torr). The net sample loading was typically five grams per liter of container volume. Paints, other coatings and adhesives were first applied to both sides of aluminum plates. The containers were then heated to 49° C for 72 hours, after which samples of headspace gas were collected and analyzed. The results were reported as µg of compound emitted per gram of material.

The static-headspace method served its purpose in the NASA study as a relatively simple screening tool for identifying high emitting materials among a large number of materials. However, since the method uses closed containers, the concentrations of VOC entering the gas phase are limited by equilibrium. Partitioning between organic and aqueous phases may also limit emissions. Therefore, gasphase concentrations of VOC may not directly correspond to compositions of these compounds in the materials or to the emissions of these compounds under actual conditions in buildings. For example, one study reported that for certain materials and compounds, static-headspace results and environmental-chamber results did not agree (Colombo et al., 1990). In this study, emissions of VOC from several household cleaners, waxes and polishes were measured using both a 7.5-L chamber and a static-headspace technique. The relative compositions of VOC in chamber and headspace air were compared for three products. Polar compounds generally had considerably higher relative abundances in chamber air. In fact, some of the major VOC components detected in the chamber experiments were below limits of detection in the headspace experiments.

Small-scale Chambers

Chambers are distinguished from static-headspace devices by a controlled flow of ventilation air. If the ventilation rate is sufficiently high, concentrations of VOC in the bulk air will be below their room-temperature equilibrium vapor pressures and emission rates (e.g., mass of compound emitted per unit time) can be determined. Small-scale chambers ranging in volume from 0.08 L to one cubic meter, or more, have been used to measure the emissions and emission rates of VOC from a variety of materials and

products. The design and operation of these chambers have varied considerably depending upon the objectives of the studies.

In their simplest form, small-scale chambers can be considered to be dynamic-headspace devices. These simple devices often have relatively small volumes and environmental parameters which are not necessarily scaled to rooms or buildings. Therefore, they are most appropriately used as a screening tool for qualitative and semi-quantitative analysis of emissions or for the relative ranking of materials with respect to emissions. For example, dynamic-headspace devices have been used in conjunction with building studies to help identify the sources of compounds found in air samples (Sheldon et al., 1986; Hodgson and Girman, 1989). In these studies, samples of materials and products were collected from buildings and their emissions of VOC were examined in the laboratory using chambers with volumes of 0.08 or 4 L.

If precise environmental controls are provided, small-scale chambers can be used to examine the effects of environmental variables on emissions. Tichenor et al. (1990) measured the emission rates of p-dichlorobenzene (DCB) from moth crystal cakes as a function of temperature, relative humidity and ventilation rate using 166-L stainless-steel chambers. Emissions of DCB were found to vary considerably with temperature, less dramatically with ventilation rate and only slightly with relative humidity. Significant losses of DCB to the walls of the chamber were discovered.

If the factors which control emissions of VOC from a material are sufficiently well understood, data produced in small-scale chambers can be used in models to predict indoor concentrations of VOC with a high degree of accuracy. In the study of DCB cited above, a model was developed to estimate indoor concentrations in houses in which moth crystal cakes were used (Tichenor et al., 1990). When appropriate values for source emission rates, air exchange rate, in-house air movement, and losses to sinks were provided, model predictions of concentrations were in close agreement with actual concentrations in a test house. However, it should be noted that the sink term, which is dependent upon the types of surfaces present, was determined in the same house.

The need for standardized designs and protocols for small-scale chambers is being addressed. An ASTM subcommittee on methods for indoor air (D22.05) has developed a document entitled, "Standard Guide for Small-scale Chamber Measurements of Organic Emissions." This document was approved by the subcommittee and full committee in April, 1990. An earlier version was published as a U.S. EPA report (Tichenor, 1989). The ASTM document is a guide not a method. As a guide, it primarily discusses the general considerations for making these types of measurements. There are chapters on mass-transfer considerations, facility design, sample collection, experimental design, experimental procedures, quality assurance and control, data analysis, and data reporting.

Although small-scale chambers are applicable for measuring emission rates of VOC from many types of materials and products, there are limitations to their use. Clearly, large assemblages of building materials or large pieces of furniture can not be placed into small chambers. Small-scale chambers are also not appropriate for evaluating emissions from consumer products if the highest emissions and exposures result from the actual application and use of these products. This may be true for a number of consumer products (e.g., paints, polishes, and various aerosol sprays). Another problem is that it may be more difficult to properly scale air mixing and air velocities to rooms and buildings with small-scale chambers

than with large-scale chambers. Finally, sink effects caused by losses of compounds to chamber walls are accentuated in small-scale chambers because of the relatively high surface-to-volume ratios.

