FINAL REPORT

Environmental Fate of Low Vapor Pressure – Volatile Organic Compounds from Consumer Products: A Modeling Approach

(Contract Number: 13-304)

Prepared for:

The California Air Resources Board and the California Environmental Protection Agency

Prepared by:

Principal Investigator:
Deborah H. Bennett

Department of Public Health Sciences
University of California, Davis
One Shields Avenue
Davis, CA 95616
(530)754-8282

Co-Investigators:
Hyeong-Moo Shin[1], Thomas E. McKone[2]

[1]Department of Public Health Sciences, University of California, Davis
[2]School of Public Health, University of California, Berkeley

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DISCLAIMER

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ABSTRACT

Low vapor pressure-volatile organic compounds (LVP-VOCs) are exempt from the VOC content limits for consumer products and are defined in the California Code of Regulations. To evaluate the availability of LVP-VOCs that may contribute towards ozone formation from the use of consumer products, this report describes the development of modeling tools for two potential modes of releases during the use of consumer products (i.e., direct release to the outdoor air and disposed down the drain). For the fate of LVP-VOCs found in some consumer products used in down-the-drain applications (e.g., laundry detergents, fabric softeners, dishwashing detergents, and other laundry products), we applied a wastewater treatment plant (WWTP) fate model to predict the fraction of LVP-VOCs that may volatilize at WWTPs. For the portion of the LVP-VOCs volatilized to air during product use, we applied a multi-compartment mass-balance model to track the fate of LVP-VOCs in a multimedia urban environment. Based on the modeling results for the selected 33 LVP-VOCs, loss by volatilization in a WWTP is negligible for most compounds, suggesting that a majority of the LVP-VOCs will not be available for ozone formation reactions in the atmosphere once they are disposed down the drain. In contrast, for the LVP-VOCs in a consumer product that is volatilized to air and is assumed to be in the gas phase, greater than 90% will remain in the air and may participate in photochemical reactions either at the source location or in the downwind areas. Comparing results from these two modes of releases emphasizes the importance of determining the fraction of LVP-VOCs volatilized versus the fraction disposed down the drain when a product is used by consumers. The results from this study can provide important information and modeling tools to evaluate the impact of LVP-VOCs on air quality.

EXECUTIVE SUMMARY

Background: The amounts of low vapor pressure-volatile organic compounds (LVP-VOCs) in some consumer products are not currently included in determining compliance with the VOC limits in the California Air Resources Board (CARB)'s Consumer Products Regulations [1]. Many LVP-VOCs do not volatilize quickly enough to be emitted into the atmosphere under normal conditions of consumer products use. Compounds that are not emitted into the atmosphere (i.e., do not evaporate) are not available to react in the atmosphere to form ozone. CARB's LVP-VOC exemption was designed to account for the fact that in some product formulations, under certain conditions of use, some LVP-VOCs will evaporate very slowly or not at all due to low vapor pressures. However, some LVP-VOCs have been found to evaporate nearly as rapidly as the traditional high-volatility solvents [2] and thus can be additional contributors to ozone formation depending on their emission rate, the portion remaining in the gas phase, and their reactivity.

To evaluate the availability of LVP-VOCs that may contribute towards ozone formation requires an estimation of: (1) the fraction of LVP-VOCs that may evaporate during the use of consumer products and the fraction that is disposed of down the drain, (2) for the fraction that evaporates during use, the portion that remains in the gas phase, and (3) for the fraction of the product going down the drain, the portion that is subsequently emitted into the gas phase from a wastewater treatment plant (WWTP) or from subsequent surface water discharge. After estimating the total amount of LVP-VOCs emitted from the use of consumer products, one then needs to run an atmospheric chemistry model to determine the contribution of emitted LVP-VOCs towards ozone formation.

The scope of this work was the estimation of what portion of the LVP-VOCs emitted during product use remains in the gas phase, and the estimation of the fraction of LVP-VOCs that is subsequently emitted into the gas phase from products disposed of down the drain. Thus, multi-compartment models that are capable of modeling the fate of LVP-VOCs need to be carefully evaluated with regard to forecasting the fraction of LVP-VOCs that leads to formation of ozone following emissions. Compared to those directly emitted to ambient air during product use, LVP-VOCs from consumer products that are disposed down the drain undergo different competing processes (e.g., biodegradation and partitioning between water and solid phases) in a WWTP and thus might result in emissions to atmosphere from a WWTP or from rivers to which effluent is released—releases that differ significantly from the emissions generated directly upon use of a consumer product. Thus, there is also a need to carry out research to (1) develop WWTP fate models to determine the total amount of LVP-VOCs emissions that may occur at a WWTP and from the WWTP discharge and (2) develop an integrated model that connects a multi-compartment model and a WWTP fate model that tracks emission rates from a WWTP or in the discharge zone of the facilities. We note that the environmental fate model was used in this study to estimate how much of the major LVP-VOCs used in consumer products that have already made their way into the outdoor atmosphere will remain in the air and participate in ozone formation. The question of how much LVP-VOCs will be released to outdoor air (volatilized directly outdoor, or volatilized indoor and then ventilated to outdoor) during the use of consumer products is beyond the scope of this work. We also note that this study did not determine the amount of ozone formed. More complex atmospheric chemistry models need to be used in conjunction with our results to determine the amount of ozone formed in the atmosphere.

The overall objective of this study is to develop and evaluate environmental fate modeling tools to determine (1) what portion of a LVP-VOC volatilized to air from the use of consumer products will remain in the urban air gas phase to participate in ozone formation reactions and (2) what portion of a LVP-VOC disposed down the drain from consumer product use (e.g., laundry detergents, fabric softeners, dishwashing detergents, and other laundry products, etc.) will be emitted to air and subsequently available for ozone formation. Comparing results (i.e., the overall fraction available for ozone formation) from these two modes of releases (i.e., direct release to outdoor air and disposed down the drain) allows air-quality researchers to understand the importance of determining the fraction of LVP-VOCs volatilized or disposed down the drain when the product is used by consumers.

Methods: This study calculates and compares the fraction of consumer product LVP-VOCs available for ozone formation as a result of (i) volatilization to air during product use and (ii) down-the-drain disposal. The study also investigates the impact of different modes of releases on the overall fraction available in ambient air for ozone formation. For the portion of the LVP-VOCs volatilized to air during product use, we applied a multi-compartment mass-balance model to track the fate of emitted LVP-VOCs in a multimedia urban environment. For the portion of the LVP-VOCs disposed down the drain during product use, we applied a WWTP fate model to predict the emission rates of LVP-VOCs to air at WWTPs or at the discharge zone of the plants and then used these results as emissions in the multi-compartment environmental model.

Models that describe the fate of chemicals in a WWTP or in an ambient environment system have been developed with different modeling features (e.g., biodegradation, volatilization, etc.) and different model compartments (e.g., air, water, urban film, etc.). Therefore, we reviewed existing models that are suitable for simulating the fate and transport of LVP-VOCs in an urban multimedia environment and a typical WWTP. We describe here the similarities and differences between models for each system (i.e., an urban multimedia environment and a WWTP). To address the implications of the differences between the two modes of releases on the model results (i.e., the overall fraction available for ozone formation), we also selected one representative model as optimum for each mode of release (i.e., disposed down the drain and direct release to outdoor air). In addition, to address ozone formation issues for Southern California, we described how critical it is to use input parameters and model conditions representative of the South Coast Air Basin (SoCAB), an area with an extreme ozone non-attainment. Lastly, we evaluated the necessity of a two-box regional airshed model and inclusion of dynamic conditions in the multi-compartment models and presented model results for steady-state and dynamic conditions.

Results: In a WWTP, the LVP-VOCs selected in this study are primarily either biodegraded or removed via sorption to sludge depending on the magnitude of the biodegradation half-life and the octanol-water partition coefficient (K_{ow}). The majority of the selected 33 LVP-VOCs had no evaporation from a WWTP and less than 11% is available for ozone formation for the other five compounds/mixtures. In contrast, for the LVP-VOC in a consumer product that is volatilized to air and is assumed to be in the gas phase, greater than 90% is available for photochemical reactions either at the source location or in the downwind areas. In addition, for LVP-VOCs with small Henry's law constant and high K_{ow}, model conditions such as rain events and the composition of a model compartment influence the mass distribution among environmental compartments. We also found that loss by reaction in other compartments such as soil and vegetation is negligible for most compounds, confirming that losses by reaction due to OH radicals or by air advection are the main loss mechanisms. In other words, once LVP-VOCs are volatilized into air, more than 90% is available for ozone forming reactions either on the day of releases or on the following day. Compared to daytime, the fraction of the compound degraded in all compartments can be ignored during nighttime due to small OH radical concentrations and low temperature. This fraction will be available for ozone formation the next day. We also found that LVP-VOCs discharged to surface water from a WWTP are not likely to be volatilized to air, but rather are biodegraded in water or sediment.

Conclusions: Because of the extreme differences between the predicted portion of the compounds available for ozone forming reactions from emissions to air during product use and that from down-the-drain disposal leading to a WWTP, reliable prediction of the fraction of compounds volatilized to air during the use of consumer products becomes critical for determining the fraction of LVP-VOCs available for ozone forming reactions in many product classes. The modeling effort in this study allows air-quality researchers to understand the importance of determining the fraction of LVP-VOCs volatilized or disposed down the drain when the product is used by consumers.

1. INTRODUCTION

1.1. Background

The formation of ground-level ozone is caused by the gas-phase interactions of emitted volatile organic compounds (VOCs) and oxides of nitrogen in the presence of sunlight. The top three reactivity-based anthropogenic VOC emission sources in California's South Coast Air Basin (SoCAB) are light-duty passenger cars, off-road equipment, and consumer products [3]. "Consumer product" means a chemically formulated product used by household and institutional consumers, including, but not limited to, detergents; cleaning compounds; polishes; floor finishes; cosmetics; personal care products; home, lawn, and garden products; disinfectants; sanitizers; aerosol paints; and automotive specialty products; but does not include other paint products, furniture coatings, or architectural coatings [1].

A low vapor pressure – volatile organic compound (LVP-VOC) is a chemical "compound" or "mixture" that has a relatively low vapor pressure (less than 0.1 mm Hg at 20°C) or high boiling point (greater than 216°C) and is defined by the California Air Resources Board (CARB)'s Consumer Products Regulations (Title 17, California Code of Regulations, section 94508(a)) [1]. These are compounds with low volatility and low potential to be transferred to air. The amounts of LVP-VOCs in some consumer products are not included in determining compliance with the VOC limits in the CARB's Consumer Products Regulations [1] because they are assumed to be non-volatile and thus not available for ozone formation. However, some LVP-VOCs have been found to evaporate nearly as rapidly as the traditional high-volatility solvents [2] and thus can be additional contributors to ozone formation depending on their emission rate, the portion remaining in the gas phase, and their reactivity.

One measure of the ozone formation potential of VOCs in the gas phase is the maximum incremental reactivity (MIR), which is the mass of ozone produced per unit mass of VOC precursors introduced [4-7]. Updated MIR values are available for VOCs and LVP-VOCs [8]. Some LVP-VOCs have higher MIR values than ethane, the threshold compound for negligible reactivity used by the U.S. Environmental Protection Agency (EPA) [9]. This indicates that if LVP-VOCs used in consumer products are emitted into the atmosphere, they can contribute to ozone formation. To evaluate the ozone formation potential of LVP-VOCs used in consumer products, both what is emitted from the product and what remains in the air should be considered in addition to MIR values.

For most chemicals in consumer products, only limited information is available about potential volatilization of the compound during the product use and the subsequent impact on outdoor air quality. The release rate and amount of a LVP-VOC transferred into the atmosphere depend not only on the volatility of the individual compound, but also on the type of products in which the compound is used, the product formulation, and the product form (i.e., aerosol, liquid, etc.). In addition, the variability in the way a product is used by consumers may significantly affect the atmospheric availability of released LVP-VOCs for ozone formation. For example, when a product is applied for cleaning hard surfaces such as a kitchen floor with a sponge mop and water bucket, a portion of compound may be volatilized during scrubbing and mopping while the portion in the sponge mop and bucket is disposed down the drain at the end of the cleaning. If the cleaning product was used with paper towels, then a portion of compound may be volatilized during scrubbing and wiping while the portion in the paper towels is placed into a trash can, where a portion may volatilize and a portion may be disposed of to a landfill [10].

The fraction of LVP-VOCs that are volatilized and emitted to the ambient environment can then undergo transport among multiple environmental compartments by cross-media transfers that involve dispersion, advection, precipitation, dry deposition, and diffusion between air and other compartments. LVP-VOCs also undergo many different environmental processes, including transformation within each compartment (e.g., hydrolysis, oxidation, etc.). Multi-compartment mass-balance models that account for these environmental processes have been used to simulate the fate and transport of environmental contaminants and determine the contribution of VOCs to ozone formation [11, 12]. However, LVP-VOCs with low vapor pressure (*VP*) and large octanol-water partition coefficient (K_{ow}) values might preferentially partition into non-atmospheric compartments compared to VOCs, and thus while a portion of emitted LVP-VOCs might be available for forming ozone, they may be available over a much longer time period. Therefore, multi-compartment models that are capable of modeling the fate of LVP-VOCs need to be carefully evaluated with regard to forecasting the fraction of LVP-VOCs that leads to formation of ozone following emissions.

DeLeo et al. [13] estimated the “down-the-drain” load of consumer products to a wastewater treatment plant (WWTP) using the product formulation and market sales data and found that liquid laundry detergent contributes approximately 69% of the total influent mass of fatty alcohols to the WWTP, which in turn may result in ambient ozone formation if these compounds can volatilize into the air. In contrast to atmospheric processes, LVP-VOCs that are disposed down the drain undergo different competing processes in a WWTP and thus might result in a different portion of atmospheric releases (relative to consumer use) from WWTPs or from rivers to which effluent is released. Emission rate estimates of LVP-VOCs from a WWTP are limited by the lack of understanding about the relationship among other competing processes including biodegradation and partitioning between water and solid phases. Thus, there is also a need to carry out research to develop a WWTP fate model that connects with a multi-compartment model to track emission rates from a WWTP or in the discharge zone of the WWTPs.

1.2. Objectives

The overall objective of this study is to develop and evaluate environmental modeling tools to determine (i) what portion of a LVP-VOC volatilized to air from the use of consumer products will remain in the urban air gas phase to form ozone and (ii) what portion of a LVP-VOC disposed down the drain from consumer product use will be emitted to air and subsequently form ozone. Comparing results (i.e., the overall fraction available for ozone formation) from these two modes of releases (i.e., direct release to outdoor air and disposed down the drain) allows air-quality researchers to understand the importance of determining the fraction of LVP-VOCs volatilized or disposed down the drain when the product is used by consumers.

1.3. Compounds of interest

The list of target compounds was selected by the California Air Resources Board (CARB) with input from stakeholders. According to the U.S. EPA’s Chemical and Product Categories (CPCat) database [14], many of the selected compounds are commonly used in a variety of consumer products including laundry detergents, fabric softeners, dishwashing detergents, and other laundry products. Primary chemical classes of the finalized compounds include glycols, glycol ethers, hydrocarbon solvents, and esters. In order to predict the fate, transport, and portion of emitted LVP-VOCs that form ozone, we need a set of physicochemical properties. We used chemical abstracts service (CAS) registry numbers to find physicochemical properties from various chemical property estimation programs including U.S. EPA Estimation Program Interface Suite (EPI Suite^{TM}) [15]. The complete list of selected chemicals and their three basic and important chemical properties, K_{ow}, Henry's law constant (H), and vapor pressure (VP), are provided in Table 1. If available, the experimental values which are reported in the EPI suite or in other resources are also listed in Table 1. The experimental and estimated values in the EPI Suite are for 25 °C and standard atmospheric pressure. We have another column with experimental values at 20 °C provided by a Dow material safety data sheet (MSDS) search or other resources. We note that the estimated values may differ from experimentally determined values, because theoretical estimates of physical properties may in some cases not account for aspects of molecular structure that impact intermolecular interactions and physical properties. If measured values are available, the models can be run with the measured values. Some of the selected LVP-VOC solvents are hydrocarbon distillate mixtures typically containing dozens to hundreds of compounds (e.g., Iso-paraffinic Hydrocarbons, Distillates petroleum-hydrotreated middle, Conosol 260, Conosol 340, and Solvent Naphtha (Petroleum), Heavy Aliphatic). Therefore, we used a representative CAS number recommended by the U.S. EPA [16]. If experimental values are available, experimental values are chosen over estimated values for K_{ow} and VP.

1.4. Overview and scope of this study

The overall approach involves three separate steps to develop and evaluate our modeling methods. The first step (Study 1) is to apply a WWTP fate model to predict the portion of LVP-VOCs that may be volatilized in a WWTP or in the discharge zone of these WWTPs. The second step (Study 2) is to apply a multi-compartment mass-balance model to predict the portion of emitted LVP-VOCs in the gas phase that may participate in ozone forming reactions based on the premise that LVP-VOCs are released to air. The third step (Study 3) is to integrate results from a WWTP model and a multi-compartment mass-balance model to predict the fate of down-the-drain LVP-VOCs that are both volatilized from a WWTP and discharged into surface waters. California has a unique climate relative to most other parts of the country, with large portions of the state receiving rain on typically 5 or less hours from June to September. The model results presented in this study reflect input parameters and model conditions representative of the South Coast Air Basin (SoCAB), an area with an extreme ozone non-attainment. However, we provided California climate and geographic conditions and discussed which parts of California would have similar and different results, and how areas outside of California will have different results.

In general, LVP-VOCs in consumer products are not easy to evaporate as implied by their definition (relatively low vapor pressure and high boiling point). Thus, we note that the environmental fate modeling for this project started with LVP-VOCs that have already made it into the outdoor air. Determination of the fraction of LVP-VOCs volatilized during the use of consumer products is beyond the scope of this project. Compounds reach the outdoor air through evaporation during use outdoors, evaporation and subsequent ventilation when used indoors, or volatilization from WWTPs. We also note that this study only predicts the fraction of LVP-VOCs that may react with the OH radicals. More complex atmospheric photochemical models such as the U.S. EPA Community Multi-scale Air Quality Model (CMAQ) are needed to simulate how much ozone will be formed in the atmosphere. The scope of this study is depicted in Figure 1.

Models that describe the fate of chemicals in a WWTP or in an urban environment system have been developed with different modeling features (e.g., biodegradation, volatilization, etc.) and different model compartments (e.g., air, water, urban film, etc.). This study addresses the differences and variability in model results among various models, and later focuses on the implications of the differences between the two modes of releases (i.e., direct release to outdoor air and disposed down the drain) on the model results (i.e., the overall fraction available for ozone formation) by selecting one representative model as optimum for each mode of release (i.e., disposed down the drain and direct release to outdoor air). Moreover, because not all consumer products are disposed down the drain during use, we focused here mostly on a selected set of LVP-VOCs that are commonly used in those consumer products (e.g., laundry detergents, fabric softeners, dishwashing detergents, and other laundry products, etc.) likely to be not only volatilized to air during use, but also disposed down the drain.

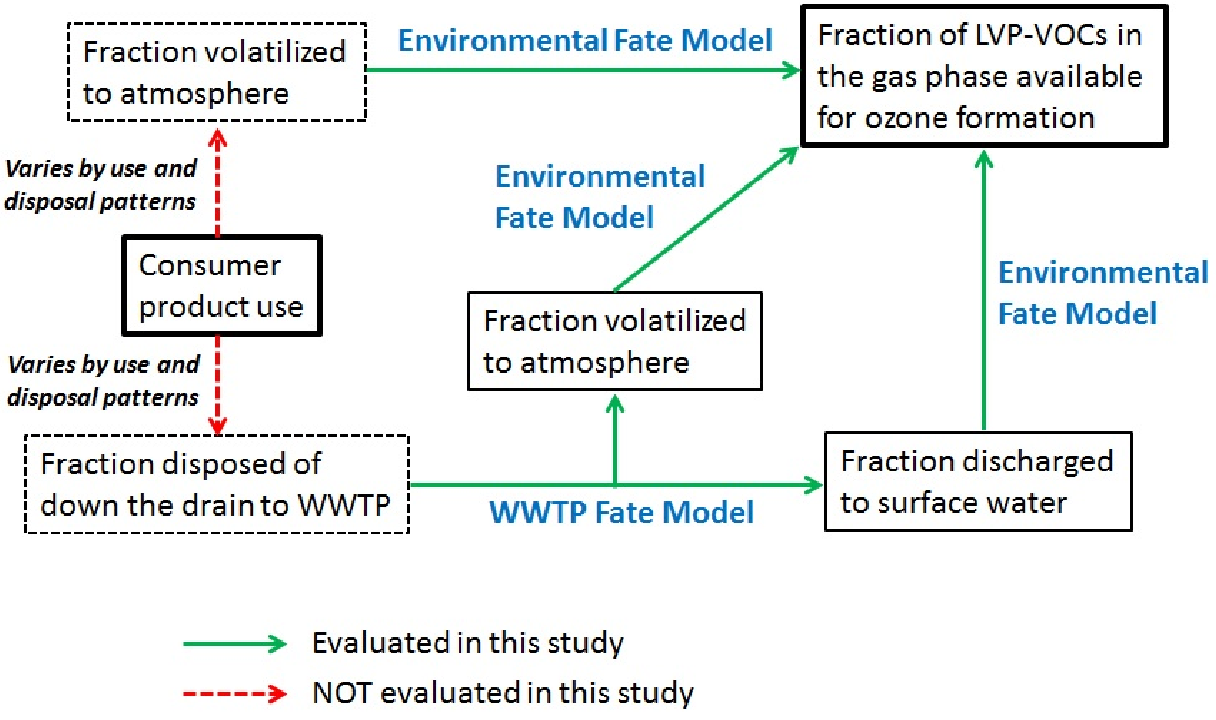

Figure 1. Schematic diagram of the scope of this study

Table 1. Estimated and experimental values of major chemical properties of target LVP-VOCs reported in the EPI Suite [15]. Experimental values reported in the EPI Suite or in other resources are listed in parenthesis where available.

Chemical class	Example compounds	CAS #	log K_{ow} (unitless)		H (Pa-m^3/mol)		VP (Pa)		
							25 °C		20 °C
Glycols (N=8)	Propylene Glycol	57-55-6	-0.8	(-0.9)	1.8E-2	(1.3E-3)	14.8	(17.2)	
	Diethylene Glycol	111-46-6	-1.5		2.1E-4		0.4	(0.8)	
	Ethylene Glycol	107-21-1	-1.2	(-1.4)	0.013	(6.1E-3)	8.1	(12.3)	
	Dipropylene Glycol	25265-71-8	-0.6		3.6E-4		1.0	(4.3)	
	Butylene Glycol	107-88-0	-0.3		0.023	(2.4E-04)	4.3	(2.7)	
	Triethylene Glycol	112-27-6	-1.8	(-1.8)	3.2E-6		0.03	(0.2)	
	Hexylene Glycol	107-41-5	0.6		4.1E-2		7.8	(1.7)	
	Polyethylene glycol	25322-68-3	-2.3		7.7E-10		4.0E-5		
Glycol Ethers (N=7)	Diethylene Glycol Ethyl Ether	111-90-0	-0.7	(-0.5)	8.7E-5	(2.3E-3)	12.5	(16.8)	(12.0) [a]
	Diethylene Glycol Monobutyl Ether	112-34-5	0.3	(0.6)	1.5E-4	(7.3E-4)	1.5	(2.9)	
	Dipropylene Glycol n-Butyl Ether	29911-28-2	1.1		2.7E-4		0.5		(5.3) [a]
	Dipropylene Glycol Methyl Ether Acetate	88917-22-0	0.7		7.6E-3		48.1		(10.7) [a]
	Dipropylene Glycol n-Propyl Ether	29911-27-1	0.6		2.0E-4		4.7		(10.7) [a]
	Ethylene Glycol Hexyl Ether	112-25-4	1.6	(1.9)	0.018	(0.032)	6.1	(20.7)	
	Triethylene Glycol Monobutyl Ether	143-22-6	0.02		2.4E-6		0.1	(0.3)	(0.2) [a]
Hydro-carbon solvents (N=6)	Iso-paraffinic Hydrocarbons	64742-47-8	6.2	(6.1)	9.5E+5	(8.3E+5)	31.5	(18.0)	
	n-Heptadecane	629-78-7	8.7		3.9E+6		0.4	(0.03)	
	n-Tridecane	629-50-5	6.7		2.9E+5	(2.9E+5)	12.3	(7.4)	
	Conosol 260	64742-46-7	7.7		1.3E+6	(1.3E+6)	2.0	(0.5)	
	Conosol 340	64742-46-7	7.7		1.3E+6	(1.3E+6)	2.0	(0.5)	
	Solvent Naphtha (Petroleum), Heavy Aliphatic	64742-96-7	6.7		1.3E+6	(2.9E+5)	12.3	(7.4)	
Esters (N=8)	Dimethyl Glutarate	1119-40-0	0.9	(0.6)	0.075	(0.065)	23.7	(24.0)	(13.3)[b]
	Methyl Palmitate	112-39-0	7.3	(7.4)	1.5E+3		0.06	(0.006)	
	2-ethylhexyl Benzoate	5444-75-7	5.2		26		0.1		
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	25265-77-4	3.0		8.3E-3		0.6	(1.3)	
	Glyceryl Triacetate	102-76-1	0.4	(0.3)	1.8E-4	(1.2E-3)		(0.3)	
	Isopropyl Palmitate	142-91-6	8.2		1.7E+3		0.03	(0.008)	
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	6846-50-0	4.9		0.95		1.1		
	Alkyl (C16-C18) Methyl Esters	67784-80-9	6.8		1.3E+3		0.013	(4.9E-4)	
Others (N=4)	Triethanolamine	102-71-6	-2.5	(-1.0)	4.2E-7	(4.1E-8)	4.5E-4	(4.8E-4)	
	Glycerol	56-81-5	-1.7	(-1.8)	6.4E-3	(1.8E-3)	0.01	(0.02)	
	Benzyl Alcohol	100-51-6	1.1	(1.1)	2.2E-2	(3.4E-2)	7.1	(12.5)	
	Stearyl Alcohol	112-92-5	7.7		53	(85)	2.6E-4	(3.6E-4)	

Note: The values from EPI Suite are for 25 °C and standard atmospheric pressure.
a. Dow MSDS search. b. http://www.epa.gov/hpv/pubs/summaries/dbe/c13453rt.pdf

2. WASTEWATER TREATMENT PLANT (WWTP) FATE MODELS

2.1. Introduction

2.1.1. Background

For some consumer products in the specific categories of laundry detergents, fabric softeners, dishwashing detergents, and other laundry products, a large portion is disposed down the drain during use and enters a wastewater treatment plant (WWTP). Thus, for LVP-VOCs used in these types of consumer products, it is critical to understand how those chemicals are treated in typical wastewater treatment processes. The most common method for treating sewage is to inject air (or oxygen) and active biological material (also known as activated sludge) in the sewage tank. A typical activated-sludge-type sewage treatment process is shown in Figure 2. In each tank, organic compounds in the influent are either (i) removed with the sludge, (ii) conveyed in a dissolved or suspended form to the subsequent treatment tank, (iii) volatilized from the water surface to the air, or (iv) biodegraded (decomposed by bacteria or other living organisms) [17]. In the primary and secondary settling tanks (see Figure 2 below), organic compounds adsorbed to solids, which are capable of settling, are removed by gravitational settling. In the aeration tank, depending on their properties, chemicals are biodegraded or leave the system in the effluent or by volatilization due to diffusion or aeration (the process by which air is circulated through). For simplicity, loss to air by aeration is referred to as a volatilization process. In the secondary settling tank, although the ratio of recycled activate sludge rate to waste activated sludge can be highly variable based on the operator and influent wastewater characteristics, most of the settled sludge (~98%) is returned to the aeration tank to maintain the concentration of activated sludge and the remaining sludge is removed from the system for further treatment [17].

