Chemosphere 153 (2016) 130–137

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Volatilization of low vapor pressure – volatile organic compounds (LVP–VOCs) during three cleaning products-associated activities: Potential contributions to ozone formation

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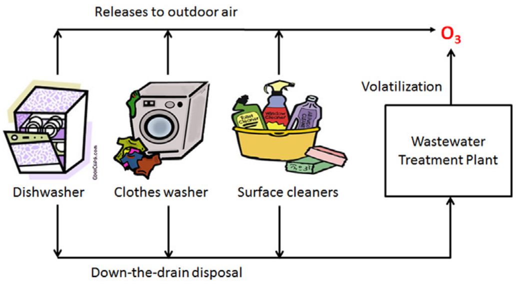
HIGHLIGHTS

- Predicts the fraction of LVP–VOCs volatilized from three cleaning product uses.
- Compares contribution to ozone formation for two modes of releases.
- Impact on ozone formation is very sensitive to what occurs during the use phase.
- This study helps evaluate the impact of LVP–VOCs on air quality.
- Shows the need for emissions of LVP–VOCs for other use categories.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form
9 February 2016
Accepted 29 February 2016

Handling Editor: I. Cousins

Keywords:
Cleaning product
Consumer product
Low vapor pressure-volatile organic compounds
Ozone
Volatilization model

ABSTRACT

There have been many studies to reduce ozone formation mostly from volatile organic compound (VOC) sources. However, the role of low vapor pressure (LVP)–VOCs from consumer products remains mostly unexplored and unaddressed. This study explores the impact of high production volume LVP–VOCs on ozone formation from three cleaning products-associated activities (dishwashing, clothes washing, and surface cleaning). We develop a model framework to account for the portion available for ozone formation during the use phase and from the down-the-drain disposal. We apply experimental studies that measured emission rates or models that were developed for estimating emission rates of organic compounds during the use phase. Then, the fraction volatilized ($f_{\text{volatilized}}$) and the fraction disposed down the drain ($f_{\text{down-the-drain}}$) are multiplied by the portion available for ozone formation for releases to the outdoor air ($f_{\text{O3|volatilized}}$) and down-the-drain ($f_{\text{O3|down-the-drain}}$), respectively. Overall, for chemicals used in three specific cleaning-product uses, $f_{\text{volatilized}}$ is less than 0.6% for all studied LVP–VOCs. Because greater than 99.4% of compounds are disposed of down the drain during the use phase, when combined with $f_{\text{O3|volatilized}}$ and $f_{\text{O3|down-the-drain}}$, the portion available for ozone formation from the direct releases to outdoor air and the down-the-drain disposal is less than 0.4% and 0.2%, respectively. The results from this study indicate that the impact of the studied LVP–VOCs on ozone formation is very sensitive to what occurs during the use phase and suggest the need for future research on experimental work at the point of use.

Abbreviations: CARB, California Air Resources Board; CPCat, Chemical and Product Categories; EPI Suite, Estimation Program Interface Suite; LVP–VOC, low vapor pressure – volatile organic compound; U.S. EPA, United States Environmental Protection Agency; WWTP, wastewater treatment plant.

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http://dx.doi.org/10.1016/j.chemosphere.2016.02.131

1. Introduction

The formation of ground-level ozone is caused by the gas-phase interactions of emitted volatile organic compounds (VOCs) and nitrogen oxides (NOx) in the presence of sunlight (Seinfeld, 1989). Compared to studies on the impact of anthropogenic and biogenic VOC emissions on urban ozone concentrations (Curci et al., 2009; Im et al., 2011; Lyu et al., 2016), the contribution of low vapor pressure-volatile organic compounds (LVP–VOCs) to ozone formation has received little attention. An LVP–VOC is a chemical "compound" or "mixture" that is defined by the California Air Resources Board (CARB)'s Consumer Products Regulations (CARB, 2013) as having a relatively low vapor pressure (less than 0.1 mm Hg at 20 °C) or a high boiling point (greater than 216 °C). Currently, the amounts of LVP–VOCs in some consumer products are exempted in determining compliance with the VOC limits in the CARB's Consumer Products Regulations (CARB, 2013). However, the concern over ozone formation from consumer products (Morrison et al., 2011; Chen and Luo, 2012; Dinh et al., 2015) highlights the need for addressing potential contributions of consumer product LVP–VOCs to ozone formation.