Large-scale Chambers

For the purposes of this discussion, large-scale chambers are defined as environmental chambers with volumes of five cubic meters or more. Most large environmental chambers are on the scale of small residential rooms with volumes of 20-40 m³. The considerations discussed in the ASTM standard guide for small-scale chambers are applicable to large-scale chambers as well. The design and materials of construction should be appropriate for experiments with VOC. For example, the construction materials should have low emissions of VOC and surface materials should be chosen to minimize sink effects. Adequate controls for ventilation rate, temperature and humidity must be provided to maintain these parameters within specified limits. This typically necessitates the use of elaborate air-handling systems and the placement of these chambers within temperature-controlled rooms.

Because room-size chambers are large enough to be occupied by a person, they are well suited for measuring emissions and exposures that occur during the actual use of consumer products. For example, exposures to dichloromethane from the use of paint removers and aerosol sprays were investigated using the 20-m³ environmental chamber at Lawrence Berkeley Laboratory (Girman and Hodgson, 1986). Protocols were developed which simulated typical consumer use of these products. Experiments were conducted at two different ventilation rates, and a mass-balance model for exposure as a function of ventilation rate was developed. In a follow-up study, the utility of this model for predicting exposures in various residential environments was demonstrated (Hodgson and Girman, 1987). Using the same chamber, the release of ethanol to the atmosphere during the use of liquid laundry and dish-washing detergents was investigated (Wooley et al., 1990). In these experiments, either a kitchen sink or a washing machine was set up and typical washing operations were conducted by a person in the chamber.

Large chambers can also be used to measure emissions of VOC from complete pieces of furniture and from large assemblages of building materials. If a material is not homogeneous with respect to emissions, then large material sizes can be used to provide a more representative sample.

Because large chambers are on the same scale as rooms in houses, some of the problems of scaling environmental variables are reduced. For example, if typical residential ventilation rates and material loading rates are used, the concentrations of VOC in the air should be similar to those measured in houses. Other parameters affecting mass transfer, such as air velocities at surfaces of materials, should also approach residential values.

Large-scale chambers can be used to help validate models for indoor air quality. Data generated in experiments in large-scale chambers can be compared to results predicted from experiments conducted in small-scale chambers. The advantage of this exercise is that the accuracy of small-chamber results and the efficacy of models are evaluated under carefully controlled environmental conditions. Validation experiments conducted in actual rooms and buildings may be considerably more difficult to control and characterize.

There are practical limitations to the use of large-scale chambers. There are in existence only several large-scale chambers that are appropriate for studies of VOC due, in part, to the large capital investment required for such a facility. Operating costs for large-scale chambers are also high relative to small-scale chambers because they must be contained within temperature-controlled rooms and considerable labor is needed to maintain them and keep them operating within specified limits for the environmental parameters.

In-situ Measurements of Source Strength

Emissions of VOC from sources can be sometimes be evaluated from *in-situ* measurements made in buildings. If the ventilation rate and indoor and outdoor concentrations of VOC in a building at near steady-state conditions are known, a single-equation mass-balance model can be used to calculate net specific sources strengths for VOC. This model assumes perfect mixing of air in the building. At steady-state conditions, the source strength, $S \pmod{h^{-1}}$, of a pollutant is:

$$S = V a (C - C_0)$$
 (5.1)

where V is the ventilated volume (m^3) , a is the ventilation rate (h^{-1}) , and C and C_0 are the indoor and outdoor concentrations (mg/m^3) , respectively. Non-ventilation losses are assumed to be negligible.

This method was used to evaluate both long- and short-term variations in the source strengths of total VOC, classes of VOC and individual VOC in a large office building (Hodgson and Daisey, 1989). The method works best if the emissions from the sources being evaluated are characteristic and unique. In this case, total VOC was found to be dominated by emissions of a characteristic mixture of isoparaffinic hydrocarbons from wet-process photocopiers and plotters. The source strength for total VOC which was calculated with the model agreed well with an estimate of emissions based on the average usage of solvent in these machines. The same model was used to calculate the sink term for DCB in a test house (Tichenor et al., 1990). Here, an effective emission rate was calculated from the indoor-air concentration of DCB and the ventilation rate. The difference between the emission rate calculated from the weight loss of the moth crystal cake source and the effective emission rate was attributed to losses to surfaces in the house.

Effects of Environmental Parameters

Environmental parameters have to be carefully considered and controlled in chamber experiments in order to produce data that can be reliably used in models to predict indoor concentrations. A good discussion of the effects of environmental parameters on mass-transfer processes as they relate to experiments conducted in chambers is provided by Tichenor (1989).

Temperature has large effects on mass-transfer processes. It determines the vapor pressures of the compounds, and therefore, the rates of evaporation of the compounds from materials. It affects the rates at which compounds sorb onto and desorb from surfaces. Since these rates are not necessarily equal, a change

in temperature can alter the relative partitioning of VOC between the gas phase and sinks. Temperature also affects diffusion rates both in air, and perhaps more importantly, in the materials themselves.