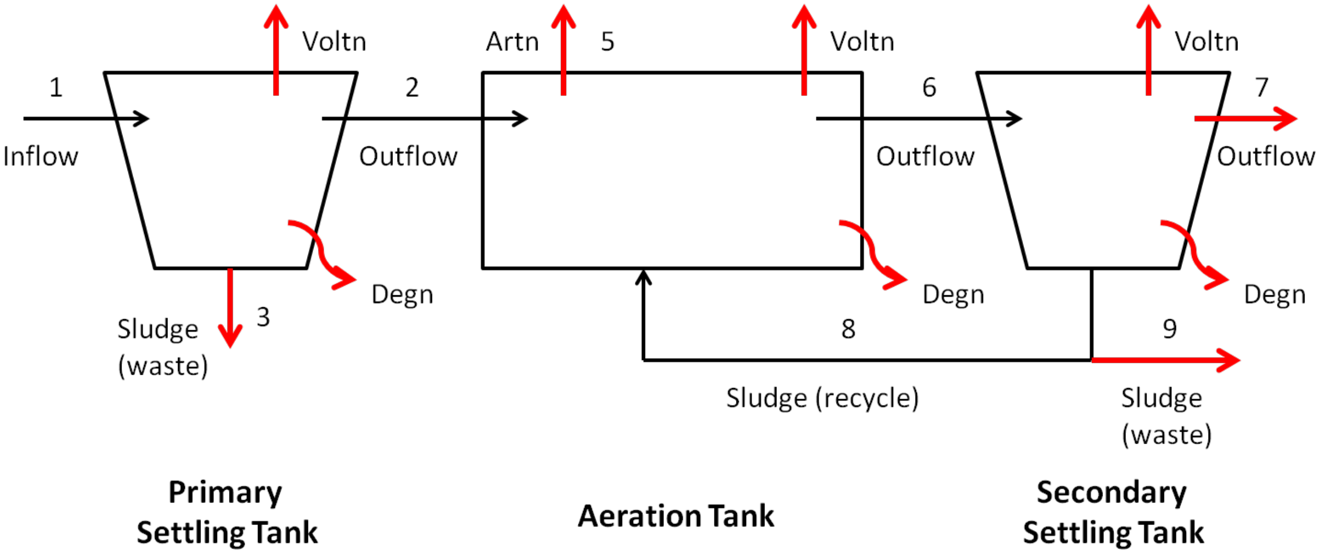

Figure 2. Schematic diagram of a typical activated sludge-type sewage treatment plant (excerpt from Seth et al. [18]). Voltn = volatilization; Artn = aeration loss; Degn = degradation. The mass transferred through the volatilization and aeration flows in the aeration tank is combined and referred to as volatilization in this analysis.

Relative removal amounts via the three removal processes (i.e., volatilization, biodegradation, sorption to sludge) depend on chemical properties including Henry's law constant (H), biodegradation half-life ($t_{1/2}$), and octanol-water partition coefficient (K_{ow}) as well as plant operating conditions (e.g., temperature, volume of tank, aeration rate, etc.). Under the same plant operating conditions, Lee et al. [19] classified compounds by chemical properties and primary removal processes. For highly hydrophobic compounds (partition coefficient between solids and water, K_d, > 0.01 m^3 water/g solids), adsorption to sludge and biodegradation are very important removal processes. For compounds with moderate to high volatilities (H = 0.001 to 0.1 m^3 water/m^3 air), the fraction of volatilization from the surface of the primary and secondary settling tanks can be important, especially when these compounds are not biodegradable. For highly volatile compounds ($H > 0.1$ m^3 water/m^3 air), aeration in the aeration tank can be a major removal process. Among input parameters, the most uncertain input variable is the biodegradation half-life during sewage treatment processes because it cannot be directly estimated from the molecular structure of a chemical.

2.1.2. Objectives

The overall objective of the wastewater treatment plant fate models is to determine the fraction of LVP-VOCs volatilized from a WWTP. Specific objectives are (i) to understand the fate of down-the-drain LVP-VOCs in a WWTP and in the discharge zone of the plants and (ii) to evaluate sensitive and uncertain input parameters and model conditions on the fate of LVP-VOCs in a WWTP.

2.2. Review: WWTP fate models

We reviewed models that were developed to predict the fate of various chemical substances in a WWTP. Depending on the compounds of interest (e.g., volatile or hydrophobic compounds), some models include all three removal processes [17-24] while others focus on studying one or two processes [25-29].

WWTP models are classified into three categories: (i) conventional concentration-based models, (ii) fugacity-based models, and (iii) combination of concentration- and fugacity-based models. Namkung and Rittmann [23], Clark et al. [17], and Struijs et al. [24] are representative models for each of these three categories, respectively. As these models were developed several years ago, all other models developed after these three models were published are descendants of each of these three models. More features of removal mechanisms and handling various types of compounds are added to later models to improve model predictions. Model names (if available), model type (conventional or fugacity or combination), a range of applicable vapor pressure, and removal processes are summarized in Table 2.

Table 2. Models describing the fate of organic chemicals in a WWTP

Model name	Model type	VP range (Pa)		Surface aeration	Bubble aeration	Volatilization	Biodegradation	Adsorption	Handling ionizing compound?	Methods available to select biodegradation rate?	Biodegradation in liquid (L) or solid (S)	Replicable?	References
		Min	Max										
	Fugacity	8.0E-05	1.7E+04	N	Y	Y	Y	Y	N	N	S	Y	Clark et al. [17]
STP-EX	Fugacity	1.3E-05	2.2E+05	Y	Y	Y	Y	Y	Y	Y	L	Y	Seth et al. [18]
SimpleTreat	Fugacity+ Conventional	1.8E+03	1.7E+04	Y	Y	N	Y	Y	Y	N	L	Y	Struijs et al. [24]; Mikkelsen et al. [30]; Franco et al. [31]
	Conventional	1.3E+03	5.8E+04	N	N	Y	Y	Y	N	N	S	Y	Namkung and Rittmann [23]
WW-TREAT	Conventional	4.8E-15	1.2E-06	N	N	Y	Y	Y	N	N	L/S	N	Cowan et al. [21]
TOXCHEM	Conventional	2.3E+02	5.8E+04	Y	Y	N	Y	Y	N	N	S	N	Melcer et al. [22]
	Conventional	2.7E-03	5.8E+04	N	Y	Y	Y	Y	N	N	L	N	Lee et al. [19]
	Conventional	1.5E-09	8.0E+04	N	N	Y	Y	Y	N	N	L	N	Byrns [20]
		1.1E+01	1.7E+04	Y	N	N	N	N	N	N	N/A	N	Hsieh et al. [26]
		1.1E+01	1.7E+04	N	Y	N	N	N	N	N	N/A	N	Hsieh et al. [25]
	Conventional	3.7E-19	1.7E-05	N	N	N	Y	Y	N	N	N/A	N	Plosz et al. [32]
	Conventional	2.5E+03	6.5E+04	Y	Y	N	N	N	N	N	N/A	N	Roberts et al. [27]
	Conventional	2.3E+02	2.7E+04	N	Y	Y	N	N	N	N	N/A	N	Tansel and Eyma [28]
	Conventional	6.8E-08	6.8E-01	N	N	N	Y	Y	N	N	S	N	Urase and Kikuta [29]

Note: Vapor pressure for the selected LVP-VOCs ranges from 4.0 × 10^{-5} to 48.1 Pa at 25 °C. Studies that include compounds with vapor pressure within the same range as the LVP-VOCs are Clark et al. [17], Byrns [20], and Seth et al. [18]. N/A: not available.

2.2.1. Conventional concentration-based models

Namkung and Rittmann [23] first developed a concentration-based fate model for VOCs which simulates all removal processes (i.e., volatilization, biodegradation, sorption to sludge). This model only accounts for the removal processes in an aeration tank. Assuming a steady-state mass flow of chemicals in the aeration tank, the model calculates individual rates for volatilization, biodegradation, and adsorption to sludge based on the steady-state chemical concentration in the aeration tank. Patterned after the Namkung and Rittmann model, Cowan et al. [21] developed a model which includes a primary settling tank as an additional module in the original Namkung and Rittmann model and modifications to the biodegradation and adsorption terms in the activated aeration tank module. Following the basic principles of the Namkung and Rittmann model, Melcer et al. [22] developed a model for VOCs by adding a secondary settling tank and a grit chamber (a pretreatment system designed to include a slow flow of wastewater so that heavy solid materials such as sand, coffee grounds, etc. can be removed due to gravitational settling) as additional modules. The Namkung and Rittmann model was also modified to simulate the fate of VOCs under dynamic conditions. As an improvement of the previous three models (Namkung and Rittmann, Cowan et al. and Melcer et al.), Lee et al. [19] developed a model for hydrophobic and volatile compounds by incorporating four additional features, which include (i) relating biodegradation processes to the growth of bacteria, (ii) the ability for biodegradation in the sorbed phase in addition to the dissolved phase, (iii) addition of the bubble volatilization of volatile compounds by surface aeration (the procedure of adding oxygen to the surface of the water), and (iv) addition of surface volatilization as a removal mechanism during bubble volatilization. Byrns [20] also developed a model following the scheme developed by Namkung and Rittmann. The major difference between the two models is that Byrns separately calculated the biodegradation rate of chemicals in a dissolved phase and those that are sorbed on the biomass solids.

2.2.2. Fugacity-based models

Clark et al. [17] developed a fugacity-based fate model for a wide range of organic compounds. As shown in Figure 2, this model includes three stages of treating the influent sewage: (i) primary settling tank, (ii) aeration tank (or biological reactor), and (iii) secondary settling tank. In each stage, mass balance equations are established for water, solids, and a chemical with the use of the fugacity approach. Here, fugacity can be regarded as the partial pressure or the tendency of a chemical to leave or escape from a given state or compartment [33]. The U.S. EPA has adopted the Clark et al. model in the EPI Suite as a tool for predicting a chemical's behavior in an activated-sludge-type sewage treatment plant. As an extended version of Clark et al. model, Seth et al. [18] presented the 'STP-EX' model, which incorporates additional features that are also included in similar models such as 'SimpleTreat' [34] and 'ASTREAT' [35]. The 'STP-EX' model includes the capability of handling ionizing compounds and the flexibility of specifying a separate biodegradation rate constant. In contrast to the Clark et al. model that calculates biodegradation rates in the solid phase, biodegradation was assumed to occur only in the aqueous (dissolved) phase in the 'STP-EX' model, as chemicals sorbed to solids may not be available for biodegradation [36]. In addition to bubble aeration, chemical loss by surface volatilization in the aeration tank is included in the 'STP-EX' model.

2.2.3. Combination of concentration- and fugacity-based models

Struijs et al. [24] developed a multimedia box model that incorporates many features used in a concentration-based model (e.g., chemical concentration in dissolved and solid phases in the primary tank and aeration tank) and applies the concept of fugacity when calculating mass balances of each box. The Struijs et al. model is widely used in European countries and has evolved with modifications to model components and features. Specifically, Mikkelsen et al. [30] presented a modified version of Struijs et al. model to apply the conditions of Danish WWTPs. They made modifications in the calculation of mass transfer by stripping, added the flexibility of the model without a primary settling tank, and used the fixed volume of the aeration tank. Franco et al. [31], another study conducted by Struijs and his colleagues to improve Struijs et al. model, also expanded the applicability of the Struijs et al. model by incorporating sorption regressions that can be used to describe the partitioning behavior of the ionized fraction of an organic chemical.

2.2.4. Selected models

Using the versions of each type of model that include all removal processes, we tried to replicate model results to determine if they are applicable for predicting the fate of a wide range of LVP-VOCs. Because the relative removal amounts via three removal processes are dependent on chemical properties [19], we did not think it was appropriate to use a model that did not include all processes and so models without all processes were not considered. We were able to replicate model results for four models (i.e., fugacity-based models by Clark et al. [17] and Seth et al. [18], conventional concentration-based models by Namkung and Rittmann [23], and combination of concentration- and fugacity-based models by Struijs et al. [24]) and these were selected for further model comparison. However, the rest of the models could not be replicated for a variety of reasons, listed below, and thus were excluded for model comparison. We excluded Byrns [20] because the mass balance for the activated sludge model is not correctly presented in their paper (i.e., the influent concentration to the biological reactor is assumed to be same as the effluent concentration from the biological reactor) and a value of hydraulic retention time for computing a biodegradation rate is not given. This model is very similar to Namkung and Rittmann, which was replicated. We excluded Cowan et al. [21] because input parameters for volatilization were not given. This model adds a primary settling tank to Namkung and Rittmann and modifies the biodegradation and adsorption terms. The added components are included in the fugacity models and thus we use those models to evaluate the impact of these components. We also excluded Melcer et al. [22] because basic input parameters such as chemical properties and plant operating variables are not given in the paper. Similarly, Melcer et al. adds additional components to the basic Namkung and Rittmann model and the impact of these components can be evaluated through the fugacity models. For Lee et al. [19], the concentration for the active biomass, a critical input parameter for biodegradation, cannot be derived from the given equations and thus this model was excluded. Nevertheless, three of four modifications added by this model to the basic Namkung and Rittmann model can be evaluated through the fugacity models.

2.2.5. Pros and cons of selected models

Namkung and Rittmann's model predicts the fate of VOCs only in an aeration tank. Because of the small K_{ow} of VOCs, predicted loss by sorption to sludge is negligible (<0.5%) compared to volatilization by diffused (bubble) aeration or biodegradation. Therefore, although this model might be applicable for estimating VOC emission rates in an aeration tank, it is not suitable to predict the fate of chemicals with a wide range of chemical properties as required for this project. In contrast, Clark et al., Seth et al., and Struijs et al. models simulate the fate of organic chemicals with a wide range of chemical properties in all three stages of a typical WWTP as shown in Table 2. For example, results from Clark et al. [17] indicate that volatile compounds are removed primarily by bubble aeration in an aeration tank (e.g., 1,1,1-trichloroethane), compounds with relatively large biodegradation rates are removed mainly by biodegradation in an aeration tank (e.g., naphthalene), and large amounts of hydrophobic compounds are adsorbed to sludge or solids in a primary settling tank or a secondary settling tank and thus removed from wastewater (e.g., pyrene).

The biodegradation rate during sewage treatment processes is not available for most chemicals. Namkung and Rittmann model and Struijs et al. model did not provide a criterion or a procedure to choose the biodegradation rate, which limits model application to LPV-VOCs in the list that the California Air Resources Board (CARB) provided. Compounds without biodegradation information were assigned '0'm^3/g of a biodegradation rate for Namkung and Rittmann. On the other hand, Seth et al. [18], an extended study of Clark et al. [17], provided a scheme to select the biodegradation half-life in wastewater from the aqueous biodegradation half-life in natural water using quantitative structure-activity (property) relationship (QSA(P)R) principles.

When ionic substances (acids or bases) dissolve in water, their ions separate from one another in a process called 'dissociation'. The ionized compounds have distinctly different chemical properties from parent compounds. The most representative example is perfluorooctanoate (PFO^-) and perfluorooctanoic acid (PFOA) [37]. There are 15 LVP-VOCs in the CARB list that dissociate in water. Therefore, the Seth et al. model and Struijs et al. model (handling ionizing compounds was added by Franco et al. study) are preferred over the Namkung and Rittmann's model because the former two models are capable of handling ionizing compounds when calculating volatilization rates using acid or base dissociation constant (pK_a or pK_b).

Compared to Clark et al. and Seth et al. fugacity-based models, the Struijs et al. model requires many more plant operating parameters (e.g., oxygen concentration in the aeration tank, sludge loading rate) and additional computational steps due to the consideration of transfer between one phase (e.g., dissolved phase) to the other (e.g., solid phase) to compute the final output (% removal via volatilization, biodegradation, and sorption to sludge). In addition, Struijs et al. model requires additional decision making procedures for selecting the biodegradation rate, which are not given in the study. Lastly, because Clark et al. and Seth et al. models are solely based on fugacity principles for which the CalTOX multimedia fate and transport model applies, they are preferred over Namkung and Rittmann model and Struijs et al. model in terms of compatibility with fugacity-based multi-compartment models such as CalTOX [38].

2.2.6. Comparison of modeled results

In order to compare results between models, we ran the Namkung and Rittmann model [23] and the Clark et al. model [17] using two compounds found in the both studies, toluene and 1,1,1-trichloroethane. Different chemical properties (e.g., H, K_{ow}) and biodegradation rates for these compounds are used in both studies. Thus, we first applied the parameter values from one study (e.g., H from the Namkung and Rittmann model) to another study (e.g., the Clark et al. model) and confirmed that model results are the same in both models. However, model results are different between the models. Figure 3 shows the fate of two compounds in a WWTP predicted from each model. Clark et al. predicts more volatilization from a WWTP for both compounds than Namkung and Rittmann.

There are several reasons of the discrepancy between Namkung and Rittmann and Clark et al. Overall, the Namkung and Rittmann model is more simplified as compared to the Clark et al. model. First, Namkung and Rittmann did not differentiate the chemical concentration between water and solid (or biomass), but used the total chemical concentration (= mass of compound/volume of tank) in an aeration tank when computing volatilization and biodegradation rates. On the other hand, Clark et al. used the concentration in the solid phase for biodegradation (Seth et al. revised this component later so that biodegradation is available only in the dissolved (=water) phase) and that in the dissolved phase for volatilization. This differentiation may be important as chemicals sorbed to solids may not be available for biodegradation [36]. Second, mass balances for the aeration tank are established differently. An aeration tank in Clark et al. has an additional inflow of water and wasted sludge recycled from a secondary settling tank while Namkung and Rittmann do not. In the typical activated-sludge-type sewage treatment plant, most of settled sludge (98%) in the secondary settling tank is returned to the aeration tank to maintain the concentration of activated sludge. Third, for computing the loss by biodegradation, Clark et al. applied different biodegradation rates to the studied compounds depending on the chemical properties while Namkung and Rittmann applied fixed biological reaction constants (0 or 0.1 m^3/g) for all compounds. Fourth, the approach to compute loss by sorption to sludge in Namkung and Rittmann model is different from that in the Clark et al. model. Clark et al. used a recommended composition of biomass (20% octanol and 80% water) [39] to estimate partitioning of chemicals between biomass (or sludge) and water (K_{bw}). On the other hand, Namkung and Rittmann computed K_{bw} using a linear relationship between the fraction of organic carbon (f_{oc}) and the octanol-water partition coefficient (K_{ow}).

We also applied the same chemical properties of the two compounds (i.e., toluene and 1,1,1-trichloroethane) to Seth et al. model. The magnitude of volatilization and biodegradation is between Clark et al. and Namkung and Rittmann primarily due to the different assumption of biodegradation as described above. These compounds were not modeled in the Seth et al. paper.

For the reasons listed above, Seth et al. model, an extended version of Clark et al. model, is considered to be more appropriate than Namkung and Rittmann model for our study objectives. Overall, the assumptions in the Seth et al. model are more representative of the actual conditions in a WWTP. Thus, we selected Seth et al. model as the best model to predict the fate of LVP-VOCs in a WWTP.

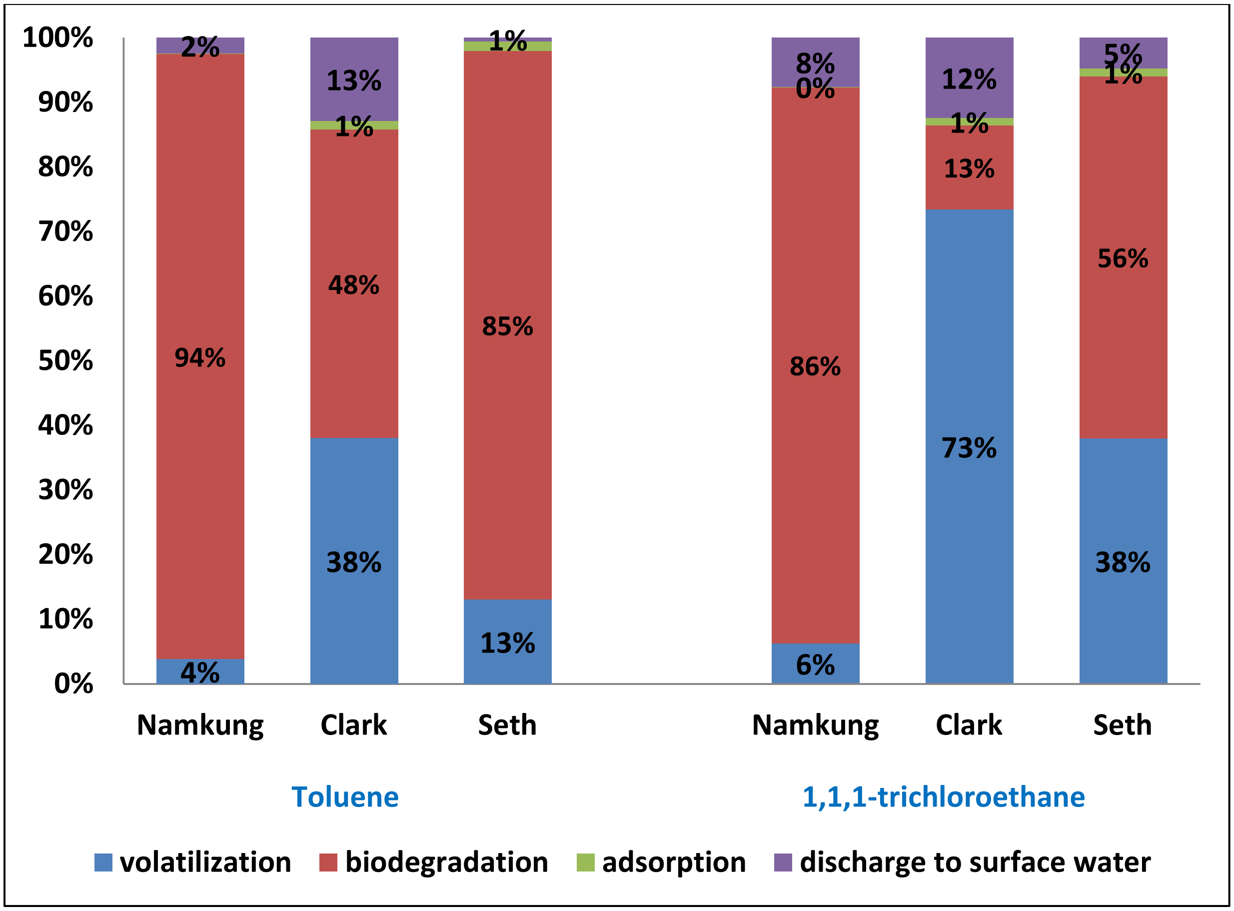

Figure 3. Fate of toluene and 1,1,1-trichloroethane in a WWTP predicted from Namkung and Rittmann [23], Clark et al. [17], and Seth et al. [18].

2.3. Methods

2.3.1. Description of the fugacity-based STP-EX model

Based on the evaluation above, we selected the Seth et al. [18] STP-EX model for our analysis. In this and other fugacity models, the fugacity and concentrations are algebraically equivalent and give identical results. Fugacity (f, Pa) is a criterion of equilibrium related to chemical potential and is used as a surrogate for chemical concentration, C (mol/m^3), which equals $Z \cdot f$, where Z is the fugacity capacity (mol/m^3-Pa). The Z-value is specific to a chemical, the phase in which it resides, and temperature. The rates of transport and transformation processes can be expressed as D-values (mol/h-Pa) or fugacity rate parameters, the rate being given by $D \cdot f$ (mol/h).