Many LVP–VOCs do not volatilize quickly enough to be emitted into the atmosphere under normal conditions of consumer product use. However, some LVP–VOCs have been found to evaporate nearly as rapidly as the traditional high-volatility solvents (Vo and Morris, 2014). In addition, some LVP–VOCs have a higher value of the maximum incremental reactivity (MIR), the mass of ozone produced per unit mass of VOC precursors introduced (Carter and Atkinson, 1987, 1989), than that of the threshold compound (i.e., ethane) for negligible reactivity (Dimitriades, 1996; Carter, 2010). Thus, LVP–VOCs that are emitted into the atmosphere can be additional contributors to ozone formation depending on their emission rate, the portion remaining in the gas phase, and their reactivity.

A previous study estimated the fraction of LVP–VOCs in the gas phase that may participate in ozone formation reactions for two modes of releases (i.e., direct release to outdoor air and down-the-drain disposal) (Shin et al., 2015). Less than 0.2% of the LVP–VOCs disposed down the drain are available for ozone formation. In contrast, when the LVP–VOC in a consumer product is volatilized from the surface to which it has been applied, greater than 90% is available for photochemical reactions either at the source location or in the downwind areas. This observation highlights that the fraction volatilized to air ($f_{\text{volatilized}}$) versus the fraction disposed down the drain ($f_{\text{down-the-drain}}$) during the use of consumer products is key to determine the overall fraction of LVP–VOCs available for ozone forming reactions. In this study we propose models that can be used to predict emissions of consumer product LVP–VOCs during each of three cleaning product-associated activities (i.e., clothes washing, dish washing, and surface cleaning) for which we were able to find models or sufficient experimental results to develop a model.

The overall objective of this effort is to estimate the overall fraction of the compound available for ozone formation (f_{O3}) by integrating $f_{\text{volatilized}}$ and $f_{\text{down-the-drain}}$ from each of three cleaning product-associated activities with the fraction available for ozone formation for releases to air ($f_{O3|\text{volatilized}}$) and for down-the-drain ($f_{O3|\text{down-the-drain}}$). To meet this goal, we (1) identify experimental studies that measured emission rates or models that were developed for estimating emission rates of organic compounds during consumer product use and (2) apply those studies and models to predict the fraction volatilized during product use.

2. Methods

2.1. Scope and overview of this study

The work here builds on our previous study (Shin et al., 2015) that has already determined (1) what portion of an LVP–VOC volatilized to air from consumer product use will remain in the urban air gas phase to participate in ozone formation reactions ($f_{O3|\text{volatilized}}$) and (2) what portion of an LVP–VOC disposed down the drain from consumer product use will be emitted to air and subsequently available for ozone formation ($f_{O3|\text{down-the-drain}}$). In general, LVP–VOCs in consumer products do not readily evaporate as implied by their definition (relatively low vapor pressure and high boiling point). Thus, the Shin et al. (2015) environmental fate modeling started with LVP–VOCs that have already made it into the outdoor air, but did not attempt to estimate the fraction that would make it to outdoor air ($f_{\text{volatilized}}$) from indoor uses. We also note that the former study did not determine the amount of ozone formed, but estimated only the portion of the compound likely to remain in the gas phase. The scope of this study is depicted in Fig. 1.

The overall approach involves two separate steps to develop and evaluate our modeling methods. The first step is to apply various consumer product volatilization models to estimate $f_{\text{volatilized}}$ during the use of each of the three products. The second step is to combine results from this present study and those from environmental fate modeling and WWTP fate modeling described in Shin et al. (2015) to show the overall impact of the two modes of releases (i.e., direct release to outdoor air and down-the-drain disposal) on the model results (i.e., the overall fraction available for ozone formation, f_{O3}). We note that there are many types of surface cleaning protocols and cleaning styles. Some cleaning products, such as spray glass cleaners, may not have a down-the-drain component because they are commonly used to clean windows or mirrors with a paper towel, which is typically placed into a trash can, where a portion may volatilize and a portion may be disposed of to a landfill. Thus, the results from this study (i.e., $f_{\text{volatilized}}$ and f_{O3}) are only valid for the three surface cleaning protocols specifically described in Section 2.3.3.