The air exchange rate and the material loading ratio (L), which is the surface area of the material per unit of chamber volume (m²/m³), largely determine the concentration of VOC in the air in the chamber. Generally, chamber experiments should be conducted using a ratio of air-exchange rate (N) to loading ratio of material that approximates the N/L ratio in the building environment the investigator is trying to simulate. This should result in concentrations of VOC in chamber air that are similar to air concentrations in the building. A decrease in air exchange rate or an increase in loading will increase the concentration in air which decreases the diffusion gradient between the material and the bulk air. This decrease in the driving force can lower the emission rates of compounds if the emissions process is limited by mass-transfer effects.

Air velocity and mixing in the chamber are important because they affect the thickness of boundary layers of air at the surfaces of materials. It may be difficult to achieve the correct air velocity and mixing in experiments conducted in environmental chambers. The average air velocity in various buildings was found to be approximately 10 cm/sec (Kovanen et al., 1987). Since chambers are typically maintained at nearly isothermal conditions, thermal gradients, which are a relatively large driving force for air movement in buildings, are minimized. Therefore, air velocities in chamber experiments that are conducted at ventilation rates that are typical for buildings are expected to be lower than 10 cm/sec. As a result, thick boundary layers can develop and emission rates can be suppressed. Often small mixing fans are added to chambers to overcome this problem. However, these fans can easily introduce too much turbulence and, therefore, artificially enhance emission rates.

The effects of water vapor on emission rates of hydrophobic organic compounds are generally minor compared to the effects of other environmental parameters. Water vapor can, however, modify sink effects. For example, an increase in humidity can reduce the number of available active sites on surfaces and reduce the amount of VOC sorbed onto these surfaces.

Sink Effects

The understanding and measurement of sink effects is essential if indoor air quality models are to be used to accurately predict concentrations of VOC in buildings. All types of materials in buildings can act as sinks. The magnitude of sorption onto these materials is determined by the composition of their surfaces and their surface areas. The amount of sorption is also dependent upon the compound. At this time, there are no general rules which can be used to predict sorption effects, except that compounds with low room-temperature equilibrium vapor pressures are expected to be most readily lost to surfaces. The net effect of sinks in a building is to spread emissions of VOC over longer time periods. The implication for human exposure, is dependent upon the behavior of the sinks and the time-activity patterns of the occupants.

Seifert and Schmahl (1987) investigated sorption effects for selected compounds and surfaces found in indoor environments. Two types of carpeting, plywood and the glass walls of the chamber were shown to remove VOC; but, the effects varied considerably for the different compounds that were examined. In experiments on the emission of DCB from moth crystal cakes, a substantial amount of DCB

was sorbed onto the walls of stainless-steel chambers (Tichenor et al., 1990). In subsequent experiments in a test house, 40 percent of the emissions of DCB were estimated to be lost to surfaces.

Data Analysis

The emission rates of VOC from materials and products are usually best expressed as mass of compound emitted per unit area or mass of source per unit time (e.g., mg/m²-h). The method for calculating emission rates depends on the emissions characteristics of the source.

The simplest case is a source which emits at a relatively constant rate over the time period of interest. In this case, the concentrations of VOC will initially exponentially increase from zero and reach and maintain a constant steady-state value. Assuming that the chamber is an ideal, continuously stirred tank reactor and that there are no losses to sinks, the steady-state source strength is calculated using Equation 5.1. The emission rate (mg/m²-h) is then calculated by dividing the source strength by the area (or mass) of the source. If the rate of loss of VOC to sinks, such as chamber walls, can be measured, this loss term can be incorporated into the calculation by adding it to the ventilation rate in Equation 5.1.

The calculation and interpretation of emission rates is more difficult for sources with high initial emission rates that rapidly decrease with time. Emissions of VOC from paints and various coatings, adhesives, and other products with relatively high solvent contents typically exhibit this temporal behavior. It is important to carefully consider the study objectives when designing experiments to measure emission rates from these products. For example, an experiment to estimate the exposure to workers applying a product might dictate different protocols and methods of data analysis than an experiment to estimate the more long-term exposure to occupants of a building in which the product has been used. In the former case, the emission rate during the usage period is of most importance. It is during this period that maximum concentrations occur which are often strongly influenced by the worker's activities, for example, brushing or rolling of a paint.