Steady-state equations can be assembled for the treatment scheme using the prevailing fugacities and D-values as shown below [17]. Knowing the D-values, these equations can then be solved for the prevailing fugacities in various stages of the treatment scheme (Please refer to Figure 2).

Primary settling tank: $E = f_P (D_2 + D_3 + D_{PV} + D_{PB})$ (1)

Aeration tank: $D_2 f_P + D_8 f_S = f_A (D_5 + D_6 + D_{AV} + D_{AB})$ (2)

Secondary settling tank: $D_6 f_A = f_S (D_7 + D_8 + D_9 + D_{SV} + D_{SB})$ (3)

Here, f is fugacity (Pa), subscripted P for primary, A for aeration, and S for settling; E is influx of chemical (mol/h) to the WWTP; D_2 is the *D*-value of stream 2 as shown in Figure 2, similarly for D_3-D_9; D_{PV}, D_{AV}, and D_{SV} are volatilization *D*-values for primary, aeration, and settling tanks; D_{PB}, D_{AB}, and D_{SB} are biodegradation *D*-values for three tanks. Stream 4 is inflow of air in which the chemical concentration is assumed to be zero and therefore has not been shown in Figure 2. Based on Equations (1)-(3), the solutions for the fugacity in each tank are as follows [17, 18]:

$$f_P = E/(D_2 + D_3 + D_{PV} + D_{PB}) \tag{4}$$

$$f_A = D_2 f_P /(D_5 + D_6 + D_{AV} + D_{AB} - (D_6 D_8/ (D_7 + D_8 + D_9 + D_{SV} + D_{SB}))) \tag{5}$$

$$f_S = D_6 f_A /(D_7 + D_8 + D_9 + D_{SV} + D_{SB}) \tag{6}$$

The expression for the various *D*-values and the corresponding chemical mass flux for the activated sludge process are summarized in Table 3. The process details for each tank and mass flows of water and solids for each stream are summarized in Tables 4 and 5, respectively. We note that the flow rates for each stream do not make a perfect mass balance. However, these are standard values.

We assumed that the density of particles (solids) is 1,000 g/L and the temperature (T) in the WWTP is at 20 °C. We assigned 0.05 m/h and 5 m/h for water-side (K_W) and air-side (K_A) mass transfer coefficients, respectively, for all compounds [17]. We solved the overall liquid mass transfer coefficient (K_V) using the following relationship [17].

$$1/K_V = 1/K_W + 1/(K_A \cdot K_{AW}) \tag{7}$$

where K_{AW} is the unitless Henry's law constant or the air-water partition coefficient ($=H/R\cdot T$). Here, R is the ideal gas constant (8.314 $Pa\cdot m^3$/mol-K). We selected bubble aeration as the primary aeration method in the U.S.

As in SimpleTreat 3.0 [34], the capability of handling ionizing chemicals is included in 'STP-EX' model by assuming that the sorption is dominated by partitioning of the unionized fraction of the chemical. This assumption is valid when $pH << (pK_a + 2)$ for organic acids and $pH >> (pK_a - 2)$ for organic bases [40]. For organic acids, the dissociation equations can be written as [18]

$$HA = H^+ + A^- \tag{8}$$
$$K_a = H^+ A^- /HA \tag{9}$$

where HA is the neutral species and A^- the conjugate base or anion. The ratio of neutral to total species of the chemical is then calculated as follows [40]:

$$\text{Ionic/neutral} = A^-/HA = 10^{(pH-pKa)} = I,$$
$$\text{Neutral/total} = 1/(I+1). \tag{10}$$

For organic bases, K_a and pK_a (of the conjugate acid) can be used. The Z-value of the neutral form of the chemical in water (Z_{WN}) for ionizing chemicals is then obtained by multiplying the Z-value in water (Z_W) by the factor, (1/(I+1)), and used for partitioning calculations.

Table 3. WWTP activated sludge processes and rate expressions [18]

Processes	Process Rates, D-values = Z× Q (mol/Pa-h)	Fugacity Rates, D × *f* (mol/h)
Primary settling tank		
Volatilization	$D_{PV} = K_{L,C} \times A_P \times Z_{WN}$	$D_{PV} \times f_P$
Biodegradation	$D_{PB} = KB_P \times V_P \times Z_W$	$D_{PB} \times f_P$
Outflow	$D_2 = GW_2 \times Z_W + GP_2 \times Z_P$	$D_2 \times f_P$
Sludge (wasted)	$D_3 = GW_3 \times Z_W + GP_3 \times Z_P$	$D_3 \times f_P$
Aeration tank		
Volatilization	$D_{AV} = K_{L,C} \times A_A \times Z_{WN}$	$D_{AV} \times f_A$
Biodegradation	$D_{AB} = KB_A \times V_A \times Z_W$	$D_{AB} \times f_A$
Aeration (surface)	$D_5 = K_{L,C}\, a \times V_A \times Z_{WN}$	$D_5 \times f_A$
Aeration (bubble)	$D_5 = Q_G \times K_{AW} \times Z_{WN}$	$D_5 \times f_A$
Outflow	$D_6 = GW_6 \times Z_W + GP_6 \times Z_P$	$D_6 \times f_A$
Secondary settling tank		
Volatilization	$D_{SV} = K_{L,C} \times A_S \times Z_{WN}$	$D_{SV} \times f_S$
Biodegradation	$D_{SB} = KB_S \times V_S \times Z_W$	$D_{SB} \times f_S$
Outflow	$D_7 = GW_7 \times Z_W + GP_7 \times Z_P$	$D_7 \times f_S$
Sludge (recycle)	$D_8 = GW_8 \times Z_W + GP_8 \times Z_P$	$D_8 \times f_S$
Sludge (wasted)	$D_9 = GW_9 \times Z_W + GP_9 \times Z_P$	$D_9 \times f_S$

Note: G = mass flow rate (m^3/h) with *W* = water and *P* = particles.

A = area (m^2) and *V* = volume (m^3)

$K_{L,C}$ = overall liquid mass transfer coefficient (MTC) (m/h), $K_{L,C}$ a = overall MTC-area term for surface aeration (1/h).

KB = aqueous phase biodegradation rate constant (1/h), Q_G = air flow rate (m^3/h).

Subscripts 2,3,…,9 = mass flow streams; N = neutral chemical species, P = primary settling tank, A = aeration tank, S = secondary settling tank.

Table 4. Process details for each tank [17]

	Primary	**Aeration**	**Settling**
Volume of water (m^3)	1,013	8,000	2,764
Volume of biomass (m^3)	5.07	20	1.52
Depth of tank (m)	3.8	10	3.8
Area of tank (m^2)	266.6	800	727.4
Aeration rate (m^3/h)		8,960	

Table 5. Flow rate of water and sludge for each stream number [17]

Stream #	Water (m^3/h)	Sludge (g/h)
1	1,000	200,000
2	998	80,000
3	2	120,000
6	1,798	4,494,000
7	982	14,700
8	800	4,397,000
9	15	82,400

2.3.2. Selected input parameters

Seth et al. suggested a scheme for converting aqueous biodegradation half-lives in natural water to those in wastewater [18]. Similar schemes to estimate the biodegradation half-life in a WWTP are implemented in the U.S. EPA Estimation Program Interface Suite (EPI Suite^{TM}) [15]. EPI Suite is one of the publically available software programs that allows one to compute chemical properties using a unique chemical abstracts service (CAS) registry number or simplified molecular-input line-entry system (SMILES) [15]. BIOWIN^{TM}, one of the estimation programs in the EPI Suite, uses two models (Biowin 3 and Biowin 5) to predict a biodegradation half-life in a WWTP. Biowin 3 is a QSA(P)R model that provides a rating (e.g., days, weeks, months) of biodegradation time for each compound based on the chemical structure such as the number of fragments and the fragment coefficient in that compound. Biowin 5 is a predictive model for assessing a compound’s biodegradability using the same principles as in Biowin 3.

The estimated biodegradation half-life in wastewater for our study compounds is either 1, 10, or 30 hours. Clark et al. [17] computed the biodegradation rate normalized to the mixed liquor suspended solids (MLSS) of 2000 mg/L using the biodegradation half-life in wastewater. Here, MLSS is the concentration of suspended solids in an aeration tank during activated sludge processes. The biodegradation rate constant normalized to MLSS of 2000 mg/L (=0.002 kg/L) was computed by dividing ln(2) by the product of the biodegradation half-life in wastewater and the fraction of compounds in solids (f_s). Using the observation that the volume of suspended solids in the tank is approximately 1/200 of water volume [17], the f_s is computed from the following.

$$f_s = 0.002 \cdot K_{bw} / (1 + 0.002 \cdot K_{bw}) \tag{11}$$

where K_{bw} is the partition coefficient between biomass (or solids) and water, which is the ratio of the fugacity capacity of biomass (Z_b) to that of water (Z_w). Z_w is an inverse of Henry’s law constant (H) and Z_b is computed from the following. Although influent wastewater characteristics can be highly variable (spatially and temporally) in their oils, fats and grease content, we assumed that the biomass is equivalent in composition to a mixture of 20% octanol and 80% water [17].

$$Z_b = 0.2 \cdot K_{ow} \cdot Z_w + 0.8 \cdot Z_w \tag{12}$$

The biodegradation rate constant is applied to the aeration and secondary settling tanks and a factor of 1/10 is applied to the rate constant in the primary settling tank because of short hydraulic retention time, a measure of the average length of time that a soluble compound remains in a constructed bioreactor [17].This is a standard assumption in WWTP modeling and does not correspond to actual residence times. Selected chemical properties of LVP-VOCs necessary for running a WWTP fate model are listed in Table 6.

We computed Henry's law constants (H) by multiplying VP by water solubility (S_w) and dividing by molecular weight (MW) instead of using either experimental or estimated values as recommended by Clark et al. [17] (see Table 1 for experimental or estimated values). Then, we used the computed H for the calculation of the air-water partition coefficient (K_{aw}). All chemical properties are either extracted from or driven by values from the EPA EPI Suite [15], except acid or base dissociation constants (pK_a or pK_b), which are extracted from SciFinder [41].

Table 6. Major chemical properties of LVP-VOCs obtained from US EPA EPI Suite [15] (#Experimental, *Estimated, **Calculated)

Chemical class	Examples of compounds	log K_{ow} (unitless)	Biodeg. Half-life* (hr)	K_{aw}** (unitless)	Deg. rate in Primary** (1/hr)
Glycols	Propylene Glycol	-0.9[#]	1	5.4E-07	42.1
	Diethylene Glycol	-1.5	1	3.3E-08	43.0
	Ethylene Glycol	-1.4[#]	1	3.1E-07	42.9
	Dipropylene Glycol	-0.6	10	2.3E-07	4.1
	Butylene Glycol	-0.3	1	9.9E-08	38.5
	Triethylene Glycol	-1.8[#]	10	1.1E-08	4.3
	Hexylene Glycol	0.6	10	8.4E-08	2.2
	Polyethylene glycol	-2.3	10	3.9E-12	4.3
Glycol Ethers	Diethylene Glycol Ethyl Ether	-0.5[#]	10	9.3E-07	4.0
	Diethylene Glycol Monobutyl Ether	0.6[#]	1	1.9E-07	22.8
	Dipropylene Glycol n-Butyl Ether	1.1	30	8.4E-07	0.3
	Dipropylene Glycol Methyl Ether Acetate	0.7	30	1.9E-05	0.7
	Dipropylene Glycol n-Propyl Ether	0.6	30	2.3E-06	0.7
	Ethylene Glycol Hexyl Ether	1.9[#]	1	1.3E-04	2.3
	Triethylene Glycol Monobutyl Ether	0.0	10	2.8E-08	3.4
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	6.1[#]	1	3.4E+02	0.1
	n-Heptadecane	8.7	1	1.0E+01	0.1
	n-Tridecane	6.7	1	1.2E+02	0.1
	Conosol 260	7.7	1	5.2E+02	0.1
	Conosol 340	7.7	1	5.2E+02	0.1
	Solvent Naphtha (Petroleum), Heavy Aliphatic	6.7	1	1.2E+02	0.1
Esters	Dimethyl Glutarate	0.6[#]	10	2.7E-05	2.1
	Methyl Palmitate	7.4[#]	10	7.7E-02	0.01
	2-ethylhexyl Benzoate	5.2	10	9.6E-03	0.01
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	3.0	10	3.7E-04	0.02
	Glyceryl Triacetate	0.3[#]	10	5.1E-07	3.0
	Isopropyl Palmitate	8.2	10	6.7E-01	0.01
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	4.9	3	1.4E-01	0.02
	Alkyl (C16-C18) Methyl Esters	6.8[#]	10	3.0E-03	0.01
Others	Triethanolamine	-1.0[#]	10	2.9E-11	4.2
	Glycerol	-1.8[#]	1	8.5E-10	43.2
	Benzyl Alcohol	1.1[#]	10	1.3E-05	1.1
	Stearyl Alcohol	7.7	10	3.6E-02	0.01

2.4. Results

2.4.1. Fate of down-the-drain LVP-VOCs in a WWTP

Because the ‘STP-EX’ model is thought to be suitable for predicting the fate of a wide range of chemical properties in a WWTP, we ran the ‘STP-EX’ model for LVP-VOCs. Table 7 summarizes the results of modeled loss of the selected LVP-VOCs, including volatilization, biodegradation, and sorption to sludge as well as removal efficiency and discharge with effluents. Except 2-ethylhexyl benzoate and texanol, the removal efficiency is greater than 90% for most of the selected 33 LVP-VOCs. For glycols and glycol ethers, they are removed in a WWTP via biodegradation in either a primary settling tank or an aeration tank because relatively small K_{aw} and K_{ow} values result in almost no removal via volatilization or sorption to sludge. For hydrocarbon solvents, biodegradation half-lives are very short (1 hour), but they are primarily removed by sorption to sludge in primary or secondary settling tanks due to the large $\log K_{ow}$ (>6.1) and less than 20% of compounds are either volatilized or biodegraded in an aeration tank. For esters and other compounds, similar to other types of chemical classes, primary removal processes are determined by the chemical properties such as K_{ow} and a biodegradation rate listed in Table 6. This is consistent with findings in Byrns [20] and Lee et al. [19].

The ‘STP-EX’ model does not include a sludge treatment module. There are four types of sludge treatment, including no treatment, aerobic digestion, anaerobic digestion, and composting [42]. Based on the EPA Clean Watershed Needs Survey [43], 50% and 35% of WWTPs in the U.S. treat the sludge via anaerobic digestion and aerobic digestion, respectively. The removal of compounds from two sludge treatment methods varies from 3% to 98%, depending on the biodegradation half-life in a WWTP [42]. About 95% of di-2(-ethylhexyl) phthalate (DEHP) in sludge was removed biologically via aerobic or anaerobic digestion [44]. During the 143 days of composting, about 60% of DEHP was removed primarily through microbial degradation [45]. All hydrocarbon solvents have 1 day of biodegradation half-life from the BIOWIN and thus most of them are expected to be biodegraded in either aerobic or anaerobic digestion or composting.

2.4.2. Sensitivity analysis on biodegradation half-lives in wastewater

In this study, due to the limited information on biodegradation half-lives in wastewater, rough numbers (i.e., 1, 10, 30 days) are selected with a scheme provided in the EPI Suite and thus a sensitivity analysis was conducted to evaluate the influence of these default values on overall model results (i.e., percent of removal via volatilization, biodegradation, and sorption to sludge). We increased and decreased the initially assigned half-lives by a factor of 10 and ran our model. Table 8 shows the results of modeled loss of the selected LVP-VOCs from the sensitivity analysis with maximum and minimum values. For two compounds (iso-paraffinic hydrocarbons and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate), the fraction that volatilizes into atmosphere is sensitive (7% and 15% changes, respectively) to the selection of the half-lives, but the changes in the half-lives did not influence significantly (>2%) the results on volatilization for the majority of the compounds. On the other hand, the changes in the half-lives did affect results (>16%) on the relative removal via biodegradation as compared to sorption to sludge for 6 compounds. This result highlights that while the uncertainty in the biodegradation half-lives can influence the fraction that volatilizes from a WWTP for some of the selected LVP-VOCs, the majority of the change relates to whether the compound is biodegraded or removed with the sludge.

Table 7. Fate of LVP-VOCs predicted from the STP-EX model. Values in bold are a primary removal process.

Chemical class	Example compounds	Removal efficiency	Volatilization *	Biodegradation	Sorption to sludge	Effluent discharge
Glycols	Propylene Glycol	100%	0%	**100%**	0%	0%
	Diethylene Glycol	100%	0%	**100%**	0%	0%
	Ethylene Glycol	100%	0%	**100%**	0%	0%
	Dipropylene Glycol	100%	0%	**100%**	0%	0%
	Butylene Glycol	100%	0%	**100%**	0%	0%
	Triethylene Glycol	100%	0%	**100%**	0%	0%
	Hexylene Glycol	100%	0%	**100%**	0%	0%
	Polyethylene glycol	100%	0%	**100%**	0%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	100%	0%	**100%**	0%	0%
	Diethylene Glycol Monobutyl Ether	100%	0%	**100%**	0%	0%
	Dipropylene Glycol n-Butyl Ether	100%	0%	**99%**	0%	0%
	Dipropylene Glycol Methyl Ether Acetate	100%	0%	**100%**	0%	0%
	Dipropylene Glycol n-Propyl Ether	100%	0%	**100%**	0%	0%
	Ethylene Glycol Hexyl Ether	100%	0%	**100%**	0%	0%
	Triethylene Glycol Monobutyl Ether	100%	0%	**100%**	0%	0%
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	95%	9%	8%	**79%**	5%
	n-Heptadecane	94%	0%	0%	**94%**	6%
	n-Tridecane	94%	3%	3%	**89%**	6%
	Conosol 260	94%	0%	0%	**93%**	6%
	Conosol 340	94%	0%	0%	**93%**	6%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	94%	3%	3%	**89%**	6%
Esters	Dimethyl Glutarate	100%	0%	**100%**	0%	0%
	Methyl Palmitate	94%	0%	0%	**94%**	6%
	2-ethylhexyl Benzoate	86%	1%	8%	**77%**	14%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	77%	0%	**74%**	3%	23%
	Glyceryl Triacetate	100%	0%	**100%**	0%	0%
	Isopropyl Palmitate	94%	0%	0%	**94%**	6%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	90%	11%	22%	**57%**	10%
	Alkyl (C16-C18) Methyl Esters	94%	0%	0%	**93%**	6%
Others	Triethanolamine	100%	0%	**100%**	0%	0%
	Glycerol	100%	0%	**100%**	0%	0%
	Benzyl Alcohol	100%	0%	**100%**	0%	0%
	Stearyl Alcohol	94%	0%	0%	**94%**	6%

*** Aeration from the aeration tank is included in the volatilization term.**

Table 8. The results from the sensitivity analysis. The model was run with increased and decreased biodegradation half-lives in wastewater by a factor of 10. The maximum and minimum values are presented for those with changes in removal.

Chemical class	Example compounds	Volatilization	Biodegradation	Sorption to sludge
Glycols	Propylene Glycol	-	-	-
	Diethylene Glycol	-	-	-
	Ethylene Glycol	-	-	-
	Dipropylene Glycol	-	-	-
	Butylene Glycol	-	-	-
	Triethylene Glycol	-	-	-
	Hexylene Glycol	-	-	-
	Polyethylene glycol	-	-	-
Glycol Ethers	Diethylene Glycol Ethyl Ether	-	-	-
	Diethylene Glycol Monobutyl Ether	-	-	-
	Dipropylene Glycol n-Butyl Ether	-	99%-100%	-
	Dipropylene Glycol Methyl Ether Acetate	-	-	-
	Dipropylene Glycol n-Propyl Ether	-	-	-
	Ethylene Glycol Hexyl Ether	-	-	-
	Triethylene Glycol Monobutyl Ether	-	-	-
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	3%-10%	1%-29%	66%-83%
	n-Heptadecane	-	-	-
	n-Tridecane	2%-3%	0%-16%	78%-91%
	Conosol 260	-	-	91%-94%
	Conosol 340	-	-	91%-94%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	2%-3%	0%-16%	78%-91%
Esters	Dimethyl Glutarate	-	-	-
	Methyl Palmitate	-	-	93%-94%
	2-ethylhexyl Benzoate	-	1%-32%	62%-81%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	-	20%-97%	2%-5%
	Glyceryl Triacetate	-	-	-
	Isopropyl Palmitate	-	-	-
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	3%-18%	3%-50%	46%-63%
	Alkyl (C16-C18) Methyl Esters	-	0%-2%	92%-94%
Others	Triethanolamine	-	-	-
	Glycerol	-	-	-
	Benzyl Alcohol	-	-	-
	Stearyl Alcohol	-	-	-

2.5. Discussion

This modeling effort has several implications for understanding the fate of LVP-VOCs in a WWTP. First, fugacity-based WWTP fate models (Clark et al. and Seth et al.) are the most suitable for simulating the fate of LVP-VOCs in a WWTP among other models because they are compatible with the CalTOX multimedia model and are algebraically simple and robust. Second, we found that the biodegradation half-life is the most uncertain input variable during sewage treatment processes among other input parameters. Third, we found that loss by volatilization is negligible for most compounds, confirming that loss by biodegradation and sorption to sludge are major loss mechanisms. In other words, once LVP-VOCs are disposed down the drain, the majority of selected compounds (=28/33) had no evaporation from a WWTP and less than 11% is evaporated for the other five compounds/mixtures during sewage treatment processes.

Limitations in regard to study results arise from the uncertainty of model input parameters. As explained in the Method section, biodegradation half-lives in wastewater are not directly measured, but rough numbers (i.e., 1, 10, 30 days) are selected based on chemical structure. This adds uncertainty to the model results. Therefore, accounting for more reliable loss rate due to biodegradation would likely improve the reliability of model predictions. In addition, because no studies clearly proved that biodegradation occurs in a dissolved (water) phase or a solid (biomass) phase or both phases, the assumption that biodegradation occurs in a dissolved (water) phase in this study might over- or under-estimate the fraction of biodegradation. We did not conduct an uncertainty analysis for the WWTP model due to insufficient information related to variability of input parameters. In future research, a detailed quantitative uncertainty assessment applied to the model results will provide an opportunity to evaluate the level of uncertainty that is attributable to lack of precision in chemical property values as well as from variability and uncertainty in input parameters, and from model uncertainty resulting from various assumptions related to environmental half-lives.

3. MULTIMEDIA FATE AND TRANSPORT MODELS

3.1. Introduction

3.1.1. Background

When LVP-VOCs are released to outdoor air, they can react with hydroxyl radicals (OH) as the first step in a series of ozone generating reactions. In addition to being degraded by reaction with the hydroxyl radical, there are three other major competing processes for LVP-VOCs in the troposphere: (i) advective loss from air and water within the air basin to outside of the air basin, (ii) inter-compartmental transfer from air to other environmental compartments (e.g., water, soil, vegetation, urban film, etc.), and (iii) degradation by reaction in environmental compartments other than air. Therefore, the fraction of LVP-VOCs available for ozone forming reactions primarily depends on the magnitude of the first-order reaction rate in air (k_{Ra}) and the advective loss rate from air (k_{Aa}), and mass distribution among all compartments along with the reaction rate in compartment i (k_{Ri}).

Multi-compartment mass-balance models have been used to simulate the fate and transport of environmental contaminants and determine the contribution of VOCs to ozone formation [11, 12, 46]. For instance, the CalTOX model allows estimation of chemical concentrations in the gas phase using fugacity principles as a result of partitioning, transformation, and transport among air, soil, water, and biota [38]. Thus, in addition to hydroxyl reaction rates, the other key element needed to understand the contribution of LVP-VOCs to ozone formation is the multimedia environmental distribution of the selected chemicals. LVP-VOCs with low vapor pressure (VP) and large octanol-water partition coefficient (K_{ow}) values might preferentially partition into non-atmospheric compartments compared to VOCs. Multi-media partitioning is a critical step in evaluating ozone forming potential because only the portion of emitted LVP-VOCs that remains in the air is available for forming ozone. Therefore, multimedia environmental modeling is needed to predict the portion of emitted LVP-VOCs resulting from consumer product use that is available to form ozone in the air.

3.1.2. Objectives

The overall objective of the multimedia fate and transport models is to determine the fraction of LVP-VOCs available for formation of ozone following emissions. Specific objectives are (1) to understand the fate and transport of emitted LVP-VOCs in an urban multimedia environment and (2) to evaluate the sensitivity and uncertainty of input parameters and model conditions on the fraction of LVP-VOCs that is available for ozone formation.

3.1.3. Overview

In this chapter, we first reviewed existing multi-compartment models that are suitable for simulating the fate and transport of LVP-VOCs in an urban multimedia environment. Second, we described the similarities and differences between models. Third, to address the ozone formation questions for Southern California, we described how critical input parameters and model conditions are selected for the South Coast Air Basin (SoCAB) and how these impact results.

Fourth, we presented model results for steady-state and dynamic conditions. Lastly, we evaluated the necessity of a two-box regional airshed model and inclusion of dynamic conditions in the multi-compartment models.

3.2. Review: Multi-compartment models

3.2.1. Model selection

Multi-compartment mass-balance models have been developed to simulate the fate, transport, and transformation of chemicals in the multimedia environment using fugacity principles as well as concentration-based mass balance approaches. Here, fugacity can be regarded physically as the partial pressure or the tendency of a chemical to leave or escape from a given state or compartment [33]. The application of the fugacity concept to these models was pioneered by Mackay and has been a commonly-used approach in the development of multi-compartment models [47]. These multi-compartment models vary depending on complexity (e.g., Levels I-IV), purpose (e.g., evaluative and "real-world"), and scale (e.g., local, regional, continental, and global) [48]. We reviewed only Level III or Level IV fugacity models because they include degradation reactions and advection as loss processes. We also reviewed evaluative models at a local or regional-scale for the purpose of our study.

A Level III model applies a constant rate of chemical discharges and steady-state conditions. The steady-state assumption no longer applies to the Level IV model which allows changes of chemical mass as a function of time. Foster et al. [11] adapted Mackay's Level III and Level IV models to assess the effects of VOC emissions on urban air quality by estimating the fraction of the mass emitted that may participate in photochemical reactions leading to ozone formation. Another representative multimedia model is the CalTOX model, which is a regional-scale Level III model designed to assess the fate, transport, and transformation of organic chemicals [38]. We selected the Foster et al. model and the CalTOX model for further review because they are formulated using the fugacity concept and are suitable for simulating the fate and transport of LVP-VOCs in a local urban environment.

3.2.2. Similarities of selected models

The Foster et al. and CalTOX multimedia models are similar in that they are formulated using the fugacity concept and are Level III multimedia chemical partitioning models with the objective of characterizing mass-transfer processes between compartments and transformation within compartments (e.g., degradation). Both models also derive environmental concentrations by determining the likelihood of competing processes by which chemicals (i) accumulate within the compartment of origin, (ii) are physically, chemically, or biologically transformed within the compartment (e.g., hydrolysis, oxidation, etc.), or (iii) are transported to other compartments by cross-media transfers that involve dispersion or advection (e.g., volatilization, precipitation, etc.). In addition, both models are based on a series of coupled mass transfer equations that are valid at any time scales. When these equations are solved using a steady-state assumption, the solution is intended for long time scales. By solving these same equations dynamically, they can be used to evaluate shorter time scales for dynamic conditions as Foster et al. did in their evaluation of low volatility compounds. The conceptual frameworks of the Foster model and the CalTOX model are illustrated in Figure A1 and Figure A2 in the Appendix.

3.2.3 Differences of selected models

The two models differ in terms of the included model compartments, input parameters, and fugacity capacity calculations. The Foster model includes five compartments including air, surface water, soil, vegetation, and urban film, whereas the CalTOX model includes eight compartments including air, surface water, ground soil, root-zone soil, vegetation (cuticle and leaf), sediment, vadose soil zone (i.e., unsaturated soil zone), and groundwater aquifer. Compared to the Foster model, the CalTOX model divides the soil compartment into three sub-compartments (i.e., ground soil, root-zone soil, vadose-zone soil), does not include a film compartment, and includes sediment and groundwater aquifer as additional compartments. For all compounds considered in this project, less than 2% of the LVP-VOCs are degraded in the last three compartments (i.e., sediment, vadose, and groundwater aquifer) of the CalTOX model. Some compounds with high K_{ow} or low Henry' law constant (H) are significantly partitioned to the film compartment in the Foster model, but the loss from reaction in this compartment is minimal (<10%) for most of the compounds considered.

Moreover, the thickness of soil compartment is different between models. The Foster model only considers 5 cm of the soil compartment whereas the soil compartment in the CalTOX model comparable to the Foster model is comprised of surface soil (1 cm) and root soil (78.5cm), and is thus thicker than that of the Foster model. In addition, the fraction of the horizontal area that is water is different between models. The fraction in the Foster model is assumed to be 0.1 for a typical city in North America. On the other hand, the fraction in the CalTOX model for California residential sites is 0.02. Increasing the fraction of the landscape that is water increases the fraction of chemicals in water. Increasing the fraction that is soil increases the fraction of chemicals in soil.

In addition to differences in the selected model compartments, the fugacity capacity calculation differs between models for the soil and vegetation compartments as shown in Table 9. Specifically, the Foster model assumes that the soil compartment only consists of soil particles, whereas the CalTOX model computes the volume-averaged fugacity capacity among air, water, and soil particles. The volumetric water content in surface soil and root soil for the California residential site in the CalTOX model is 0.192 and 0.206, respectively [38]. Clearly, the volume fraction of water in the soil compartment needs to be taken into account because the fugacity capacity of water is several orders of greater than that of soil particles for most of the compounds considered in this report, thereby increasing the fraction in soil. For the vegetation compartment, the Foster model assumes that it is only comprised of the lipid phase. On the other hand, the CalTOX model first divides the vegetation compartment into two sub-compartments (i.e., cuticles and leaves) and then considers the volume fraction of air, water, and lipid for each sub-compartment when computing the fugacity capacity.

We presented input parameters of and the results from both Forster et al. and CalTOX models to show the differences and similarities of the model results due to the differences in model compartments, input parameters, and fugacity capacity calculations. However, because CalTOX includes distribution and partitioning of compounds in the water phase in soil compartments that may potentially impact the overall fate in an outdoor environment, we selected the CalTOX model as a more appropriate model to predict the fate of LVP-VOCs in an urban atmosphere.

Table 9. Similarities and differences in fugacity capacity calculations between Foster et al. [11]and CalTOX [38]

	Foster	**CalTOX**
Pure air	$Z_{air} = \frac{1}{R \cdot T}$	$Z_{air} = \frac{1}{R \cdot T}$
Air particles	$Z_{ap} = \frac{6 \times 10^6/P}{R \cdot T}$	$Z_{ap} = \frac{0.00123 \times f_{oc\_ap} \times K_{oa}}{R \cdot T}$
Bulk Air	$Z_a = Z_{air} + Z_{ap} \cdot V_q$	$Z_a = Z_{air} + Z_{ap} \cdot \frac{\rho_{air\_dust}}{\rho_{soil}}$
Pure water		$Z_{water} = \frac{1}{H}$
Water particles		$Z_{wp} = \frac{K_{d\_d} \cdot \rho_{soil} \cdot Z_{water}}{1000}$
Water	$Z_w = \frac{1}{H}$	$Z_w = Z_{water} \cdot \left(1 - \frac{\rho_{sed\_wtr}}{\rho_{soil}}\right) + Z_{wp} \cdot \left(\frac{\rho_{sed\_wtr}}{\rho_{soil}}\right)$
Soil particles		$Z_{sp} = \frac{Z_{water} \cdot K_{oc} \cdot \rho_{soil} \cdot f_{oc}}{1000}$
(Ground) Soil	$Z_s = \frac{Z_{water} \cdot K_{oc} \cdot \rho_{soil} \cdot f_{oc,s}}{1000}$	$Z_{gs} = Z_{air} \cdot f_{a\_surf\_soil} + Z_{water} \cdot f_{w\_surf\_soil} + Z_{sp} \cdot (1 - f_{a\_surf\_soil} - f_{w\_surf\_soil})$
Root soil		$Z_{rs} = Z_{air} \cdot f_{a\_root\_soil} + Z_{water} \cdot f_{w\_root\_soil} + Z_{sp} \cdot (1 - f_{a\_root\_soil} - f_{w\_root\_soil})$
Vegetation	$Z_v = Z_{water} \cdot K_{ow} \cdot f_{oc,v}$	$Z_v = Z_c \cdot V_c/(V_l + V_c) + Z_l \cdot V_l/(V_l + V_c)$
Cuticles		$Z_c = Z_{ap} \cdot f_{ap\_c} + 0.9 \cdot K_{ow} \cdot lipid\_leaf \cdot (V_l + V_c)/V_c \cdot Z_{water} \cdot (1 - f_{ap\_c})$
Leaves		$Z_l = Z_{air} \cdot f_{air\_l} + 0.1 \cdot K_{ow} \cdot lipid\_leaf \cdot (V_l + V_c)/V_l \cdot Z_{water} + Z_{water} \cdot f_{w\_l}$
Urban film	$Z_f = Z_{water} \cdot K_{ow} \cdot f_{oc,f}$	Not available
Reaction in air	$k_{R1} = C_{OH} \cdot k_{OH}$	$k_{R1} = \ln(2)/t_{1/2\_air}$
Others	Not available	Vadose-zone, sediment, aquifer compartments

Note:

$V_q = 5.0 \times 10^{-11}$ (aerosol volume fraction)
$\rho_{air\_dust}/\rho_{soil} = 2.4 \times 10^{-11}$ (aerosol volume fraction)
$\rho_{sed\_wtr}/\rho_{soil} = 3.1 \times 10^{-4}$ (volume fraction of suspended solids in soil)
$f_{a\_surf\_soil} = 0.27$, $f_{w\_surf\_soil} = 0.19$ (air or water content in surface soil)
$f_{a\_root\_soil} = 0.25$, $f_{w\_root\_soil} = 0.21$ (air or water content in root soil)
$f_{oc\_s} = 0.02$ (organic carbon fraction in soil)
$f_{oc\_f} = 0.74$ (organic carbon fraction in urban film)
$f_{oc\_s} = 0.01$ (organic carbon fraction in vegetation)
lipid_leaf = 0.002 (volume fraction of lipid in leaf)
$f_{ap\_c} = 0.01$ (volume fraction of atmospheric particles on cuticle)
$f_{air\_l} = 0.18$, $f_{w\_l} = 0.50$ (volume fraction of air and water in leaf)
$(Vl+Vc)/Vl = 1.01$ (ratio of the volume of total vegetation to that of leaf)

3.3. Methods

3.3.1. Overview of California climate and landscape factors

Compared to other states in the United States, California has unique climate during summer. For cities with the largest population in California (Los Angeles, San Diego, San Jose, San Francisco, Fresno, Sacramento, Long Beach, Oakland, Bakersfield), the average monthly number of hours with measureable precipitation (>0.25 inches) is less than 5 hours during the period of June to September (http://www.wrcc.dri.edu/htmlfiles/hrsofppt.html), indicating that these California cities and surrounding areas have almost no rain during summer. The population density of California and the location of these cities are illustrated in Figure A3 in the Appendix. If one views the distribution of these cities throughout the state, along with the distribution of the population, assuming that the regions around these cities receive a similar amount of rain, the vast majority of the population of California lives in an area with virtually no rain during the summer ozone season. There is slightly more rain in the far northern portions of the state, and in the mountains, but these regions are relatively sparsely populated and thus not anticipated to have significant emissions of LVP-VOCs from consumer product use as compared to more populated, drier regions. The annual average precipitation in California in inches is provided in Figure A4 in the Appendix. In general, precipitation is concentrated during the winter season. In addition, except San Francisco, the average daily high temperature in the most populated cities is above 80 °F (27 °C) during the period of June to September. For two cities where the high ozone concentrations are measured (San Bernardino and Riverside) [3], the average daily high temperature reaches up to 100 °F (38 °C) and 95 °F (35 °C), respectively, from July to September. Generally ground-level ozone is more likely to reach unhealthy levels on hot sunny days in urban environments [49].

The landscape factors of California vary within the state. For example, except counties adjacent to the Pacific Ocean (e.g., San Francisco, San Mateo, Marin, Santa Barbara, Santa Cruz), the fraction of horizontal surface area that is surface water ranges from 0.3% (e.g., San Bernardino County) to 11% (e.g., Sonoma County) [50]. This indicates that for those chemicals that are likely to be partitioned in water, model results (fraction available in the air for photochemical reactions) in a region with a small fraction of water bodies would differ from those in a region with a large fraction of water bodies. Looking at Figure A3 and Figure A4 together, one can see that the vast majority of the more heavily populated southern portion of the state can be characterized as dry, and that one would anticipate the fate and transport of compounds to be similar throughout this region. In addition, the average fraction that is water for all counties in California is 5%, which differs from other states with large fractions of water bodies such as Maryland (21%), Massachusetts (15%), and Michigan (41%). Therefore, the studies of other states in the United States with different landscape and climate factors would have different results.

3.3.2. Study area

Because of its notable status with regard to ozone non-attainment during summer, the South Coast Air Basin (SoCAB) is used as our study location for the outdoor multi-compartment modeling. SoCAB encompasses the City of Los Angeles, all of Orange County, and the non-desert areas of Los Angeles, San Bernardino, and Riverside Counties (see Figure 4). Because the

SoCAB area has the San Gabriel Mountains forming a border north of the Santa Ana Mountains, which form an East-West wall through the SoCAB, we consider east and west of the Santa Anna Mountains as independent airshed areas. In general, higher concentrations of ozone are measured and predicted in downwind areas of the SoCAB (i.e., less densely populated Riverside and San Bernardino Counties) than the upwind areas of the SoCAB (i.e., more densely populated Los Angeles and Orange Counties) [3]. This is partly because winds are primarily blowing from west (the upwind areas) to east (the downwind areas) during the period of June to September [51]. Prevailing wind direction is based on the hourly data from 1992-2002 and is defined as the direction with the highest percent of frequency. To estimate the fraction of a LVP-VOC available for ozone formation from emissions during consumer product use in the SoCAB, we used the CalTOX multi-compartment mass-balance model [38] and the Foster model [11] with the particular characteristics of the SoCAB (e.g., little rain during the summer ozone-season, two airsheds separated by low mountains). We modeled a time period of June-September because these months represent the time period when ozone levels are the highest. Because radiation (or surface) inversion breaks up after sunrise [52], it is reasonable to assume that once chemicals are released outdoors during the daytime in a region with a hot summer, they are likely to be well-mixed throughout an airshed. We described how critical input parameters and model conditions are selected for the SoCAB and how that impacts results.

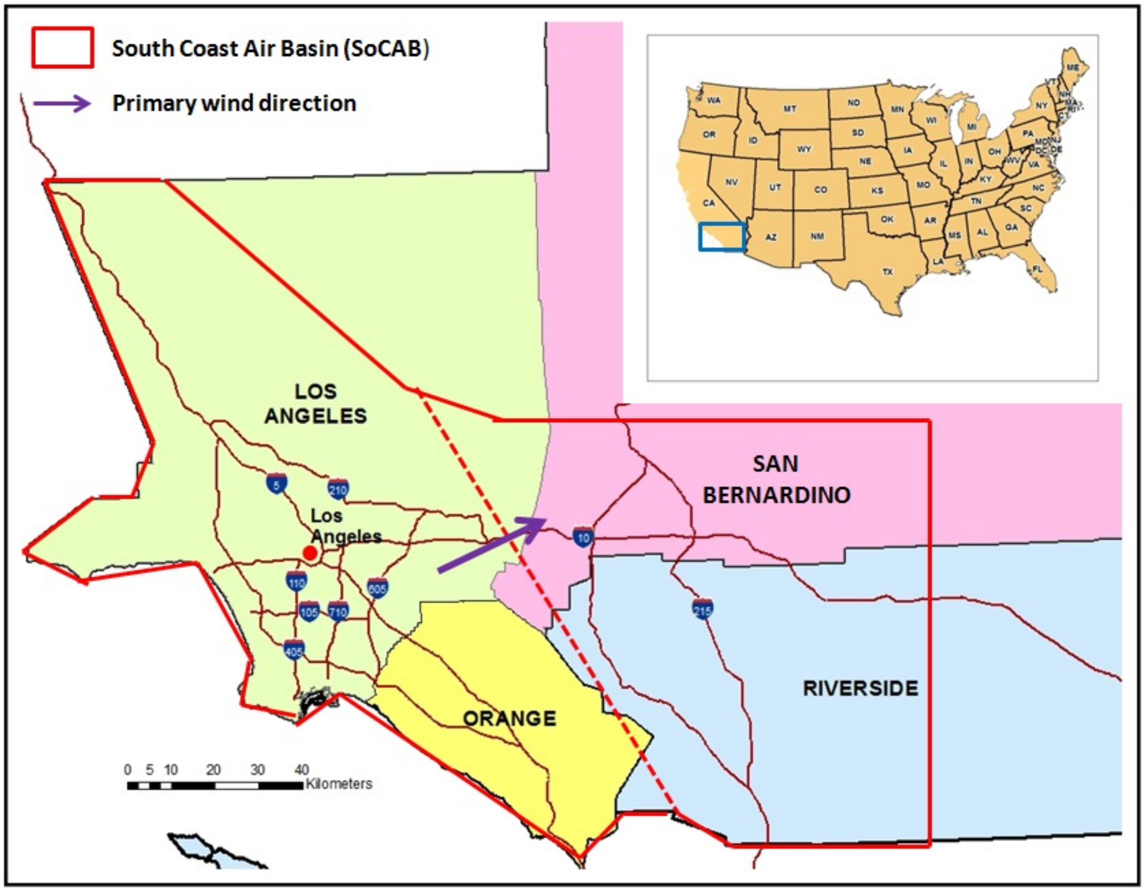

Figure 4. Study area, boundary of and two airsheds in the SoCAB, and primary wind direction [53]

3.3.3. Compartment dimensions

In contrast to VOCs that are primarily partitioned to the air compartment, LVP-VOCs with small H values and large K_{ow} values might be also partitioned to soil, water, or vegetation compartments. Thus, dimensions of model compartments influence the mass distribution of LVP-VOCs among compartments. The default dimensions of model compartments in the Foster model represent a large city with about 1-2 million population and those in the CalTOX model represent a typical residential site in California. The major difference in model dimensions between models is the fraction of total horizontal area for each model compartment. Foster et al. separated the area of soil from the area of vegetation whereas CalTOX assumes that all vegetation grows on top of the soil compartment. An urban film which coats impervious urban surfaces such as pavement, glass, roof, and concrete is one of the compartments included in the Foster model [11, 46], but the CalTOX model does not consider the surface area of the urban film. For these reasons, the fraction of total horizontal area that is soil in the CalTOX model (=0.98) is much greater than that in the Foster model (=0.1). Table A1 shows the default dimensions of compartments for both Foster and CalTOX models. We retained the included model compartments in each model to acknowledge the differences in model development. However, dimensions of important model compartments (i.e., air, water, soil, vegetation) that would influence the fate and transport of LVP-VOCs are modified to apply the same compartment dimensions to both models and the impact on model results with modified dimensions of model compartments is presented in section 3.4.1.

The size of the SoCAB is approximately 2.8×10^{10} m^2 (http://www.aqmd.gov/). Rose et al. [54] studied urban surfaces of four U.S. cities, including Salt Lake City, Sacramento, Chicago, and Houston and reported that approximately 60% of the total horizontal area for the urban environment is comprised of impervious surfaces such as roof and pavement. Chemical cannot partition or move into these impervious surfaces and so they are not included in the horizontal soil-surface area. As noted above, these non-permeable surfaces may be coated with an urban film, but this is not included in the CalTOX model. Thus, we recalculated the fraction of the total horizontal area for the soil compartment in the CalTOX model by subtracting the average fraction of horizontal surface area that is pavement and roof (=0.60) and the California-specific fraction that is water (=0.02) from the fraction of total horizontal area (=1). The ground-soil compartment is directly above the root-zone compartment, which in turn is directly above the vadose zone compartment. The water compartment is directly above the sediment compartment. The aquifer underlies the entire area. We obtained the fraction of horizontal area that is surface water and the height (or depth for soil and water) of each compartment for the residential site of California from the CalTOX database. The modified dimensions of compartments (e.g., from 0.98 to 0.38 for the soil compartment in CalTOX) used in both Foster model and the CalTOX model are listed in Table 10.

Table 10. SoCAB-specific dimensions of model compartments used in Foster et al. [11] and CalTOX [38] models ($^{\#}$only used in Foster et al., *only used in CalTOX)

	Compartment	Height/depth (m)	Surface area (m^2)	Fraction of total horizontal area (unitless)	Volume (m^3)
Foster et al.	Bulk air	700	1.4E+10	1	9.7E+12
	Water	5	2.5E+08	0.02	1.4E+09
	Soil	0.05	2.6E+09	0.19	1.3E+08
	Vegetation	0.001	2.6E+09	0.19	2.6E+06
	Urban film$^{\#}$	5.00E-8	4.2E+10	0.6	2.1E+03
CalTOX	Bulk air	700	1.4E+10	1	9.7E+12
	Water	5	2.5E+08	0.02	1.3E+09
	Vegetation	0.0014	5.3E+09	0.38	7.4E+06
	Ground-soil	0.01	5.3E+09	0.38	5.3E+07
	Root-zone*	0.785	5.3E+09	0.38	4.2E+09
	Vadose*	0.557	5.3E+09	0.38	3.0E+09
	Sediment*	0.05	2.5E+08	0.02	1.3E+07
	Aquifer*	3	1.4E+10	1	4.2E+10

Note: The fraction of the horizontal surface that is pavement and roof (=0.6) is not modeled in CalTOX.

3.3.4. First-order degradation rate in air (k_{Ra}, $hour^{-1}$)

The first-order degradation rate in air due to OH radical reaction (k_{Ra}) can be estimated by multiplying the OH radical concentration in air (C_{OH}, molecules/cm^3) and the overall OH radical rate constant (k_{OH}, cm^3/molecules-sec) or can be estimated by dividing ln(2) by the half-life in air ($t_{1/2\_air}$, hour), assuming the half-life is based on OH radical reaction.

$$k_{A1} = C_{OH} \cdot k_{OH} \quad \text{or} \quad = \ln(2)/t_{1/2\_air} \tag{1}$$

Model results on the fraction of LVP-VOCs for ozone forming reactions are sensitive to the selection of the OH radical concentration because it varies diurnally over six orders of magnitude, ranging from 4.5×10^0 to 8.0×10^6 molecules/cm^3 [55]. In addition, the OH radical concentration varies zonally (i.e., latitude), monthly, and vertically [56]. Estimated seasonal variation of the OH radical concentration in Los Angeles (35°N) ranges from 0.23×10^6 to 1.87×10^6 molecules/cm^3 with an annual average of 0.96×10^6 molecules/cm^3 [56]. The measured daily maximum OH radical concentration in Los Angeles during September 1993 was about 7.0×10^6 molecules/cm^3 [57]. For fast reacting chemicals, 12-hour daylight OH radical concentrations are reasonable to use for computing the first-order degradation rate, whereas for chemicals that react more slowly (> a few days), the 24 hour average is suggested to be used [15]. For the diurnally and annually averaged 12-hour daylight OH radical concentration, the Atmospheric Oxidation Program for Microsoft Windows (AOPWIN^{TM}), one of the chemical-property estimation programs in the EPI Suite [15], recommends using 1.5×10^6 molecules/cm^3

[15]. For seasonally and diurnally 24-hour averaged OH radical concentration in the northern hemisphere, Atkinson [58] suggested using 0.5×10^6 molecules/cm^3. Because of the wide range of the OH radical concentrations, the selection of the value of this property in the multimedia outdoor model is critical for determining the fraction of LVP-VOCs available for ozone.

In contrast to the OH radical concentration, estimated OH radical rate constants (k_{OH}) from the AOPWIN program are uncertain rather than variable. Among the 667 compounds evaluated in the AOPWIN program, 90% of estimates are within a factor of two of the experimental values and the correlation coefficient between estimated and experimental values is 0.96 [15]. Most experimental values were taken from Atkinson [58, 59] and Kwok and Atkinson [60]. In the CARB list, alkyl (C16-C18) methyl esters has additional an O_3 (k_{O3}) reaction rate, but it is approximately 6 ($=4.0 \times 10^{-16}$ cm^3/ molecules-sec) orders of magnitude smaller than the k_{OH} values. Thus, we assumed in this study that reactions with OH radical are the only degradation process in air for all LVP-VOCs. For the first-order degradation rate in air (k_{Ra}), we multiplied the experimental or estimated values of k_{OH} listed in Table 11 by the half of the recommended 12-hour daylight C_{OH} (1.5×10^6 molecules/cm^3). We selected experimental values over estimated values. CalTOX requires the user enter the half-life in air ($t_{1/2\_air}$), which can be computed by dividing ln(2) by the degradation reaction rate (the product of C_{OH} and k_{OH}) [38]. We used the half-life estimated from the AOPWIN program, which uses the same C_{OH} and k_{OH} used for the calculation of k_{Ra} [15].

3.3.5. Degradation half-lives in other compartments ($t_{1/2}$, hour)

The estimated half-lives of LVP-VOCs in other environmental compartments are listed in Table 11. Diamond and co-workers have emphasized the role of the urban film in multimedia urban models [11, 46, 61, 62] and Kahan et al. [63] showed that reaction loss from films can be a significant loss process for low volatility polycyclic aromatic hydrocarbons (PAHs). However, the degradation half-life in the urban film is not consistently used across studies even with the same compound. Specifically, Diamond et al. [46] did not specify how the half-life in the film was computed, but the half-life for five compounds (i.e., phenanthrene, fluoranthene, tetra-chlorinated dibenzodioxins (CDD), penta-CDD, octa-CDD) used in their study is approximately 62% smaller than that in the air, ranging from 5 to 2252 hours. Foster et al. [11] computed a degradation rate in the film by assuming that the half-life in the film is 100 hours for five volatile organic compounds (i.e., pentane, toluene, naphthalene, anthracene, and pyrene). The estimated half-lives of five PAHs (i.e., naphthalene, anthracene, fluoranthene, phenanthrene, and pyrene) in the film from Kahan et al. [63] are 4.7, 6.0, 2.0, 7.8, 2.0 hours, respectively. Kwamena et al. [62] also estimated half-lives of six PAHs (i.e., naphthalene, anthracene, fluoranthene, phenanthrene, pyrene, benzo(a)pyrene) in the film by interpolating from the kinetic study of Kahan et al. [63]. The half-life in the film for six PAHs in Kwamena et al. are 292, 108, 2092, 650, 417, 61 hours, respectively. The reported half-lives of compounds in the film for above four studies are listed in Table A2. There are difficulties in obtaining reliable estimates on the importance of the urban film. First, for the limited number of compounds with estimated values, there are large discrepancies between the values used. Second, neither the degradation half-life in the film nor its estimation method is available for any compounds in the CARB list. Therefore, we applied a half-life of 100 hours for all compounds. We acknowledge that predicted losses in the film are therefore very uncertain in the Foster et al. model.