Tichenor (1989) described a method of data analysis for calculating an emission rate for the initial, undisturbed drying period after applying a wet source such as a paint. Typically, the change in the emission rate, R, can be approximated by a first-order decay of the form:

$$R = R_0 e^{-kt} (5.2)$$

where R_0 is the initial emission rate (mg/m^2-h) , k is the first-order rate constant, and t is time (h). Using a non-linear, least squares regression of the concentration versus time data from the chamber, values of R_0 and t are obtained. A similar method of data analysis is described by Colombo *et al.* (1990). This method empirically fits an equation to the data that describes concentrations in a chamber which increase from zero, pass through a maximum and then decline toward zero or some intermediate plateau.

For many products, calculation of emission rates during undisturbed drying may not provide a realistic estimate of exposures to VOC during actual usage by workers or consumers. For example, in chamber experiments in which paint removers and aerosol sprays containing dichloromethane were used by a worker, source strengths and personal exposures were found to be highest when brushing or spraying the products (Girman and Hodgson, 1986). Emissions during undisturbed drying of the products were relatively very low. In these experiments, concentrations of dichloromethane were continuously measured.

Exposures were calculated by integrating the areas under the concentration versus time curves. Theoretical estimates of concentration versus time were also developed from the measured average usage of the products during the experimental periods. Exposures obtained by integrating the theoretical curves closely agreed with the measured exposures.

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Glossary of Terms

Abbreviation Definition

ABS Acrylonitrile-butadiene-styrene plastic

BTU British Thermal Unit

°C degrees Celsius

C.C. Contra Costa

Cn n-carbon alkane

CARB California Air Resources Board

cig. cigarette

cm² square centimeter conc. concentration

CTCP Clinical Toxicology of Commercial Products

2,4-D an insecticide
DCB p-dichlorobenzene

DEHP di(2-ethylhexyl)phthalate
DFBA decaflourobenzaldehyde azine

dia. diameter

DNPH 2,4-dinitrophenyl hydrazine
EPA Environmental Protection Agency
ETS environmental tobacco smoke

g gram

GC gas chromatography

GC/ECD gas chromatography / electron capture detection GC/FID gas chromatography / flame ionization detection

GC/MS gas chromatography / mass spectrometry
GC/TEA gas chromatography / thermal energy analysis

 $\begin{array}{ll} h & \quad \ \ \, hour \\ h^{-1} & \quad \ \, per \ hour \end{array}$

HPLC high performance liquid chromatography

HSDB Hazardous Substances Data Bank IACP Integrated Air Cancer Project

IARC International Agency for Research on Cancer

kg kilogram l liter

L.A. Los Angeles

l/min. liters per minute (flow rate)

LOD limit of detection

 $\begin{array}{ccc} m & meter \\ m^2 & square meter \\ m^3 & cubic meter \end{array}$

MDA 4,4'-methylenedianiline

μg microgram

μg/g microgram per gram (concentration)

Abbreviation Definition

 μ g/h microgram per hour (emission rate) μ g/l microgram per liter (concentration)

μg/m³ microgram per cubic meter (concentration)

 $\mu g/m^2$ -h microgram per square meter per hour (specific emission rate) $\mu g/m^3$ -h microgram per cubic meter per hour (specific emission rate)

mg milligram

mg/cm²-h milligram per square centimeter per hour (specific emission rate)

mg/kg milligram per kilogram (concentration)
mg/h milligram per hour (emission rate)

mg/m³ milligram per cubic meter (concentration)
mg/person-day milligram per person per day (emission rate)

ml milliliter

ml/min. milliliters per minute (flow rate)

N number of items in set

NASA National Aeronautics and Space Administration

NDEA N-nitrosodiethylamine NDMA N-nitrosodimethylamine

ng nanogram

ng/kJ nanogram per kilojoule NMOR N-nitrosomorpholine

No. number

NVOC National Volatile Organic Compound Database

PCP pentachlorophenol

POM particulate organic matter

pos. positive

ppb part per billion (by weight)
ppbv part per billion by volume
ppm part per million (by weight)
ppmv part per million by volume

PTEAM Particulate Total Exposure Assessment Methodology

PVC polyvinyl chloride

SASS Source Assessment Sampling System

SUMMA passivation process for sampling containers

TCE 1,1,1-trichloroethane
TEA thermal energy analysis

TEAM Total Exposure Assessment Methodology

vent. ventilation

VOC volatile organic compound

% (w/w) weight percent

XAD styrene-divinylbenzene polymeric resin

APPENDIX

Bibliographic Database

The following is a listing of all of the reference citations contained in the bibliographic database that was created as part of this study. This database contains the citations that were found on the indoor sources, indoor concentrations, and source emissions of the 47 compounds under review and on methods used to measure emissions of VOC. The database was created using an IBM-compatible personal computer and "Pro-Cite," a bibliographic software package developed by Personal Bibliographic Software, Inc. (Ann Arbor, MI). Most of the records contain abstracts, key words, and compound and subject index terms. The database can be searched and sorted by any of more than twenty fields for each record.

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