Table 11. OH radical rate constant (*k*$_{OH}$, m^3/mol-sec) and estimated half-lives ($t_{1/2}$, hour) of LVP-VOCs in four environmental compartments from the EPI Suite [15] (*Estimated, $^{\#}$Experimental)

Chemical class	Example compounds	k_{OH} *	k_{OH} $^{\#}$	$t_{1/2}$ *			
				air	water	soil	veget-ation
Glycols	Propylene Glycol	1.28E-11	1.20E-11	21	208	416	17
	Diethylene Glycol	2.23E-11	3.00E-11	9	208	416	7
	Ethylene Glycol	8.32E-12	7.70E-12	33	208	416	26
	Dipropylene Glycol	3.13E-11		8	360	720	6
	Butylene Glycol	1.42E-11		18	208	416	14
	Triethylene Glycol	3.64E-11		7	360	720	6
	Hexylene Glycol	1.42E-11		18	360	720	14
	Polyethylene glycol	6.44E-11		4	360	720	3
Glycol Ethers	Diethylene Glycol Ethyl Ether	3.14E-11	5.72E-11	4	360	720	4
	Diethylene Glycol Monobutyl Ether	3.75E-11	7.44E-11	3	208	416	3
	Dipropylene Glycol n-Butyl Ether	4.97E-11		5	360	720	4
	Dipropylene Glycol Methyl Ether Acetate	3.36E-11		8	360	720	6
	Dipropylene Glycol n-Propyl Ether	4.78E-11		5	360	720	4
	Ethylene Glycol Hexyl Ether	2.63E-11		10	208	416	8
	Triethylene Glycol Monobutyl Ether	5.15E-11		5	360	720	4
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	1.39E-11	1.42E-11	18	208	416	14
	n-Heptadecane	2.10E-11		12	208	416	10
	n-Tridecane	1.53E-11	1.16E-11	16	208	416	12
	Conosol 260	1.82E-11	2.22E-11	12	208	416	9
	Conosol 340	1.82E-11	2.22E-11	12	208	416	9
	Solvent Naphtha (Petroleum), Heavy Aliphatic	1.53E-11	1.60E-11	16	208	416	12
Esters	Dimethyl Glutarate	2.56E-12	3.30E-12	78	360	720	61
	Methyl Palmitate	1.88E-11		14	360	720	11
	2-ethylhexyl Benzoate	1.15E-11		22	360	720	17
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	1.62E-11		16	360	720	12
	Glyceryl Triacetate	8.50E-12		30	360	720	24
	Isopropyl Palmitate	2.21E-11		12	360	720	9
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	1.15E-11		22	900	1800	17
	Alkyl (C16-C18) Methyl Esters	1.43E-10		1	360	720	1
Others	Triethanolamine	1.11E-10		2	360	720	2
	Glycerol	1.87E-11		14	208	416	11
	Benzyl Alcohol	8.25E-12	2.29E-12	11	360	720	9
	Stearyl Alcohol	2.67E-11		10	360	720	8

3.3.6. Advective loss rate from air (k_{Aa}, hour^{-1})

Another important parameter that influences the fraction of LVP-VOCs available for ozone forming reactions in the initial airshed is the advective loss rate from air (k_{Aa}). The faster the loss rates in the air basin of concern, the smaller the fraction of LVP-VOCs available for ozone formation reaction in the initial airshed. However, the fraction transported out of the air basin is still available for ozone formation in the downwind area. This may be of concern especially if the downwind region is not in compliance. The loss rate varies depending on the wind speed and direction, time of day, and the topography and size of the air basin [11]. The advective loss rate can be estimated by dividing the wind speed by the size of the area (e.g., air basin) of concern using the following equation:

$$\mathrm{k_{Aa}} = 0.23 \cdot \mathrm{V_{wind}}/(\mathrm{Area}^{0.5}) \qquad (2)$$

where k_{Aa} is the advective loss rate from air (1/hour), V_{wind} is the wind speed (km/hour or m/hour), and *Area* is the size of the study area (m^2). The default yearly average wind speed for the California residential site in the CalTOX model is 11.6 km/hour [38]. This is very similar to the value reported in the National Oceanic and Atmospheric Administration (NOAA) as the annual mean wind speed for the SoCAB is about 12.0 km/hour (=7.5 mile/hour) (http://www.currentresults.com/Weather/US/wind-speed-city-annual.php). Thus, we used 11.6 km/hour as the average wind speed for the SoCAB. We used the size of the study area provided in Table 10. This loss rate can be also estimated by the air residence time (τ), which is inversely proportional to k_{Aa} and wind speed.

3.3.7. Rain events

For compounds with a small *H* value such as glycols, glycol ethers, esters, and alcohols, they are likely to be distributed in the water phase in the ambient environment because the fugacity capacity (i.e., holding capacity of a material or a compartment for a chemical substance) of the water compartment (Z_W, mol/m^3-Pa), which is an inverse of *H*, is about 4 to 8 orders of magnitude greater than that of the air compartment ($Z_A = 4.0 \times 10^{-4}$ mol/m^3-Pa). Thus, the mode of rain events (e.g., intermittent, continuous, or no rain) in the model significantly affects the distribution of LVP-VOCs among compartments As a default setting, the CalTOX model applies an average daily precipitation rate of a specific model area by distributing the annual average precipitation rate throughout the whole year as a continuous rainfall scenario. For example, for a steady-state or Level III version of the model with a continuous rainfall scenario, more than 90% of the compounds whose *H* value is smaller than approximately 0.0001 Pa-m^3/mol are distributed to the water compartment. This indicates that the fraction of these compounds in the air compartment is very small in the continuous rainfall scenario. Refer to Tables A3-A4 in the Appendix for the mass distribution of LVP-VOCs in the continuous rainfall scenario. The ozone problem in California becomes more severe during summer when rain is not expected to occur often, if at all. The average monthly number of hours with measureable precipitation (>0.25 inches) for most of the major cities in California is less than 5 hours during the period of June to September (http://www.wrcc.dri.edu/htmlfiles/hrsofppt.html), indicating that the more heavily populated regions of California have almost no rain during summer. When we assume no rain, less than 5% of compounds whose *H* values are smaller than approximately 1 Pa-m^3/mol would partition into the water compartment, implying that a large fraction of LVP-VOCs is available for ozone forming reactions on days with no rain. Thus, we used the no rain scenario, because SoCAB has very little rain, if any, during summer.

There are three different transport processes from air to other environmental compartments (water, soil, and vegetation), including particle-bound dry deposition, wet deposition driven by precipitation, and diffusion between compartments. With a no rain scenario, we found the modeled diffusion process primarily drives transfer from air to other compartments for the majority of the selected LVP-VOCs, compared to the transfer by dry deposition. However, for those compounds with large K_{ow}, dry deposition is a driving transfer factor over molecular diffusion.

3.3.8. Steady-state vs. dynamic

Emission information could include the rate of release, location of release, and time of release. These three factors would dictate whether LVP-VOCs would contribute to ozone formation locally or regionally because night-time releases could be transferred out of local areas before conditions were met for reactions with OH radicals. Moreover, as LVP-VOCs in the air compartment are depleted due to ozone formation during the day, mass-transfer of LVP-VOCs from other compartments (e.g., soil, water, and vegetation) to air could be another source to the air compartment and result in further ozone formation reactions. In other words, changes in the emission profiles with regard to the above three factors would influence availability of LVP-VOCs for atmospheric reactions leading to ozone formation. To determine the direction of transfers between compartments, we compared the fugacity of each compartment during daytime and nighttime. In addition to emission profiles, another important variable in determining the necessity of additional model complexity is the OH radical concentration (C_{OH}, molecules/cm^3) because it varies diurnally according to the following equation [11]:

$$C_{OH} = (8 \times 10^6) \times e^{-0.1(t-11)^2} \tag{3}$$

where t is time on the 24 hour clock. Foster et al. used the above diurnally varying OH concentration throughout each day in the Level IV calculations. Compared to Level III calculations, different wind speeds and diurnally changing OH radical concentrations can be applied to the Level IV calculations, which allow environmental parameters and conditions to be changed over time. Thus, we ran the Foster model in the dynamic condition (i.e., Level IV version) to evaluate the degree of diurnal changes in concentrations of LVP-VOCs in air.

3.4. Results

3.4.1. Steady-state (Level III) results

We ran both the Foster and CalTOX models in a steady-state condition (Level III version) for both daytime (8 am to 8 pm) and nighttime (8 pm to 8 am) using the dimensions of model compartments that are specific to the SoCAB listed in Table 10. The percent losses by reaction and advection in each compartment for both models and for both time periods are provided in Tables 12-15. During the daytime, both models predict that compounds are primarily either degraded in air due to the reaction with OH radicals or transported out of the air basin by air advection. To run both models for a nighttime scenario, we used Equation 3 to calculate the average 12-hour nighttime OH radical concentration. Due to the small OH radical concentration during the night (1.8× 10^3 molecules/cm^3), which is three orders of magnitude smaller than 12-hour daytime average concentration, loss by reaction in air with OH radicals is negligible (<7%) for all chemicals during the night for both models. As explained in the 'Rain events' section, for compounds that are likely to be distributed in the water phase as a result of small Henry's law constant (H) values, the total loss in the air compartment due to the reaction with OH radicals and advection is negligible in the case of a continuous rainfall scenario. The results of mass distribution with the continuous rainfall scenario are provided in Tables A3-A4 in the Appendix.

For the majority of the compounds in the Foster model, more than 50% of the LVP-VOCs are transported out of the air basin by air advection during the night (see Table 13). On the other hand, as explained in the earlier section about the model differences, large amounts of chemicals are estimated to be in the soil compartment in the simulations using the CalTOX model. Compared to the soil depth (5cm) of the Foster et al model, the soil compartment of the CalTOX model is deeper (approximately 80cm). In addition, the CalTOX model takes into account the water phase (approximately 20%) in the soil compartment whereas the Foster model assumes that the soil compartment only consists of soil particles. Thus, the primary loss pathways during the night from the CalTOX model are either reaction in soil or air advection depending on the magnitude of mass distributed among air and soil. Yadav et al. [64] reported that biodegradation of toluene is decreased by a factor of 2 for every 10°C decrease. As the average difference in temperature between daytime and nighttime is expected to be about 10 °C in Southern California (www.WeatherSpark.com), biodegradation in soil during nighttime will be about a factor of 2 smaller than that during daytime. We acknowledge that there is little data on changes in biodegradation rates in soil by temperature. Thus, the primary loss pathway during the night will be advection from air in the CalTOX model. Overall, the two models produce similar results for both daytime and nighttime modeling scenarios. The percent differences of each loss process between models for both time periods are provided in Tables A5-A6. In addition, the percent loss and the percent difference of each loss process using the default dimensions of model compartments are provided in Tables A7-A12 in the Appendix.

In addition, for dipropylene glycol n-propyl ether, the estimated value of vapor pressure at 25 °C (=48.1 Pa) from the EPI Suite is much higher than the experimental value at 20 °C (=10.7 Pa) (See Table 1). To evaluate the impact of this discrepancy in vapor pressure on the model results, we also ran the CalTOX model with the experimental value at 20 °C and found no changes at the level of five significant figures, confirming that this amount of discrepancy in vapor pressure has no significant impact on the overall model results.

Table 12. Percent loss by reaction and advection in each compartment predicted from the Foster model during daytime

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	film	other	air	water
Glycols	Propylene Glycol	68%	0%	1%	1%	24%	0%
	Diethylene Glycol	80%	0%	1%	1%	11%	0%
	Ethylene Glycol	59%	0%	2%	1%	32%	0%
	Dipropylene Glycol	80%	0%	1%	1%	11%	0%
	Butylene Glycol	63%	0%	1%	1%	19%	0%
	Triethylene Glycol	82%	0%	1%	1%	9%	0%
	Hexylene Glycol	62%	0%	1%	1%	18%	0%
	Polyethylene glycol	88%	0%	1%	1%	3%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	90%	0%	0%	0%	7%	0%
	Diethylene Glycol Monobutyl Ether	90%	0%	0%	0%	5%	0%
	Dipropylene Glycol n-Butyl Ether	85%	0%	0%	0%	7%	0%
	Dipropylene Glycol Methyl Ether Acetate	84%	0%	1%	1%	10%	0%
	Dipropylene Glycol n-Propyl Ether	85%	0%	0%	0%	7%	0%
	Ethylene Glycol Hexyl Ether	78%	0%	1%	1%	12%	0%
	Triethylene Glycol Monobutyl Ether	86%	0%	0%	0%	7%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	76%	0%	0%	0%	23%	0%
	n-Heptadecane	71%	0%	1%	0%	14%	0%
	n-Tridecane	70%	0%	1%	0%	25%	0%
	Conosol 260	80%	0%	1%	0%	15%	0%
	Conosol 340	80%	0%	1%	0%	15%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	75%	0%	1%	0%	21%	0%
Esters	Dimethyl Glutarate	35%	0%	3%	2%	45%	0%
	Methyl Palmitate	69%	0%	1%	0%	15%	0%
	2-ethylhexyl Benzoate	58%	0%	1%	0%	21%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	66%	0%	1%	1%	17%	0%
	Glyceryl Triacetate	50%	0%	1%	1%	25%	0%
	Isopropyl Palmitate	72%	0%	1%	0%	13%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	60%	0%	1%	0%	22%	0%
	Alkyl (C16-C18) Methyl Esters	94%	0%	0%	0%	2%	0%
Others	Triethanolamine	93%	0%	0%	0%	3%	0%
	Glycerol	69%	0%	1%	1%	15%	0%
	Benzyl Alcohol	76%	0%	1%	1%	14%	0%
	Stearyl Alcohol	75%	0%	1%	1%	8%	0%

Table 13. Percent loss by reaction and advection in each compartment predicted from the Foster model during nighttime

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	film	other	air	water
Glycols	Propylene Glycol	0%	0%	4%	4%	73%	0%
	Diethylene Glycol	0%	0%	3%	3%	56%	0%
	Ethylene Glycol	0%	0%	4%	4%	79%	0%
	Dipropylene Glycol	0%	0%	3%	3%	55%	0%
	Butylene Glycol	0%	0%	3%	3%	50%	0%
	Triethylene Glycol	1%	0%	3%	3%	52%	0%
	Hexylene Glycol	0%	0%	3%	3%	48%	0%
	Polyethylene glycol	1%	0%	4%	4%	24%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	1%	0%	4%	3%	63%	0%
	Diethylene Glycol Monobutyl Ether	1%	0%	3%	3%	48%	0%
	Dipropylene Glycol n-Butyl Ether	1%	0%	3%	3%	48%	0%
	Dipropylene Glycol Methyl Ether Acetate	1%	0%	4%	3%	63%	0%
	Dipropylene Glycol n-Propyl Ether	1%	0%	3%	3%	51%	0%
	Ethylene Glycol Hexyl Ether	0%	0%	3%	3%	58%	0%
	Triethylene Glycol Monobutyl Ether	1%	0%	3%	3%	48%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	0%	0%	2%	0%	96%	0%
	n-Heptadecane	0%	0%	3%	0%	49%	0%
	n-Tridecane	0%	0%	4%	0%	84%	0%
	Conosol 260	0%	0%	4%	0%	74%	0%
	Conosol 340	0%	0%	4%	0%	74%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	0%	4%	0%	84%	0%
Esters	Dimethyl Glutarate	0%	0%	4%	3%	69%	0%
	Methyl Palmitate	0%	0%	3%	0%	47%	0%
	2-ethylhexyl Benzoate	0%	0%	3%	1%	49%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	0%	3%	3%	50%	0%
	Glyceryl Triacetate	0%	0%	3%	3%	49%	0%
	Isopropyl Palmitate	0%	0%	3%	0%	47%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	0%	0%	3%	0%	56%	0%
	Alkyl (C16-C18) Methyl Esters	2%	0%	4%	3%	34%	0%
Others	Triethanolamine	1%	0%	4%	4%	33%	0%
	Glycerol	0%	0%	3%	3%	48%	0%
	Benzyl Alcohol	0%	0%	3%	3%	56%	0%
	Stearyl Alcohol	0%	0%	4%	2%	33%	0%

Table 14. Percent loss by reaction and advection in each compartment predicted from the CalTOX model during daytime

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	70%	0%	3%	0%	24%	0%
	Diethylene Glycol	82%	0%	3%	0%	11%	0%
	Ethylene Glycol	59%	1%	5%	0%	32%	0%
	Dipropylene Glycol	86%	0%	1%	0%	11%	0%
	Butylene Glycol	71%	0%	4%	0%	21%	0%
	Triethylene Glycol	81%	0%	4%	1%	9%	0%
	Hexylene Glycol	69%	0%	4%	1%	20%	0%
	Polyethylene glycol	89%	0%	2%	0%	6%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	92%	0%	1%	0%	7%	0%
	Diethylene Glycol Monobutyl Ether	93%	0%	1%	0%	5%	0%
	Dipropylene Glycol n-Butyl Ether	91%	0%	1%	0%	8%	0%
	Dipropylene Glycol Methyl Ether Acetate	88%	0%	1%	0%	11%	0%
	Dipropylene Glycol n-Propyl Ether	91%	0%	1%	0%	8%	0%
	Ethylene Glycol Hexyl Ether	84%	0%	1%	0%	13%	0%
	Triethylene Glycol Monobutyl Ether	86%	0%	3%	0%	7%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	76%	0%	1%	0%	22%	0%
	n-Heptadecane	80%	0%	2%	1%	16%	0%
	n-Tridecane	77%	0%	1%	0%	20%	0%
	Conosol 260	83%	0%	1%	0%	16%	0%
	Conosol 340	83%	0%	1%	0%	16%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	77%	0%	1%	0%	20%	0%
Esters	Dimethyl Glutarate	41%	1%	3%	0%	52%	0%
	Methyl Palmitate	74%	0%	3%	2%	16%	0%
	2-ethylhexyl Benzoate	70%	0%	2%	1%	25%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	77%	0%	1%	0%	20%	0%
	Glyceryl Triacetate	63%	0%	3%	0%	31%	0%
	Isopropyl Palmitate	78%	0%	3%	2%	15%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	71%	0%	1%	0%	26%	0%
	Alkyl (C16-C18) Methyl Esters	98%	0%	0%	0%	1%	0%
Others	Triethanolamine	94%	0%	1%	0%	4%	0%
	Glycerol	55%	0%	19%	1%	12%	0%
	Benzyl Alcohol	82%	0%	1%	0%	15%	0%
	Stearyl Alcohol	80%	0%	3%	2%	13%	0%

Table 15. Percent loss by reaction and advection in each compartment predicted from the CalTOX model during nighttime

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	0%	2%	10%	1%	80%	0%
	Diethylene Glycol	1%	1%	20%	1%	65%	0%
	Ethylene Glycol	0%	2%	12%	1%	78%	0%
	Dipropylene Glycol	1%	1%	9%	1%	79%	0%
	Butylene Glycol	0%	1%	15%	1%	73%	0%
	Triethylene Glycol	1%	1%	22%	3%	50%	0%
	Hexylene Glycol	0%	1%	14%	3%	67%	0%
	Polyethylene glycol	1%	1%	20%	3%	54%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	1%	1%	7%	1%	83%	0%
	Diethylene Glycol Monobutyl Ether	2%	1%	14%	4%	72%	0%
	Dipropylene Glycol n-Butyl Ether	1%	1%	8%	0%	80%	0%
	Dipropylene Glycol Methyl Ether Acetate	1%	1%	5%	0%	87%	0%
	Dipropylene Glycol n-Propyl Ether	1%	1%	6%	0%	85%	0%
	Ethylene Glycol Hexyl Ether	1%	1%	7%	0%	86%	0%
	Triethylene Glycol Monobutyl Ether	1%	1%	22%	4%	51%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	0%	0%	5%	0%	92%	0%
	n-Heptadecane	0%	0%	9%	5%	79%	0%
	n-Tridecane	0%	0%	6%	0%	89%	0%
	Conosol 260	1%	0%	6%	0%	89%	0%
	Conosol 340	1%	0%	6%	0%	89%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	0%	6%	0%	89%	0%
Esters	Dimethyl Glutarate	0%	1%	5%	0%	87%	0%
	Methyl Palmitate	0%	1%	13%	9%	63%	0%
	2-ethylhexyl Benzoate	0%	1%	6%	2%	83%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	1%	5%	0%	88%	0%
	Glyceryl Triacetate	0%	1%	8%	1%	82%	0%
	Isopropyl Palmitate	0%	1%	12%	8%	66%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	0%	0%	3%	0%	90%	0%
	Alkyl (C16-C18) Methyl Esters	6%	1%	12%	8%	59%	0%
Others	Triethanolamine	2%	1%	19%	3%	55%	0%
	Glycerol	0%	0%	42%	3%	27%	0%
	Benzyl Alcohol	1%	1%	7%	0%	84%	0%
	Stearyl Alcohol	0%	1%	13%	9%	62%	0%

3.4.2. Dynamic (Level IV) results

We ran the Foster et al. model in a dynamic condition (Level IV version) for four compounds representing each chemical class listed in Table 1. Figure 5 shows the time-dependent concentrations of propylene glycol, diethylene glycol ethyl ether, iso-paraffinic hydrocarbons, and dimethyl glutarate in the air compartment from the Level IV model with 1000 kg/hour of continuous emission. In addition to diurnally changing OH concentrations, this simulation applies step changes of the advection rate with a period of typical (8 hour) ventilation (days 0-3), followed by a period of reduced (96 hour) ventilation (day 4-6) and finally a return to typical ventilation until day 9. The results reflect these step changes, reaching a new pseudo steady-state with approximately 2 days for all compounds. When applying the high ventilation scenario (8 hour) and 1000 kg/hour of emission to the Level III model, the average concentration of propylene glycol, diethylene glycol ethyl ether, iso-paraffinic hydrocarbons, and dimethyl glutarate in the air compartment is 2.3, 1.0, 2.5, and 3.1 μg/m^3 respectively. This indicates that even if the model runs with dynamic conditions, concentration changes over the entire period are within a factor of 2 or 3 of the mean concentration.

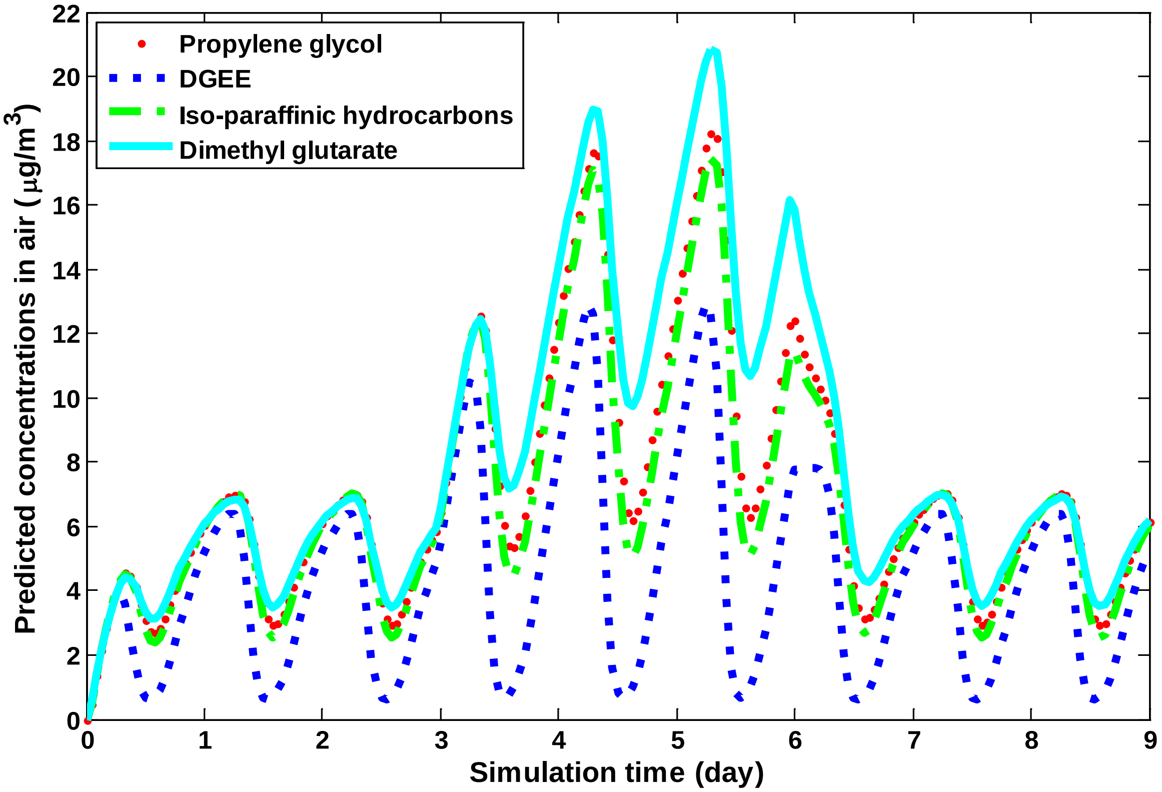

Figure 5. Dynamic predictions of the concentration of three compounds (propylene glycol, diethylene glycol ethyl ether (DGEE), and dimethyl glutarate) and a mixture (iso-paraffinic hydrocarbons) in the air compartment. Concentration increases reflect the low ventilation period (96 hour) from day 4 to day 6

3.4.3. VOC results

To compare the fate of LVP-VOCs with that of VOCs, we ran both the Foster and CalTOX models for 6 VOCs recommended by CARB. The recommended VOCs are acetone, toluene, ethyl acetate, methyl ethyl ketone, 2-butoxyethanol, and isopropyl alcohol. Three major chemical properties including K_{ow}, H, and VP as well as OH radical rate constants and $t_{1/2}$ for all environmental compartments are provided in Tables A13-A14. Note that $t_{1/2\_air}$ of the selected VOCs is much longer than that of the selected LVP-VOCs. The percent losses by reaction and advection in each compartment for both models and for both time periods (daytime and nighttime) are provided in Tables 16-17. During the daytime, both models predict that compounds are primarily either degraded in air due to the reaction with OH radical or transported out of the air basin by air advection with no reactions occurring in water or soil compartments. The proportion that is lost by reaction in air versus by advection to the next air basin where it will eventually be lost by reaction in air is influenced by the magnitude of OH radical rate constants (=ln(2)/$t_{1/2\_air}$). For example, the half-lives in air for acetone, ethyl acetate, and methyl ethyl ketone are 1170, 160, and 223 hours, respectively. Therefore, percent loss by reaction with OH radicals for these three VOCs (i.e., acetone, ethyl acetate, and methyl ethyl ketone) is less than 30% from both models. In contrast, for the LVP-VOCs, the volatility of the compound also influences the results, with some of the compounds having some reaction loss in other compartments. The selected set of LVP-VOCs used in this modeling efforts have shorter half-lives in air (refer to Table 11), with dimethyl glutarate having the longest half-life of 76 hours, than those for acetone, ethyl acetate, and methyl ethyl ketone (refer to Table A14). Thus, median percent loss by reaction with OH radicals for the selected LVP-VOCs is approximately 76% and 77% from the Foster model and the CalTOX model, respectively. From this comparison of fate between the selected LVP-VOCs and the selected VOCs, we learned that OH radical rate constants or half-lives in air are the most influential parameters on the fate of volatilized LVP-VOCs.

Table 16. Percent loss by reaction and advection of VOCs in each compartment predicted from the Foster model and CalTOX model during daytime

Models	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Foster	Acetone	5%	0%	0%	0%	95%	0%
	Toluene	55%	0%	0%	0%	44%	0%
	Ethyl acetate	29%	0%	0%	0%	71%	0%
	Methyl ethyl ketone	24%	0%	0%	0%	75%	0%
	2-butoxyethanol	83%	0%	0%	0%	15%	0%
	Isopropyl Alcohol	61%	0%	0%	0%	35%	0%
CalTOX	Acetone	5%	0%	0%	0%	94%	0%
	Toluene	59%	0%	0%	0%	41%	0%
	Ethyl acetate	28%	0%	0%	0%	72%	0%
	Methyl ethyl ketone	21%	0%	0%	0%	78%	0%
	2-butoxyethanol	81%	0%	0%	0%	18%	0%
	Isopropyl Alcohol	51%	0%	0%	0%	42%	0%

Table 17. Percent loss by reaction and advection of VOCs in each compartment predicted from the Foster model and CalTOX model during nighttime

Models	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Foster	Acetone	0%	0%	0%	0%	99%	0%
	Toluene	0%	0%	0%	0%	100%	0%
	Ethyl acetate	0%	0%	0%	0%	99%	0%
	Methyl ethyl ketone	0%	0%	0%	0%	99%	0%
	2-butoxyethanol	1%	0%	1%	2%	89%	0%
	Isopropyl Alcohol	0%	0%	0%	1%	91%	0%
CalTOX	Acetone	0%	0%	0%	0%	99%	0%
	Toluene	0%	0%	0%	0%	100%	0%
	Ethyl acetate	0%	0%	0%	0%	100%	0%
	Methyl ethyl ketone	0%	0%	0%	0%	99%	0%
	2-butoxyethanol	0%	1%	4%	0%	93%	0%
	Isopropyl Alcohol	0%	2%	6%	1%	87%	0%

3.4.4. Uncertainty analysis

We performed a Monte Carlo uncertainty analysis to determine the relative contribution of input parameters to the output uncertainty (i.e., the fraction available for OH reaction) for each study compound using the CalTOX model. Distributions of input variables used for the uncertainty analysis, including the mean and coefficient of variation (CV) are provided in Table A15. Also, we used a log-normal distribution for all physicochemical properties with the following CVs recommended by McKone [38]: VP = 0.38; H = 0.45; K_{ow} = 0.37; D_{air} (diffusion coefficient in air) = 0.1; $t_{1/2\_air}$ = 1.0. Due to the large number of input variables (n = 74), we used a stepwise method to perform a multiple linear regression on the fraction available for OH reaction and included only the variables whose regression coefficients have a p-value less than 0.05 in the final model. Then, we calculated pairwise correlation coefficients between the output variable and each of the included inputs and computed the percent contribution of the included input parameters to output (the fraction available for OH reaction) uncertainty. We acknowledge that the stepwise regression may inflate the appearance of an effect of the tested parameters and is controversial to use, but it is a standard method in data mining when searching a large space of possible models.

Figure 6 illustrates the relative contribution of each input parameter to the output uncertainty from the Monte Carlo uncertainty analysis. Overall, wind speed and the reaction half-life in air are the two most influential parameters on the overall fraction available for ozone formation.

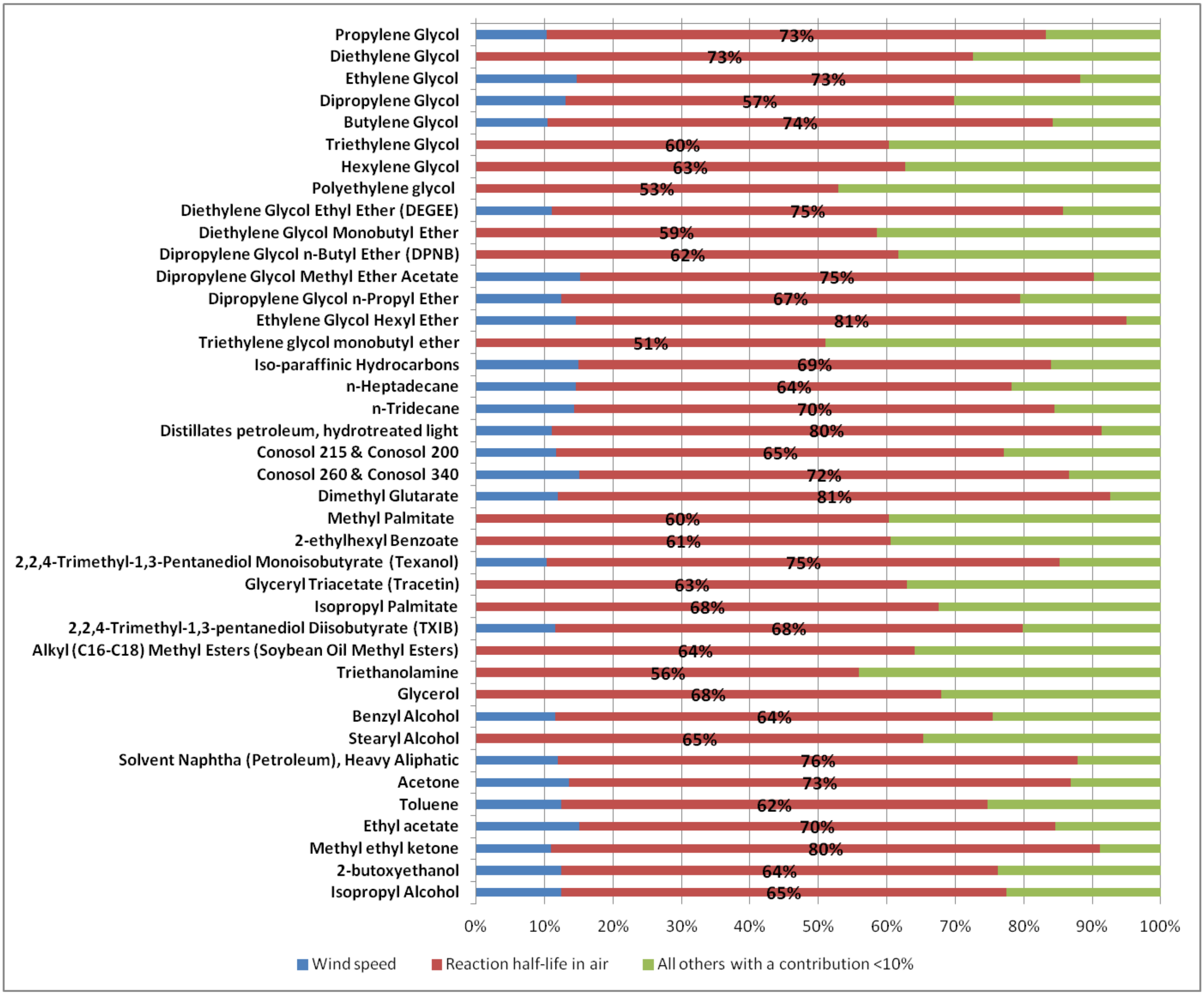

Figure 6. Percent contribution of model inputs on the uncertainty of the overall fraction available for ozone formations for studied compounds from the multiple linear regression analysis. Input parameters with a p-value less than 0.05 from the multiple linear regression with a contribution to output uncertainty less than 10% are included together as "All others with a contribution <10%"

3.5. Discussion

3.5.1. Two-box model and dynamic conditions

One question of interest is whether LVP-VOCs transported outside of the air basin will react with OH radicals in the downwind areas during daytime either on the day of release or on the following day. The yearly average wind direction for the SoCAB is eastward (http://www.currentresults.com/Weather/US/wind-speed-city-annual.php). This is consistent with findings that high concentrations of ozone were predicted in downwind areas of the SoCAB, such as Azusa, Rubidoux, and San Bernardino [3]. This indicates that for those downwind areas, the sources of LVP-VOCs should include not only the emissions from the use of consumer products during the daytime, but also the inflow from upwind areas during both nighttime and daytime. However, the results from the Level III version of both models (Foster et al. and CalTOX) for daytime and nighttime scenarios show that loss by degradation from other environmental compartments is much smaller than loss by degradation due to OH radical reaction and by advection from air. In other words, we found that except glycerol (19% biodegraded in soil during the daytime), more than 90% of the selected LVP-VOCs in the CARB list will be available for ozone forming reactions in air during the day either in the air basin that has releases or in the adjacent air basin which receives advective flows. Thus, if the area of air basin is located downwind of highly populated urban area such as Riverside and San Bernardino Counties, additional inflow of chemicals needs to be considered in multi-compartment models.

We compared results of air concentrations from the Level III and Level IV versions of the Foster model for three compounds and a mixture and confirmed that concentrations responding to step changes to the varying advective rate and to the diurnally changing OH radical concentrations can be reasonably assumed to be the same as the results from the Level III model. In other words, as the mass of LVP-VOCs in the air compartment is computed as a product of the concentration and the volume of the air compartment, the average fraction of LVP-VOCs for ozone formation from the Level IV version is similar to that from the Level III version.

3.5.2. Implications/Limitations

This modeling effort has several implications for determining the fraction of LVP-VOCs available for ozone formation reactions. First, fugacity-based multi-compartment models are suitable for simulating the fate and transport of LVP-VOCs following emissions and two different models applied in this study produce similar results in the loss by reaction due to OH radicals or transported out of the air basin by air advection. Second, for LVP-VOCs with small H and high K_{ow}, model conditions such as rain events and composition of model compartments influence the mass distribution among environmental compartments. Third, we found that loss by reaction in other compartments such as soil, vegetation, and film is negligible for most compounds, confirming that loss by reaction due to OH radical or transported out of the air basin by air advection are major loss mechanisms. In other words, once the selected LVP-VOCs are released outdoors, then more than 90% is available for ozone forming reactions either on the day of release or on the following day. We also found that compared to daytime, the fraction of the compound degraded in all compartments can be ignored during nighttime due to small OH radical concentrations and low temperature.

Limitations of this study are related to the uncertainty and variability of model input parameters. As provided in Table 11, many of the compounds have estimated OH radical rate constants and half-lives in each compartment are not directly measured, but estimated based on its chemical structure. In addition, because half-lives in the film are not available for all compounds, the same 100 hours of half-life were applied to the Foster model. Thus, we might over- or under-estimate the loss by degradation in some of the compartments. Moreover, the actual OH radical concentration in the study area might be different from the value used in this study. Therefore, accounting for measured OH radical concentrations in the different California residential areas would likely improve the reliability of model predictions.

4. MODEL INTEGRATION

4.1. Introduction

In the wastewater treatment model evaluation, we modeled the fate of low vapor pressure - volatile organic compounds (LVP-VOCs) and determined the fraction volatilized from the wastewater treatment plant (WWTP). Additionally, in a multi-compartment model, we determined the fraction of LVP-VOCs available for formation of ozone following emissions to air using the multi-compartment fate and transport model (i.e., CalTOX). To understand the ultimate fate of LVP-VOCs that are discharged from a WWTP to surface water and that are volatilized from a WWTP, we integrated two model results in this chapter.

4.2. Methods and Results

For the fate of the selected LVP-VOCs that are discharged from a WWTP to surface water, we ran the CalTOX model with a surface water release scenario to determine the fate of the compound discharged with sewer effluent to surface water. Table18 illustrates the modeled distribution of the LVP-VOCs among different environmental compartments, including air, water, and sediment for a surface water release from the CalTOX model. Overall, our study compounds are likely to be present in water due to their high water solubility while hydrophobic compounds (e.g., iso-paraffinic hydrocarbons, isopropyl palmitate and stearyl alcohol, etc.) are likely to be in sediment due to a large K_{ow} value. Because of this mass distribution in water and sediment, all the selected 33 LVP-VOCs are biodegraded in water or sediment and no significant volatilization is expected to occur from surface water. We multiplied the fraction that is discharged from a WWTP model ('Effluent discharge' column in Table 7) by the fraction of reaction in air from the CalTOX model with a surface water release (Table 19).

The portion of down-the-drain LVP-VOCs that may form ozone can be estimated as a product of the results from a WWTP model (i.e., the fraction volatilized) and those from emissions to outdoor air or surface water from the CalTOX model (i.e., the fraction reacted with OH radicals). Thus, we multiplied the fraction of volatilization from a WWTP model ('Volatilization' column in Table 7) by the fraction of reaction in air from the CalTOX model with an air release (Table 13).

Tables 20-21 show the fate of the LVP-VOCs that are discharged into surface water in an outdoor environment and that are volatilized from a WWTP, respectively. Because none of the compounds has a significant fraction of volatilization from the WWTP (<9%) and from the surface water (<2%), once LVP-VOCs are disposed down the drain at the end of the consumer product use, the potential for ozone formation is negligible.

Table 18. Distribution of LVP-VOCs among different environmental compartments in a surface water release scenario

Chemical class	Example compounds	air	water	sediment
Glycols	Propylene Glycol	0%	100%	0%
	Diethylene Glycol	0%	100%	0%
	Ethylene Glycol	0%	100%	0%
	Dipropylene Glycol	0%	100%	0%
	Butylene Glycol	0%	100%	0%
	Triethylene Glycol	0%	100%	0%
	Hexylene Glycol	0%	100%	0%
	Polyethylene glycol	0%	100%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	100%	0%
	Diethylene Glycol Monobutyl Ether	0%	100%	0%
	Dipropylene Glycol n-Butyl Ether	0%	100%	0%
	Dipropylene Glycol Methyl Ether Acetate	0%	100%	0%
	Dipropylene Glycol n-Propyl Ether	0%	100%	0%
	Ethylene Glycol Hexyl Ether	0%	98%	2%
	Triethylene Glycol Monobutyl Ether	0%	100%	0%
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	0%	4%	96%
	n-Heptadecane	0%	4%	96%
	n-Tridecane	0%	4%	96%
	Conosol 260	0%	4%	96%
	Conosol 340	0%	4%	96%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	4%	96%
Esters	Dimethyl Glutarate	0%	100%	0%
	Methyl Palmitate	0%	4%	96%
	2-ethylhexyl Benzoate	0%	7%	93%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	83%	17%
	Glyceryl Triacetate	0%	100%	0%
	Isopropyl Palmitate	0%	4%	96%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	0%	9%	91%
	Alkyl (C16-C18) Methyl Esters	0%	4%	96%
Others	Triethanolamine	0%	100%	0%
	Glycerol	0%	100%	0%
	Benzyl Alcohol	0%	100%	0%
	Stearyl Alcohol	0%	4%	96%

Table 19. Percent loss of LVP-VOCs by reaction and advection in each compartment predicted from the CalTOX model during daytime with a surface water release scenario

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	sediment	other	air	water
Glycols	Propylene Glycol	0%	0%	0%	0%	0%	0%
	Diethylene Glycol	0%	0%	0%	0%	0%	0%
	Ethylene Glycol	0%	0%	0%	0%	0%	0%
	Dipropylene Glycol	0%	0%	0%	0%	0%	0%
	Butylene Glycol	0%	0%	0%	0%	0%	0%
	Triethylene Glycol	0%	0%	0%	0%	0%	0%
	Hexylene Glycol	0%	0%	0%	0%	0%	0%
	Polyethylene glycol	0%	0%	0%	0%	0%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	0%	0%	0%	0%	0%
	Diethylene Glycol Monobutyl Ether	0%	0%	0%	0%	0%	0%
	Dipropylene Glycol n-Butyl Ether	0%	0%	0%	0%	0%	0%
	Dipropylene Glycol Methyl Ether Acetate	0%	0%	0%	0%	0%	0%
	Dipropylene Glycol n-Propyl Ether	0%	0%	0%	0%	0%	0%
	Ethylene Glycol Hexyl Ether	0%	0%	0%	0%	0%	0%
	Triethylene Glycol Monobutyl Ether	0%	0%	0%	0%	0%	0%
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	0%	5%	0%	0%	0%	0%
	n-Heptadecane	0%	6%	0%	0%	0%	0%
	n-Tridecane	0%	6%	0%	0%	0%	0%
	Conosol 260	0%	6%	0%	0%	0%	0%
	Conosol 340	0%	6%	0%	0%	0%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	6%	0%	0%	0%	0%
Esters	Dimethyl Glutarate	0%	0%	0%	0%	0%	0%
	Methyl Palmitate	0%	6%	0%	0%	0%	0%
	2-ethylhexyl Benzoate	0%	14%	0%	0%	0%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	23%	0%	0%	0%	0%
	Glyceryl Triacetate	0%	0%	0%	0%	0%	0%
	Isopropyl Palmitate	0%	6%	0%	0%	0%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	1%	8%	0%	0%	0%	0%
	Alkyl (C16-C18) Methyl Esters	0%	6%	0%	0%	0%	0%
Others	Triethanolamine	0%	0%	0%	0%	0%	0%
	Glycerol	0%	0%	0%	0%	0%	0%
	Benzyl Alcohol	0%	0%	0%	0%	0%	0%
	Stearyl Alcohol	0%	6%	0%	0%	0%	0%

Table 20. Fate of LVP-VOCs that are discharged from a wastewater treatment plant to surface water in an outdoor environment

Chemical class	Example compounds	Reaction in air	Advection from air	Degradation in other compartments
Glycols	Propylene Glycol	0%	0%	0%
	Diethylene Glycol	0%	0%	0%
	Ethylene Glycol	0%	0%	0%
	Dipropylene Glycol	0%	0%	0%
	Butylene Glycol	0%	0%	0%
	Triethylene Glycol	0%	0%	0%
	Hexylene Glycol	0%	0%	0%
	Polyethylene glycol	0%	0%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	0%	0%
	Diethylene Glycol Monobutyl Ether	0%	0%	0%
	Dipropylene Glycol n-Butyl Ether	0%	0%	0%
	Dipropylene Glycol Methyl Ether Acetate	0%	0%	0%
	Dipropylene Glycol n-Propyl Ether	0%	0%	0%
	Ethylene Glycol Hexyl Ether	0%	0%	0%
	Triethylene Glycol Monobutyl Ether	0%	0%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	0%	0%	5%
	n-Heptadecane	0%	0%	6%
	n-Tridecane	0%	0%	6%
	Conosol 260	0%	0%	6%
	Conosol 340	0%	0%	6%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	0%	0%
Esters	Dimethyl Glutarate	0%	0%	0%
	Methyl Palmitate	0%	0%	6%
	2-ethylhexyl Benzoate	0%	0%	14%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	0%	23%
	Glyceryl Triacetate	0%	0%	0%
	Isopropyl Palmitate	0%	0%	6%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	**1%**	0%	8%
	Alkyl (C16-C18) Methyl Esters	0%	0%	6%
Others	Triethanolamine	0%	0%	0%
	Glycerol	0%	0%	0%
	Benzyl Alcohol	0%	0%	0%
	Stearyl Alcohol	0%	0%	6%

Table 21. Fate of LVP-VOCs that are volatilized from a wastewater treatment plant in an outdoor environment

Chemical class	Example compounds	Reaction in air	Advection from air	Degradation in other compartments
Glycols	Propylene Glycol	0%	0%	0%
	Diethylene Glycol	0%	0%	0%
	Ethylene Glycol	0%	0%	0%
	Dipropylene Glycol	0%	0%	0%
	Butylene Glycol	0%	0%	0%
	Triethylene Glycol	0%	0%	0%
	Hexylene Glycol	0%	0%	0%
	Polyethylene glycol	0%	0%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	0%	0%
	Diethylene Glycol Monobutyl Ether	0%	0%	0%
	Dipropylene Glycol n-Butyl Ether	0%	0%	0%
	Dipropylene Glycol Methyl Ether Acetate	0%	0%	0%
	Dipropylene Glycol n-Propyl Ether	0%	0%	0%
	Ethylene Glycol Hexyl Ether	0%	0%	0%
	Triethylene Glycol Monobutyl Ether	0%	0%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	**7%**	2%	0%
	n-Heptadecane	0%	0%	0%
	n-Tridecane	**2%**	1%	0%
	Conosol 260	0%	0%	0%
	Conosol 340	0%	0%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	**2%**	1%	0%
Esters	Dimethyl Glutarate	0%	0%	0%
	Methyl Palmitate	0%	0%	0%
	2-ethylhexyl Benzoate	**1%**	0%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	0%	0%
	Glyceryl Triacetate	0%	0%	0%
	Isopropyl Palmitate	0%	0%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	**8%**	3%	0%
	Alkyl (C16-C18) Methyl Esters	0%	0%	0%
Others	Triethanolamine	0%	0%	0%
	Glycerol	0%	0%	0%
	Benzyl Alcohol	0%	0%	0%
	Stearyl Alcohol	0%	0%	0%

5. SUMMARY AND CONCLUSIONS

5.1. Summary of findings

In general, LVP-VOCs in consumer products are not easy to evaporate due to their relatively low vapor pressure and high boiling point. We note that it was beyond the scope of this study to determine the faction of LVP-VOCs that volatilizes at the point of use and thus the environmental fate modeling for this project started with compounds in the outdoor air. To evaluate ozone formation potential of LVP-VOCs that may be evaporated during the use of consumer products, we determined the fraction of emitted LVP-VOCs in the gas phase that is available for ozone formation reactions via a modeling exercise. We also note that this study did not determine the amount of ozone formed. More complex atmospheric photochemical models need to be used in conjunction with our results to simulate how much ozone will be formed in the atmosphere.

The followings are a summary of findings from our studies.

1. We compared the WWTP model results between concentration-based and fugacity-based WWTP fate models, and found that fugacity-based models (Clark et al. [17] and Seth et al. [18]) are the most suitable for simulating the fate of selected LVP-VOCs in a WWTP because they are compatible with other fugacity-based multimedia models and are algebraically simple and robust.

2. The biodegradation half-life in wastewater is the most uncertain input variable during sewage treatment processes among other input parameters. Biodegradation half-life values are roughly estimated and generally not measured. The sensitivity analysis on the half-life highlights that while the uncertainty in the biodegradation half-lives can influence the fraction that volatilizes from a WWTP for some of the selected LVP-VOCs, the majority of the change relates to whether the compound is biodegraded or removed with the sludge.

3. Loss by volatilization in a WWTP is negligible for most compounds, confirming that losses by biodegradation or sorption to sludge are major loss mechanisms. Also, for only one compound, less than 2% is volatilized from surface water. In other words, once the selected 33 LVP-VOCs are disposed down the drain, then the majority of compounds (=28/33) had no evaporation from a WWTP and for the other five compounds/mixtures studied less than 11% is volatilized and may participate in the ozone formation reactions in the atmosphere (refer to Table 21).

4. Fugacity-based multi-compartment models (Foster et al. [11] and CalTOX [38]) are suitable for simulating the fate and transport of LVP-VOCs following emissions and two models produce similar results in the overall fate of LVP-VOCs in an urban multimedia environment.

5. For LVP-VOCs with small Henry's law constant (H) and high octanol-water partition coefficient (K_{ow}), model conditions such as rain events and composition of model compartments influence the mass distribution among environmental compartments. Specifically, the values of the input parameters (e.g., precipitation rate, the fraction of the

horizontal area that is surface water) implemented in this study (i.e., Southern California during the dry, hot summer season) differ from those that would be implemented in other states. Therefore, the studies of other states in the United States with different landscape and climate factors would have very different results. However, the vast majority of the population of California lives in a region with a dry summer and little surface water, and therefore results are expected to be similar.

6. Loss by reaction in other compartments such as soil, vegetation, and film is negligible for most compounds, confirming that losses by reaction due to OH radical or transported out of the air basin by air advection are major loss mechanisms. In other words, once the selected LVP-VOCs are in the outdoor air, then more than 90% is available for ozone forming reactions during the day either in the air basin that has releases or in the adjacent air basin which receives advective flows.

7. Compared to daytime, the fraction of the compound degraded in all compartments can be ignored during nighttime due to small OH radical concentrations and low temperature.

8. From the results of the Level III (steady state) and Level IV (dynamic) versions of the Foster model, the average fraction of the selected LVP-VOCs available for ozone formation from the Level IV version is similar to that from the Level III version, indicating that dynamic conditions do not significantly impact the predictions of multi-compartment models

5.2. Conclusions

When comparing results (i.e., the overall fraction available for ozone formation) from two modes of releases (i.e., direct release to outdoor air and disposed down the drain), we realized the importance of determining the fraction of LVP-VOCs volatilized or disposed down the drain when the product is used by consumers. Because of the extreme differences in the portion of the compounds available for ozone forming potential from emissions to air during use and from down-the-drain disposal, reliable prediction of the fraction of compounds volatilized to air during the use of cleaning products becomes critical for determining the fraction of LVP-VOCs available for ozone forming reactions in many product classes. In addition, many of the compounds have estimated OH radical rate constants and half-lives in each compartment are not directly measured, but estimated based on its chemical structure. Thus, a robust method to estimate environmental half-lives or measured values would improve the overall results on the fraction available for ozone formation. The results from this study can provide important information and modeling tools to evaluate the impact of LVP-VOCs on air quality.

6. RECOMMENDATIONS

In future research, a detailed quantitative uncertainty assessment applied to the model results is needed to evaluate the level of uncertainty that is attributable to lack of precision in chemical property values as well as from variability and uncertainty in input parameters, and from model uncertainty resulting from various assumptions related to environmental half-lives. In addition, future research needs the development and evaluation of volatilization models regarding various cleaning product-associated human activities, including washing clothes, dishwashing, and surface cleaning as well as other use activities associated with fabric softeners, soaps and liquids for hand washing, cosmetics, fragrances, sunscreens, adhesives, sealants, paints, bleaching agents, etc. Future research including measurements of LVP-VOCs at different locations of the WWTP such as before and after the aeration tank will be helpful.

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LIST OF PUBLICATIONS

Shin, H.M.; McKone, T.E.; Bennett, D.H., Contribution of Low Vapor Pressure - Volatile Organic Compounds (LVP-VOCs) from Consumer Products to Ozone Formation in Urban Atmospheres. *Atmospheric Environment* **2015**, 108: 98-106.

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

AEF	adjusted emission factor
AOPWIN	Atmospheric Oxidation Program for Microsoft Windows
CARB	California Air Resources Board
CAS	chemical abstracts service
CDD	chlorinated dibenzodioxins
C_{OH}	OH radical concentration in air
CPCat	Chemical and Product Categories
CV	coefficient of variation
EPI Suite	Estimation Program Interface Suite
H	Henry’s law constant
k_{Aa}	advective loss rate from air
K_d	partition coefficient between solids and water
K_LA	effective mass transfer coefficient
k_{OH}	overall OH radical rate constant
K_{OW}	octanol-water partition coefficient
k_{Ra}	first-order degradation rate in air due to OH radical reaction
LVP-VOC	low vapor pressure - volatile organic compound
MIR	maximum incremental reactivity
MLSS	mixed liquor suspended solids
MTC	overall liquid mass transfer coefficient
MW	molecular weight
NOAA	National Oceanic and Atmospheric Administration
NOx	nitrogen oxides
O_3	ozone
PAH	polycyclic aromatic hydrocarbons
PFO^-	perfluorooctanoate
PFOA	perfluorooctanoic acid
QSA(P)R	quantitative structure-activity (property) relationship
SMILES	simplified molecular-input line-entry system
SoCAB	South Coast Air Basin
STP	sewage treatment plant
S_w	water solubility
$t_{1/2}$	half-life
U.S. EPA	United States Environmental Protection Agency
VOC	volatile organic compound
VP	vapor pressure
WWTP	wastewater treatment plant
Z	fugacity capacity

APPENDIX

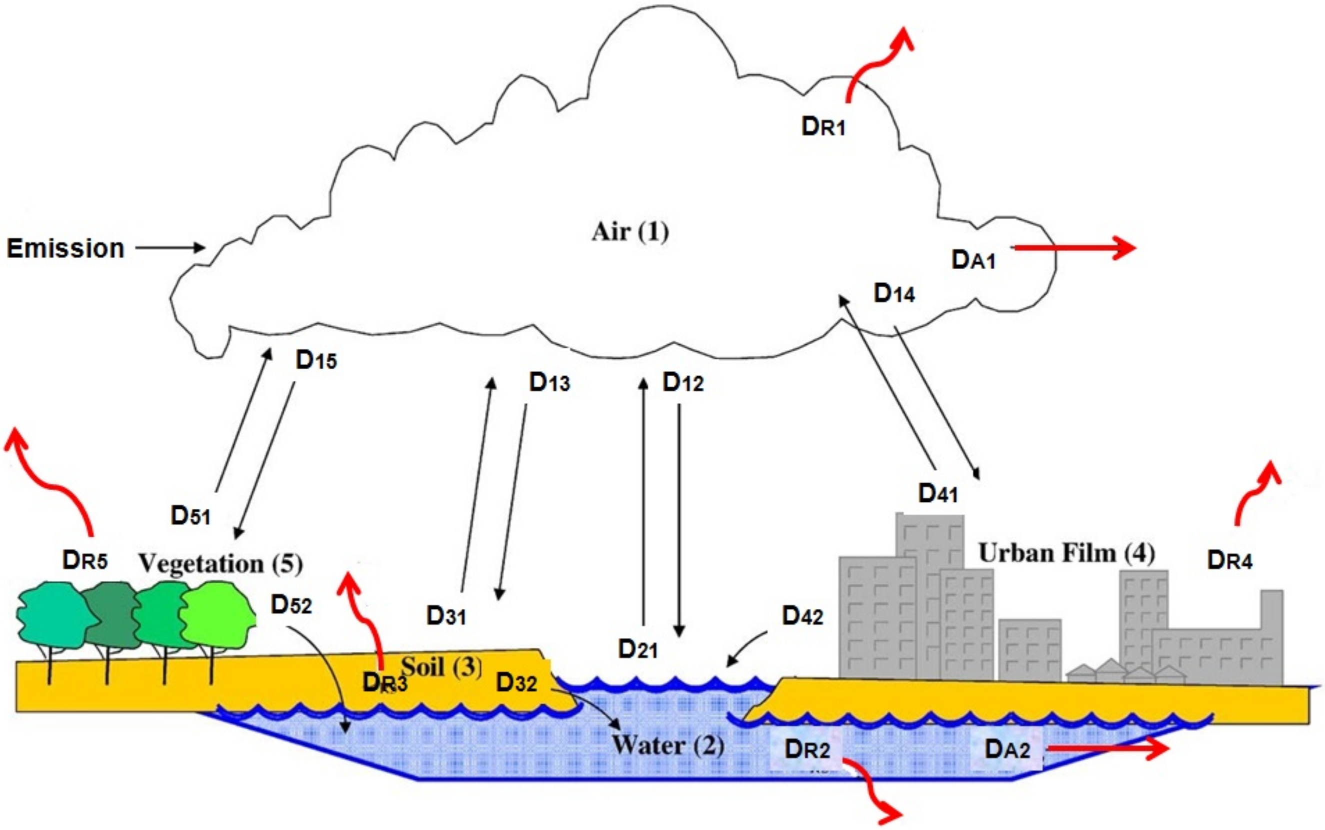


Figure A1. Foster Model: Urban model environment with reaction, advection, and inter-compartmental transfer *D* values (excerpt from Foster et al. [11]). Numbers in parenthesis are a compartmental number (e.g., 1 for air, 2 for water, etc.).

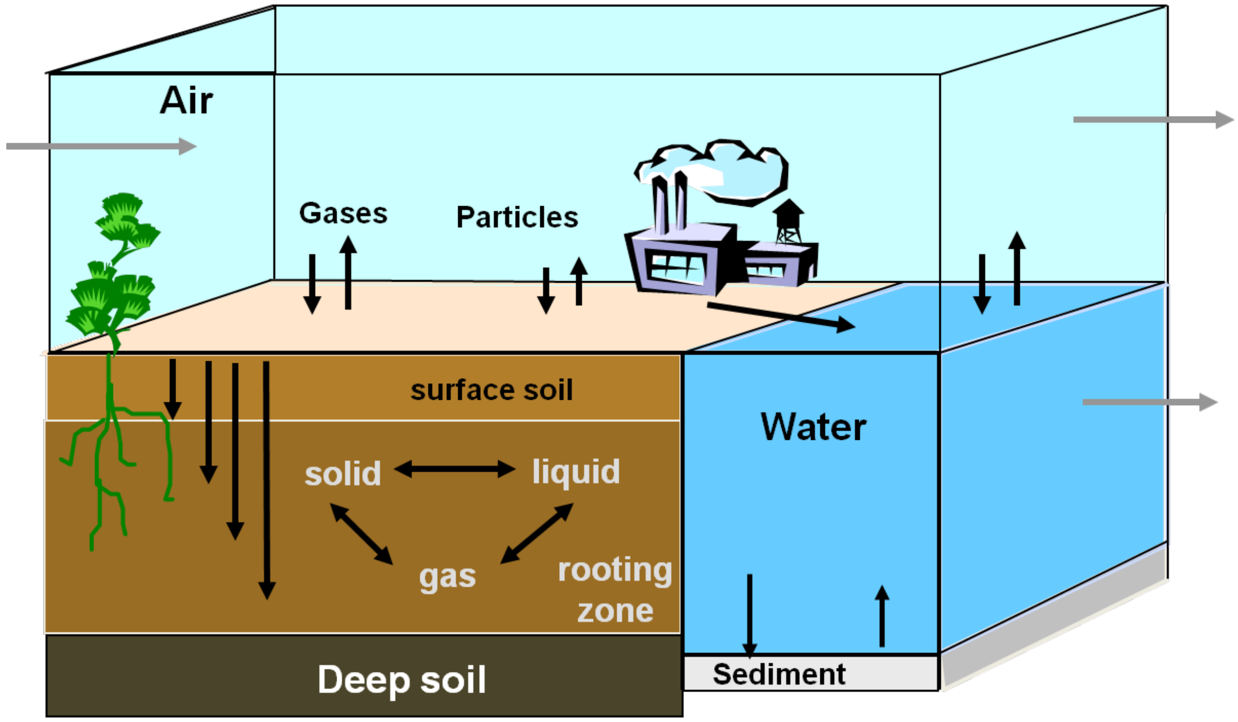
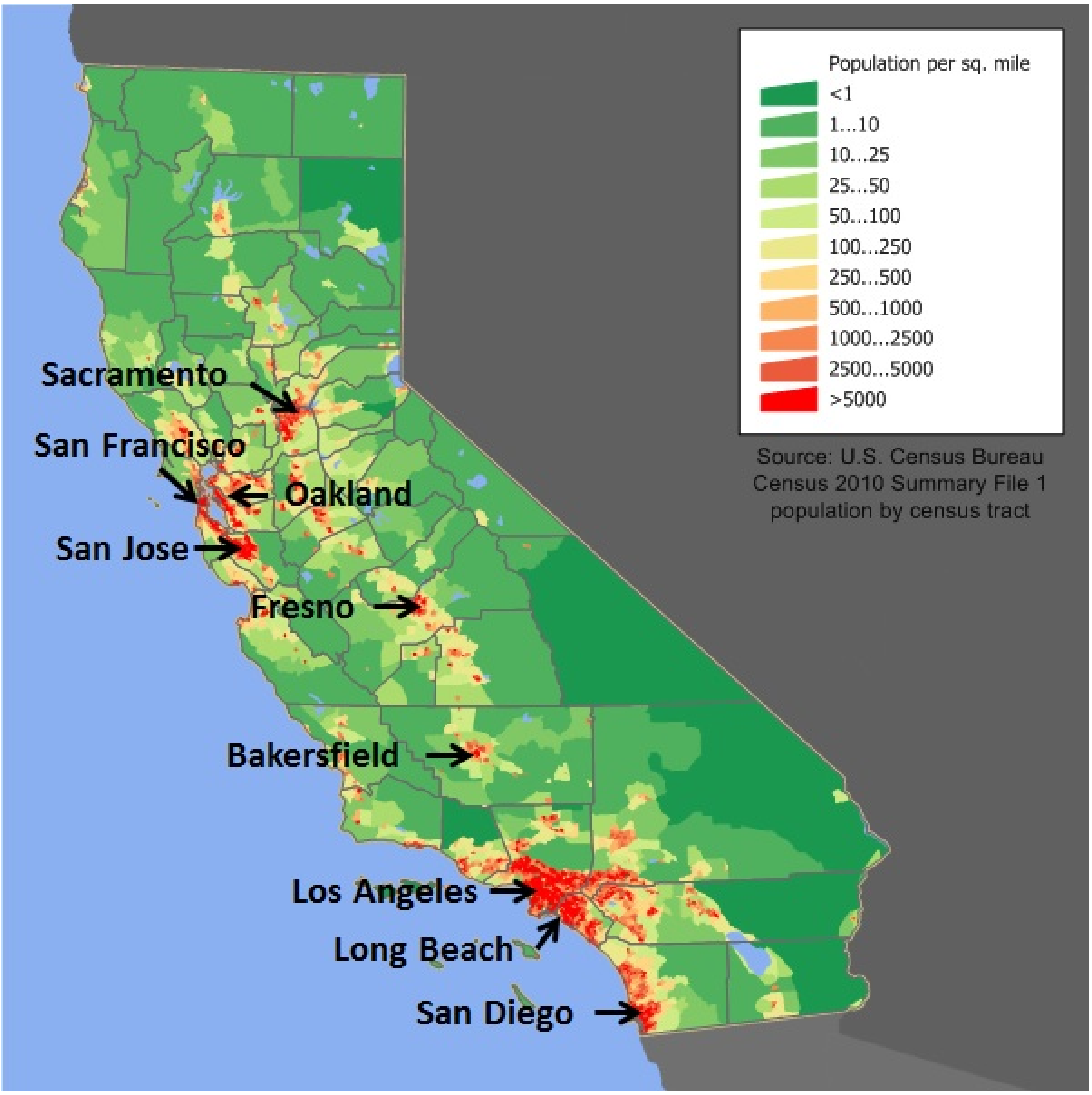


Figure A2. Mass-exchange processes in the CalTOX model among seven compartments.



Source: U.S. Census Bureau Census 2010 Summary File 1 population by census tract

Figure A3. Population density in California and locations of major cities with large population (Source: U.S. Census Bureau, 2010).

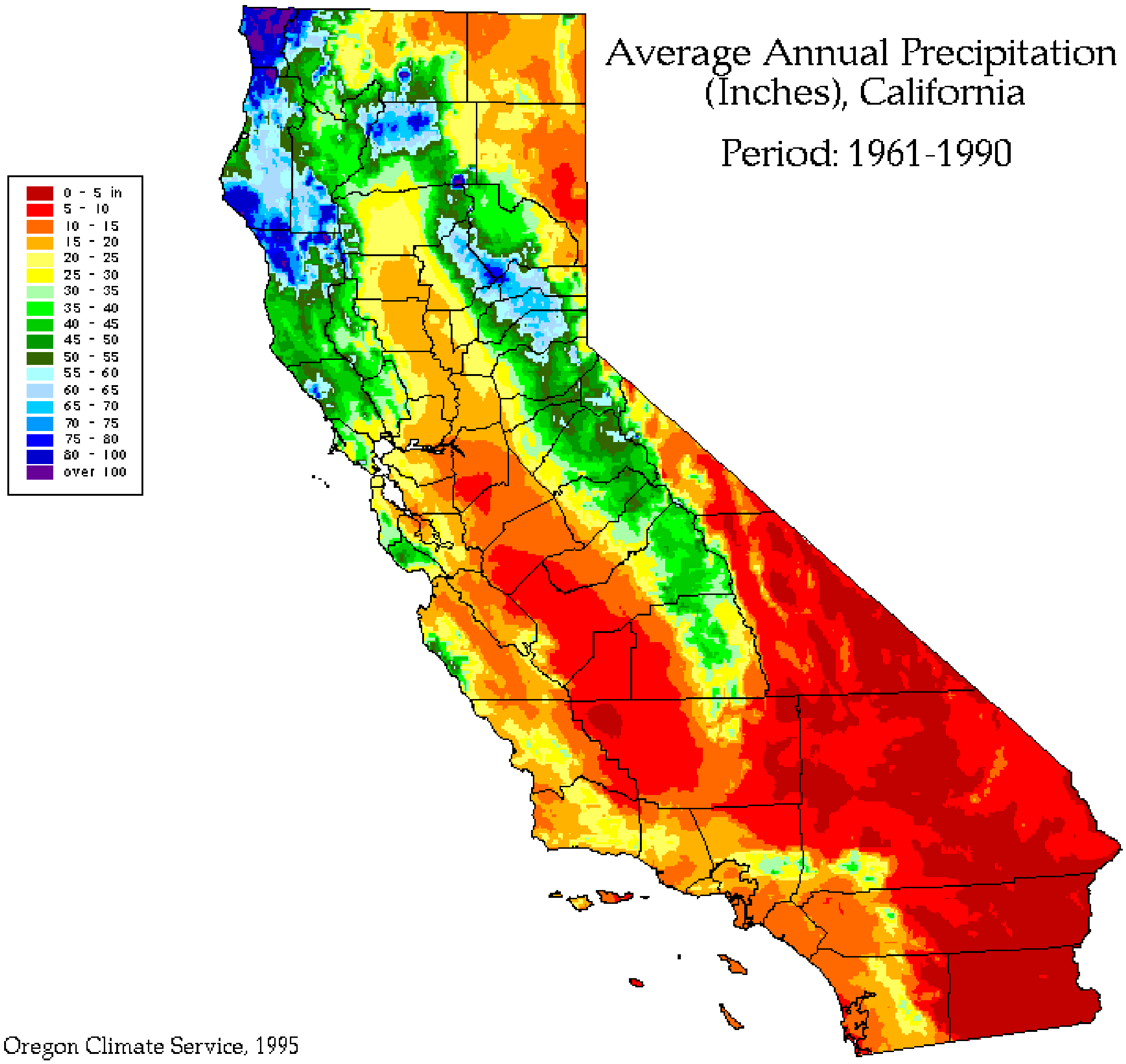


Figure A4. Average annual precipitation rate (in inches) in California over the period of 1961 to 1990 (Source: Oregon Climate Service, 1995).

Table A1. Default dimensions of model compartments used in Foster et al. [11] and CalTOX [38] models (#only used in Foster et al., *only used in CalTOX)

		Height/depth (m)	Surface area (m^2)	Fraction of total horizontal area (unitless)	Volume (m^3)
Foster et al.	Bulk air	1000	1.0E+09	1	1.0E+12
	Water	2	1.0E+08	0.1	2.0E+08
	Soil	0.05	1.0E+08	0.1	5.0E+06
	Vegetation	0.001	5.0E+08	0.1	5.0E+05
	Urban film#	5.00E-8	3.5E+09	0.7	175
CalTOX	Bulk air	700	4.1E+11	1	2.9E+14
	Water	5	7.5E+09	0.02	3.7E+10
	Vegetation	0.0014	4.0E+11	0.98	5.7E+08
	Ground-soil	0.01	4.0E+11	0.98	4.0 E+09
	Root-zone*	0.785	4.0E+11	0.98	3.2 E+11
	Vadose*	0.557	4.0E+11	0.98	2.3 E+11
	Sediment*	0.05	7.5E+09	0.02	3.7 E+08
	Aquifer*	3	4.1E+11	1	1.2 E+12

Table A2. Reported half-lives (hours) of compounds on organic film from four studies

	Diamond et al. [46]	Foster et al. [11]	Kahan et al. [63]	Kwamena et al. [62]
naphthalene		100	4.7	292
anthracene		100	6	108
phenanthrene	5		7.8	650
fluoranthene	11		2	2092
tetra-CDD[1]	111			
penta-CDD	205			
octa-CDD	2252			
pentane		100		
toluene		100		
pyrene		100	2	417
benzo(a)pyrene				61

Note: 1. chlorinated dibenzodioxins

Table A3. Percent mass distribution among each compartment predicted from the Foster model using a continuous rainfall scenario

Chemical class	Example compounds	Distribution			
		air	water	film	other
Glycols	Propylene Glycol	0%	99%	0%	1%
	Diethylene Glycol	0%	98%	0%	2%
	Ethylene Glycol	0%	99%	0%	1%
	Dipropylene Glycol	0%	97%	0%	3%
	Butylene Glycol	0%	96%	0%	4%
	Triethylene Glycol	0%	97%	0%	3%
	Hexylene Glycol	0%	95%	0%	5%
	Polyethylene glycol	0%	96%	0%	4%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	98%	0%	2%
	Diethylene Glycol Monobutyl Ether	0%	95%	0%	5%
	Dipropylene Glycol n-Butyl Ether	0%	92%	0%	7%
	Dipropylene Glycol Methyl Ether Acetate	1%	92%	0%	6%
	Dipropylene Glycol n-Propyl Ether	0%	94%	0%	5%
	Ethylene Glycol Hexyl Ether	6%	64%	3%	27%
	Triethylene Glycol Monobutyl Ether	0%	96%	0%	4%
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	100%	0%	0%	0%
	n-Heptadecane	32%	16%	49%	3%
	n-Tridecane	96%	1%	3%	0%
	Conosol 260	90%	2%	8%	0%
	Conosol 340	90%	2%	8%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	96%	1%	3%	0%
Esters	Dimethyl Glutarate	2%	91%	0%	6%
	Methyl Palmitate	15%	28%	52%	5%
	2-ethylhexyl Benzoate	15%	29%	48%	8%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	4%	55%	12%	28%
	Glyceryl Triacetate	0%	96%	0%	4%
	Isopropyl Palmitate	18%	23%	56%	4%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	44%	18%	32%	6%
	Alkyl (C16-C18) Methyl Esters	5%	30%	54%	11%
Others	Triethanolamine	0%	96%	0%	4%
	Glycerol	0%	96%	0%	4%
	Benzyl Alcohol	1%	87%	1%	11%
	Stearyl Alcohol	6%	30%	55%	10%

Table A4. Percent mass distribution among each compartment predicted from the CalTOX model using a continuous rainfall scenario

Chemical class	Example compounds	Distribution			
		air	water	soil	other
Glycols	Propylene Glycol	0%	34%	43%	23%
	Diethylene Glycol	0%	29%	36%	35%
	Ethylene Glycol	0%	34%	42%	24%
	Dipropylene Glycol	0%	39%	39%	21%
	Butylene Glycol	0%	30%	39%	32%
	Triethylene Glycol	0%	36%	35%	29%
	Hexylene Glycol	0%	34%	40%	26%
	Polyethylene glycol	0%	32%	31%	37%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	41%	43%	16%
	Diethylene Glycol Monobutyl Ether	0%	25%	42%	32%
	Dipropylene Glycol n-Butyl Ether	0%	32%	52%	16%
	Dipropylene Glycol Methyl Ether Acetate	0%	34%	61%	5%
	Dipropylene Glycol n-Propyl Ether	0%	38%	50%	12%
	Ethylene Glycol Hexyl Ether	1%	20%	75%	3%
	Triethylene Glycol Monobutyl Ether	0%	32%	35%	33%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	86%	0%	14%	0%
	n-Heptadecane	8%	1%	34%	56%
	n-Tridecane	46%	0%	53%	1%
	Conosol 260	38%	0%	61%	1%
	Conosol 340	38%	0%	61%	1%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	46%	0%	53%	1%
Esters	Dimethyl Glutarate	0%	32%	64%	4%
	Methyl Palmitate	2%	1%	55%	42%
	2-ethylhexyl Benzoate	4%	3%	67%	27%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	1%	11%	84%	4%
	Glyceryl Triacetate	0%	30%	50%	20%
	Isopropyl Palmitate	2%	1%	52%	45%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	9%	4%	78%	9%
	Alkyl (C16-C18) Methyl Esters	2%	2%	57%	40%
Others	Triethanolamine	0%	32%	32%	36%
	Glycerol	0%	24%	30%	46%
	Benzyl Alcohol	0%	33%	63%	4%
	Stearyl Alcohol	2%	2%	54%	42%

Table A5. Percent difference of loss between the CalTOX model and the Foster model during daytime. Percent loss from the Foster model is subtracted from that from the CalTOX model

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	2%	0%	2%	-1%	1%	0%
	Diethylene Glycol	2%	0%	3%	0%	0%	0%
	Ethylene Glycol	0%	1%	3%	-1%	0%	0%
	Dipropylene Glycol	5%	0%	1%	0%	1%	0%
	Butylene Glycol	8%	0%	3%	-1%	2%	0%
	Triethylene Glycol	-1%	0%	4%	0%	0%	0%
	Hexylene Glycol	7%	0%	3%	0%	2%	0%
	Polyethylene glycol	2%	0%	2%	0%	3%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	2%	0%	0%	0%	0%	0%
	Diethylene Glycol Monobutyl Ether	3%	0%	1%	0%	0%	0%
	Dipropylene Glycol n-Butyl Ether	5%	0%	0%	0%	0%	0%
	Dipropylene Glycol Methyl Ether Acetate	4%	0%	0%	-1%	0%	0%
	Dipropylene Glycol n-Propyl Ether	5%	0%	0%	0%	0%	0%
	Ethylene Glycol Hexyl Ether	6%	0%	0%	-1%	1%	0%
	Triethylene Glycol Monobutyl Ether	1%	0%	3%	0%	0%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	-1%	0%	1%	0%	0%	0%
	n-Heptadecane	9%	0%	2%	0%	2%	0%
	n-Tridecane	8%	0%	1%	-1%	-5%	0%
	Conosol 260	3%	0%	1%	-1%	1%	0%
	Conosol 340	3%	0%	1%	-1%	1%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	2%	0%	1%	-1%	0%	0%
Esters	Dimethyl Glutarate	5%	1%	1%	-2%	7%	0%
	Methyl Palmitate	5%	0%	3%	1%	2%	0%
	2-ethylhexyl Benzoate	12%	0%	2%	-1%	4%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	11%	0%	0%	-1%	3%	0%
	Glyceryl Triacetate	12%	0%	1%	-1%	6%	0%
	Isopropyl Palmitate	6%	0%	3%	1%	2%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	11%	0%	1%	-1%	4%	0%
	Alkyl (C16-C18) Methyl Esters	4%	0%	0%	0%	-1%	0%
Others	Triethanolamine	1%	0%	1%	0%	1%	0%
	Glycerol	-14%	0%	18%	0%	-3%	0%
	Benzyl Alcohol	7%	0%	0%	-1%	1%	0%
	Stearyl Alcohol	5%	0%	2%	1%	4%	0%

Table A6. Percent difference of loss between the CalTOX model and the Foster model during nighttime. Percent loss from the Foster model is subtracted from that from the CalTOX model

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	0%	2%	7%	-3%	7%	0%
	Diethylene Glycol	0%	1%	16%	-2%	9%	0%
	Ethylene Glycol	0%	2%	8%	-3%	-1%	0%
	Dipropylene Glycol	0%	1%	6%	-2%	24%	0%
	Butylene Glycol	0%	1%	12%	-2%	23%	0%
	Triethylene Glycol	0%	1%	19%	0%	-2%	0%
	Hexylene Glycol	0%	1%	11%	0%	18%	0%
	Polyethylene glycol	0%	1%	16%	-1%	30%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	1%	3%	-3%	20%	0%
	Diethylene Glycol Monobutyl Ether	1%	1%	11%	0%	24%	0%
	Dipropylene Glycol n-Butyl Ether	0%	1%	5%	-1%	31%	0%
	Dipropylene Glycol Methyl Ether Acetate	0%	1%	2%	-3%	24%	0%
	Dipropylene Glycol n-Propyl Ether	0%	1%	3%	-2%	34%	0%
	Ethylene Glycol Hexyl Ether	0%	1%	4%	-3%	28%	0%
	Triethylene Glycol Monobutyl Ether	0%	1%	19%	1%	3%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	0%	0%	5%	-1%	-3%	0%
	n-Heptadecane	0%	0%	9%	2%	30%	0%
	n-Tridecane	0%	0%	6%	-4%	6%	0%
	Conosol 260	0%	0%	6%	-4%	15%	0%
	Conosol 340	0%	0%	6%	-4%	15%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	0%	6%	-4%	6%	0%
Esters	Dimethyl Glutarate	0%	1%	2%	-3%	18%	0%
	Methyl Palmitate	0%	1%	13%	6%	16%	0%
	2-ethylhexyl Benzoate	0%	1%	5%	-1%	34%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	1%	2%	-2%	38%	0%
	Glyceryl Triacetate	0%	1%	5%	-2%	33%	0%
	Isopropyl Palmitate	0%	1%	12%	5%	19%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	0%	0%	2%	-3%	35%	0%
	Alkyl (C16-C18) Methyl Esters	4%	1%	9%	3%	25%	0%
Others	Triethanolamine	0%	1%	16%	-2%	21%	0%
	Glycerol	0%	0%	39%	0%	-21%	0%
	Benzyl Alcohol	0%	1%	3%	-3%	28%	0%
	Stearyl Alcohol	0%	1%	11%	4%	29%	0%

Table A7. Percent loss by reaction and advection in each compartment predicted from the Foster model during daytime using default dimensions of model compartments

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	film	other	air	water
Glycols	Propylene Glycol	68%	0%	2%	0%	24%	0%
	Diethylene Glycol	81%	0%	1%	0%	11%	0%
	Ethylene Glycol	59%	0%	3%	1%	32%	1%
	Dipropylene Glycol	81%	0%	1%	0%	11%	0%
	Butylene Glycol	65%	0%	2%	0%	19%	0%
	Triethylene Glycol	83%	0%	1%	0%	10%	0%
	Hexylene Glycol	64%	0%	2%	0%	19%	0%
	Polyethylene glycol	89%	0%	1%	0%	3%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	90%	0%	1%	0%	7%	0%
	Diethylene Glycol Monobutyl Ether	90%	0%	1%	0%	5%	0%
	Dipropylene Glycol n-Butyl Ether	86%	0%	1%	0%	7%	0%
	Dipropylene Glycol Methyl Ether Acetate	84%	0%	1%	0%	10%	0%
	Dipropylene Glycol n-Propyl Ether	86%	0%	1%	0%	8%	0%
	Ethylene Glycol Hexyl Ether	79%	0%	1%	0%	13%	0%
	Triethylene Glycol Monobutyl Ether	86%	0%	1%	0%	7%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	76%	0%	1%	0%	22%	0%
	n-Heptadecane	73%	0%	2%	0%	14%	0%
	n-Tridecane	70%	0%	2%	0%	25%	0%
	Conosol 260	80%	0%	2%	0%	15%	0%
	Conosol 340	80%	0%	2%	0%	15%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	75%	0%	2%	0%	21%	0%
Esters	Dimethyl Glutarate	36%	0%	5%	1%	45%	1%
	Methyl Palmitate	70%	0%	2%	0%	15%	0%
	2-ethylhexyl Benzoate	59%	0%	2%	0%	21%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	67%	0%	2%	0%	17%	0%
	Glyceryl Triacetate	52%	0%	3%	1%	26%	0%
	Isopropyl Palmitate	73%	0%	2%	0%	13%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	61%	0%	2%	0%	22%	0%
	Alkyl (C16-C18) Methyl Esters	95%	0%	0%	0%	2%	0%
Others	Triethanolamine	93%	0%	1%	0%	3%	0%
	Glycerol	70%	0%	2%	0%	15%	0%
	Benzyl Alcohol	76%	0%	2%	0%	14%	0%
	Stearyl Alcohol	77%	0%	2%	0%	8%	0%

Table A8. Percent loss by reaction and advection in each compartment predicted from the Foster model during nighttime using default dimensions of model compartments

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	film	other	air	water
Glycols	Propylene Glycol	0%	0%	2%	0%	94%	0%
	Diethylene Glycol	0%	0%	2%	0%	89%	0%
	Ethylene Glycol	0%	0%	2%	0%	95%	0%
	Dipropylene Glycol	0%	0%	2%	0%	88%	0%
	Butylene Glycol	0%	0%	2%	0%	87%	0%
	Triethylene Glycol	0%	0%	2%	0%	87%	0%
	Hexylene Glycol	0%	0%	2%	0%	86%	0%
	Polyethylene glycol	0%	0%	4%	1%	67%	1%
Glycol Ethers	Diethylene Glycol Ethyl Ether	0%	0%	2%	0%	91%	0%
	Diethylene Glycol Monobutyl Ether	0%	0%	2%	0%	85%	0%
	Dipropylene Glycol n-Butyl Ether	0%	0%	2%	0%	86%	0%
	Dipropylene Glycol Methyl Ether Acetate	0%	0%	2%	0%	91%	0%
	Dipropylene Glycol n-Propyl Ether	0%	0%	2%	0%	87%	0%
	Ethylene Glycol Hexyl Ether	0%	0%	2%	0%	89%	0%
	Triethylene Glycol Monobutyl Ether	0%	0%	2%	0%	85%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	0%	0%	1%	0%	99%	0%
	n-Heptadecane	0%	0%	2%	0%	86%	0%
	n-Tridecane	0%	0%	2%	0%	96%	0%
	Conosol 260	0%	0%	2%	0%	94%	0%
	Conosol 340	0%	0%	2%	0%	94%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	0%	0%	2%	0%	96%	0%
Esters	Dimethyl Glutarate	0%	0%	2%	0%	93%	0%
	Methyl Palmitate	0%	0%	2%	0%	85%	0%
	2-ethylhexyl Benzoate	0%	0%	2%	0%	86%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	0%	0%	2%	0%	86%	0%
	Glyceryl Triacetate	0%	0%	2%	0%	86%	0%
	Isopropyl Palmitate	0%	0%	2%	0%	85%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	0%	0%	2%	0%	88%	0%
	Alkyl (C16-C18) Methyl Esters	1%	0%	3%	0%	76%	0%
Others	Triethanolamine	1%	0%	3%	1%	76%	0%
	Glycerol	0%	0%	2%	0%	85%	0%
	Benzyl Alcohol	0%	0%	2%	0%	89%	0%
	Stearyl Alcohol	0%	0%	3%	0%	75%	0%

Table A9. Percent loss by reaction and advection in each compartment predicted from the CalTOX model during daytime using default dimensions of model compartments

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	79%	1%	9%	1%	5%	0%
	Diethylene Glycol	82%	0%	9%	1%	2%	0%
	Ethylene Glycol	68%	1%	14%	1%	7%	0%
	Dipropylene Glycol	90%	0%	3%	0%	2%	0%
	Butylene Glycol	76%	0%	11%	1%	4%	0%
	Triethylene Glycol	76%	0%	10%	2%	2%	0%
	Hexylene Glycol	70%	0%	11%	3%	4%	0%
	Polyethylene glycol	87%	0%	5%	1%	1%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	96%	0%	1%	0%	1%	0%
	Diethylene Glycol Monobutyl Ether	94%	0%	3%	0%	1%	0%
	Dipropylene Glycol n-Butyl Ether	94%	0%	2%	0%	1%	0%
	Dipropylene Glycol Methyl Ether Acetate	94%	0%	2%	0%	2%	0%
	Dipropylene Glycol n-Propyl Ether	95%	0%	1%	0%	2%	0%
	Ethylene Glycol Hexyl Ether	92%	0%	3%	0%	3%	0%
	Triethylene Glycol Monobutyl Ether	82%	0%	7%	2%	1%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	90%	0%	4%	0%	5%	0%
	n-Heptadecane	86%	0%	5%	3%	3%	0%
	n-Tridecane	89%	0%	4%	0%	4%	0%
	Conosol 260	92%	0%	3%	0%	3%	0%
	Conosol 340	92%	0%	3%	0%	3%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	89%	0%	4%	0%	4%	0%
Esters	Dimethyl Glutarate	60%	1%	12%	1%	14%	0%
	Methyl Palmitate	73%	0%	9%	6%	3%	0%
	2-ethylhexyl Benzoate	80%	0%	6%	2%	5%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	88%	0%	3%	0%	4%	0%
	Glyceryl Triacetate	74%	0%	9%	2%	7%	0%
	Isopropyl Palmitate	78%	0%	7%	5%	3%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	86%	0%	2%	0%	6%	0%
	Alkyl (C16-C18) Methyl Esters	98%	0%	1%	0%	0%	0%
Others	Triethanolamine	92%	0%	3%	0%	1%	0%
	Glycerol	39%	0%	35%	2%	2%	0%
	Benzyl Alcohol	90%	0%	3%	0%	3%	0%
	Stearyl Alcohol	79%	0%	7%	5%	2%	0%

Table A10. Percent loss by reaction and advection in each compartment predicted from the CalTOX model during nighttime using default dimensions of model compartments

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	0%	3%	43%	3%	24%	0%
	Diethylene Glycol	1%	1%	51%	4%	12%	0%
	Ethylene Glycol	0%	3%	44%	3%	21%	0%
	Dipropylene Glycol	1%	2%	34%	5%	22%	0%
	Butylene Glycol	0%	2%	47%	4%	17%	0%
	Triethylene Glycol	0%	1%	42%	6%	7%	0%
	Hexylene Glycol	0%	1%	38%	9%	13%	0%
	Polyethylene glycol	1%	1%	41%	6%	8%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	3%	2%	31%	4%	28%	0%
	Diethylene Glycol Monobutyl Ether	2%	1%	43%	10%	17%	0%
	Dipropylene Glycol n-Butyl Ether	2%	2%	32%	9%	23%	0%
	Dipropylene Glycol Methyl Ether Acetate	2%	3%	28%	2%	35%	0%
	Dipropylene Glycol n-Propyl Ether	2%	2%	30%	3%	31%	0%
	Ethylene Glycol Hexyl Ether	1%	3%	38%	1%	33%	0%
	Triethylene Glycol Monobutyl Ether	1%	0%	41%	8%	7%	0%
Hydrocarbon solvents	Iso-paraffinic Hydrocarbons	1%	0%	33%	1%	47%	0%
	n-Heptadecane	1%	0%	35%	20%	22%	0%
	n-Tridecane	1%	0%	37%	1%	38%	0%
	Conosol 260	1%	0%	36%	1%	39%	0%
	Conosol 340	1%	0%	36%	1%	39%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	1%	0%	37%	1%	38%	0%
Esters	Dimethyl Glutarate	0%	3%	30%	2%	34%	0%
	Methyl Palmitate	0%	1%	32%	23%	11%	0%
	2-ethylhexyl Benzoate	0%	2%	30%	10%	27%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	1%	2%	29%	3%	35%	0%
	Glyceryl Triacetate	0%	2%	33%	5%	25%	0%
	Isopropyl Palmitate	0%	1%	32%	22%	13%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	1%	1%	17%	1%	41%	0%
	Alkyl (C16-C18) Methyl Esters	6%	1%	30%	21%	10%	0%
Others	Triethanolamine	1%	1%	41%	6%	8%	0%
	Glycerol	0%	0%	57%	4%	3%	0%
	Benzyl Alcohol	1%	3%	32%	2%	29%	0%
	Stearyl Alcohol	0%	1%	32%	23%	11%	0%

Table A11. Percent difference of loss between the CalTOX model and the Foster model during daytime. Percent loss from the Foster model is subtracted from that from the CalTOX model using default dimensions of model compartments

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	11%	0%	9%	-2%	-19%	0%
	Diethylene Glycol	1%	0%	9%	-1%	-9%	0%
	Ethylene Glycol	9%	1%	14%	-2%	-25%	-1%
	Dipropylene Glycol	9%	0%	3%	-1%	-9%	0%
	Butylene Glycol	11%	0%	11%	-1%	-15%	0%
	Triethylene Glycol	-7%	0%	10%	1%	-8%	0%
	Hexylene Glycol	6%	0%	11%	1%	-15%	0%
	Polyethylene glycol	-2%	0%	5%	0%	-2%	0%
Glycol Ethers	Diethylene Glycol Ethyl Ether	5%	0%	1%	-1%	-5%	0%
	Diethylene Glycol Monobutyl Ether	4%	0%	2%	0%	-4%	0%
	Dipropylene Glycol n-Butyl Ether	8%	0%	2%	0%	-6%	0%
	Dipropylene Glycol Methyl Ether Acetate	10%	0%	2%	-1%	-8%	0%
	Dipropylene Glycol n-Propyl Ether	9%	0%	1%	-1%	-6%	0%
	Ethylene Glycol Hexyl Ether	13%	0%	3%	-1%	-10%	0%
	Triethylene Glycol Monobutyl Ether	-4%	0%	7%	1%	-6%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	14%	0%	4%	-1%	-18%	0%
	n-Heptadecane	13%	0%	5%	1%	-11%	0%
	n-Tridecane	19%	0%	4%	-2%	-21%	0%
	Conosol 260	12%	0%	3%	-1%	-12%	0%
	Conosol 340	12%	0%	3%	-1%	-12%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	14%	0%	4%	-2%	-16%	0%
Esters	Dimethyl Glutarate	24%	1%	11%	-4%	-32%	-1%
	Methyl Palmitate	3%	0%	9%	4%	-12%	0%
	2-ethylhexyl Benzoate	21%	0%	6%	0%	-16%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	21%	0%	3%	-2%	-13%	0%
	Glyceryl Triacetate	22%	0%	8%	-1%	-19%	0%
	Isopropyl Palmitate	5%	0%	7%	3%	-11%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	25%	0%	2%	-2%	-17%	0%
	Alkyl (C16-C18) Methyl Esters	3%	0%	1%	0%	-2%	0%
Others	Triethanolamine	-1%	0%	3%	0%	-2%	0%
	Glycerol	-31%	0%	34%	1%	-14%	0%
	Benzyl Alcohol	13%	0%	3%	-1%	-11%	0%
	Stearyl Alcohol	2%	0%	7%	3%	-6%	0%

Table A12. Percent difference of loss between the CalTOX model and the Foster model during nighttime. Percent loss from the Foster model is subtracted from that from the CalTOX model using default dimensions of model compartments

Chemical class	Example compounds	Loss by reaction				Loss by advection	
		air	water	soil	other	air	water
Glycols	Propylene Glycol	0%	3%	43%	1%	-70%	0%
	Diethylene Glycol	0%	1%	50%	2%	-77%	0%
	Ethylene Glycol	0%	3%	44%	2%	-74%	0%
	Dipropylene Glycol	1%	2%	34%	3%	-66%	0%
	Butylene Glycol	0%	2%	47%	2%	-70%	0%
	Triethylene Glycol	0%	0%	42%	5%	-80%	0%
	Hexylene Glycol	0%	1%	37%	7%	-73%	0%
	Polyethylene glycol	0%	1%	41%	2%	-59%	-1%
Glycol Ethers	Diethylene Glycol Ethyl Ether	2%	2%	30%	3%	-63%	0%
	Diethylene Glycol Monobutyl Ether	2%	1%	43%	8%	-69%	0%
	Dipropylene Glycol n-Butyl Ether	2%	2%	31%	7%	-63%	0%
	Dipropylene Glycol Methyl Ether Acetate	2%	2%	28%	1%	-56%	0%
	Dipropylene Glycol n-Propyl Ether	2%	2%	29%	2%	-56%	0%
	Ethylene Glycol Hexyl Ether	1%	3%	38%	0%	-57%	0%
	Triethylene Glycol Monobutyl Ether	0%	0%	41%	6%	-79%	0%
Hydro-carbon solvents	Iso-paraffinic Hydrocarbons	1%	0%	33%	0%	-52%	0%
	n-Heptadecane	1%	0%	35%	18%	-64%	0%
	n-Tridecane	1%	0%	37%	-1%	-59%	0%
	Conosol 260	1%	0%	36%	-1%	-56%	0%
	Conosol 340	1%	0%	36%	-1%	-56%	0%
	Solvent Naphtha (Petroleum), Heavy Aliphatic	1%	0%	37%	-1%	-58%	0%
Esters	Dimethyl Glutarate	0%	3%	29%	1%	-59%	0%
	Methyl Palmitate	0%	1%	32%	21%	-74%	0%
	2-ethylhexyl Benzoate	0%	2%	29%	9%	-59%	0%
	2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol)	1%	2%	28%	2%	-51%	0%
	Glyceryl Triacetate	0%	2%	33%	3%	-61%	0%
	Isopropyl Palmitate	0%	1%	31%	20%	-72%	0%
	2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate	1%	1%	17%	0%	-47%	0%
	Alkyl (C16-C18) Methyl Esters	5%	1%	30%	18%	-66%	0%
Others	Triethanolamine	1%	1%	40%	3%	-68%	0%
	Glycerol	0%	0%	56%	3%	-83%	0%
	Benzyl Alcohol	1%	3%	31%	1%	-60%	0%
	Stearyl Alcohol	0%	1%	32%	19%	-65%	0%

Table A13. Major chemical properties of VOCs predicted from EPI Suite [15]. Experimental values are in parenthesis.

Chemical class	Example compounds	log K_{ow} (unitless)	H (Pa-m^3/mol)	VP (Pa)
VOCs	Acetone	-0.2 (-0.2)	5.0E+00 (3.5E+00)	3.3E+04 (3.1E+04)
	Toluene	2.5 (2.7)	6.0E+02 (6.7E+02)	3.2E+03 (3.8E+03)
	Ethyl acetate	0.9 (0.7)	2.4E+01 (1.4E+01)	1.3E+04 (1.2E+04)
	Methyl ethyl ketone	0.3 (0.3)	6.7E+00 (5.8E+00)	1.3E+04 (1.2E+04)
	2-butoxyethanol	0.6 (0.8)	9.9E-03 (1.6E-01)	6.3E+01 (1.2E+02)
	Isopropyl Alcohol	0.3 (0.1)	7.6E-01 (8.2E-01)	6.6E+03 (6.1E+03)

Table A14. OH radical rate constant (k_{OH}, m^3/mol-sec) and estimated half-lives ($t_{1/2}$, hour) of VOCs in four environmental compartments from the EPI Suite [15] (*Estimated, $^{\#}$Experimental)

				$t_{1/2}$ *			
Chemical class	**Example compounds**	**k_{OH} ***	**k_{OH} $^{\#}$**	**air**	**water**	**soil**	**vegetation**
VOCs	Acetone	2.0E-13	2.2E-13	1170	360	720	720
	Toluene	5.2E-12	6.0E-12	43	360	720	720
	Ethyl acetate	1.7E-12	1.6E-12	160	360	720	720
	Methyl ethyl ketone	1.3E-12	1.2E-12	223	360	720	720
	2-butoxyethanol	2.4E-11	1.9E-11	13.8	208	416	416
	Isopropyl Alcohol	7.3E-12	5.1E-12	51	360	720	39

Table A15. Distribution of input variables used in the CalTOX model [38] for uncertainty analysis: mean and coefficient of variation (CV) for lognormal distribution

Input parameter (units)	symbol	mean	CV
contaminated area in m^2	Area	1.4×10^{10}	0.1
annual average precipitation (m/d)	rain	0	0.56
Flux; surface water into landscape (m/d)	inflow	0	0.1
Land surface runoff (m/d)	runoff	0	1.0
Atmospheric dust load (kg/m^3)	rhob_a	6.15×10^{-8}	0.2
Dry deposition velocity, air particles (m/d)	v_d	500	0.3
Aerosol organic fraction	foc_ap	0.2	0.1
Volume fraction of water in leaf	beta_leaf	0.5	0.05
Volume fraction of air in leaf	alpha_leaf	0.18	0.2
Volume fraction of lipid in leaf	lipid_leaf	0.002	0.2
Volume fraction of water in stem	beta_stem	0.4	0.15
Volume fraction of water in root	beta_root	0.6	0.15
Primary production dry vegetation(kg/m^2/y)	veg_prod	0.9	1.0
Wet interception fraction	IF_w	0.1	0.1
Avg thickness of leaf surface(cuticle)(m)	d_cuticle	2.0×10^{-6}	0.2
Stem wet density (kg/m^3)	rho_stm	830	0.2
Leaf wet density (kg/m^3)	rho_leaf	820	0.3
Root wet density (kg/m^3)	rho_root	800	0.05
Veg attenuation fctr, dry interception(m^2/kg)	atf_leaf	2.9	0.01
Stomata area fraction(area stomata/area leaf)	na_st	0.007	0.2
Effective pore depth	del_st	2.0×10^{-5}	0.2
Boundary layer thickness over leafs	del_a	0.002	1.0
Leaf surface erosion half-life (d)	Thalf_le	14	1.0
Ground-water recharge (m/d)	recharge	1.6×10^{-4}	1.0
Evaporation of water from surface water (m/d)	evaporate	4.3×10^{-4}	1.0
Thickness of the ground soil layer (m)	d_g	0.01	1.0
Soil particle density (kg/m^3)	rhos_s	2600	0.05
Water content in surface soil (vol fraction)	beta_g	0.18	0.33
Air content in the surface soil (vol fraction)	alpha_g	0.28	0.29
Erosion of surface soil (kg/m^2-d)	erosion_g	5.5×10^{-4}	1.0
Bioturbation (m^2/d)	D_bio	1.2×10^{-4}	1.0
Thickness of the root-zone soil (m)	d_s	0.15	0.47

Table A15 (continued). Distribution of input variables used in the CalTOX model [38]for uncertainty analysis: mean and coefficient of variation (CV) for lognormal distribution

Input parameter (units)	symbol	mean	CV
Water content of root-zone soil (vol. frctn.)	beta_s	0.2	0.34
Air content of root-zone soil (vol. frctn.)	alpha_s	0.24	0.31
Thickness of the vadose-zone soil (m)	d_v	0.57	0.37
Water content; vadose-zone soil (vol. frctn.)	beta_v	0.19	0.32
Air content of vadose-zone soil (vol. frctn.)	alpha_v	0.2	0.3
Thickness of the aquifer layer (m)	d_q	3	0.3
Solid material density in aquifer (kg/m^3)	rhos_q	2600	0.05
Porosity of the aquifer zone	beta_q	0.2	0.2
Fraction of land area in surface water	f_arw	0.02	0.2
Average depth of surface waters (m)	d_w	5	1.0
Suspended sediment in surface water (kg/m^3)	rhob_w	0.8	1.0
Suspended sediment deposition (kg/m^2/d)	deposit	10.5	0.3
Thickness of the sediment layer (m)	d_d	0.05	1.0
Solid material density in sediment (kg/m^3)	rhos_d	2600	0.05
Porosity of the sediment zone	beta_d	0.2	0.2
Sediment burial rate (m/d)	bury_d	1.0×10^{-6}	5.0
Ambient environmental temperature (K)	Temp	298	0.06
Surface water current in m/d	current_w	0	1.0
Organic carbon fraction in upper soil zone	foc_s	0.008	1.98
Organic carbon fraction in vadose zone	foc_v	0.002	0.96
Organic carbon fraction in aquifer zone	foc_q	0.002	0.96
Organic carbon fraction in sediments	foc_d	0.02	1
Boundary layer thickness in air above soil (m)	del_ag	0.005	0.2
Yearly average wind speed (m/d)	v_w	2.8×10^{5}	0.17