2.2. Selected compounds

Because not all types of cleaning 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 types of consumer products (e.g., laundry detergents, dishwashing detergents, and surface cleaners) that have a use phase where they can be volatilized to air, but are also disposed of down the drain. Our selected compounds include six glycols, six glycol ethers, and six other compounds. We selected these compounds because they are commonly found in the types of consumer products listed above (see Table A1 in the Appendix) and are all high production volume chemicals in the U.S. whose annual production volume exceeds 1 million pounds or 500 metric tons (U.S. EPA, 2015a). A list of selected LVP–VOCs is provided in Table 1 along with key chemical properties, which were obtained from the U.S. Environmental Protection Agency (EPA) Estimation Program Interface Suite (EPI Suite) (U.S. EPA, 2015b). When available, we selected measured values because they are more reliable than estimated values. For the Henry's law constant, when experimental values are not available, but experimental vapor pressure (VP) and water solubility (Sw) data are available, the VP/Sw estimate is used.

2.3. Consumer product volatilization models

Several volatilization models are available for estimating

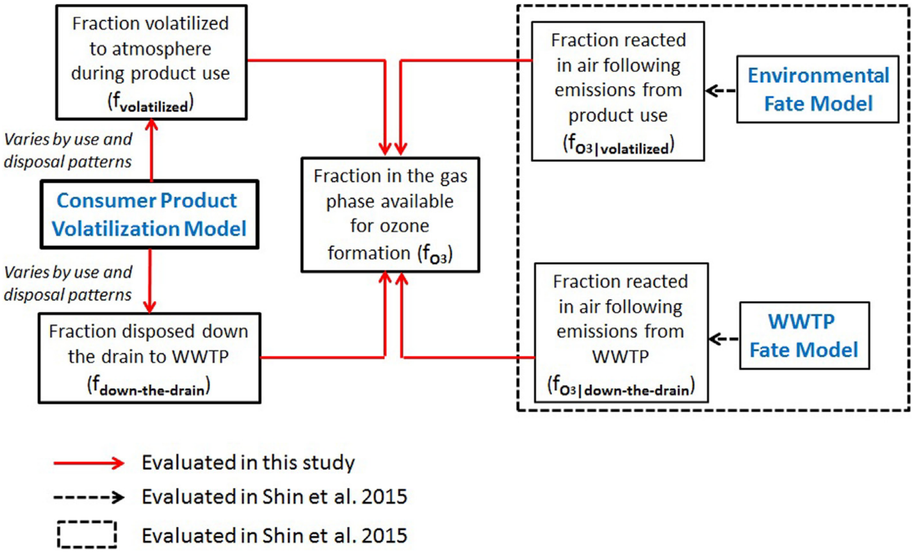

Fig. 1. Scope of this study.

Table 1
Chemical properties of selected LVP–VOCs.

Chemical class	Compounds	CAS#[a]	MW[b]	H[c]	VP[d]	Sw[e]
Glycols (N = 6)	Ethylene glycol	107-21-1	62	6.1E-03	0.09	1.0E+06
	Propylene glycol	57-55-6	76	1.3E-03[j]	0.08[g]	1.0E+06
	Dipropylene glycol	25265-71-8	134	3.6E-04[f]	0.03	1.0E+06
	Hexylene glycol[i]	107-41-5	118	4.1E-02[f]	0.01	1.0E+06
	Diethylene glycol	111-46-6	106	2.1E-04[f]	0.006	1.0E+06
	Polyethylene glycol	25322-68-3	238	7.7E-10[f]	3.0E-07[f]	1.0E+06[f]
Glycol Ethers (N = 6)	Diethylene glycol monoethyl ether	111-90-0	134	2.3E-03[j]	0.095[g]	1.0E+06
	Ethylene glycol hexyl ether[i]	112-25-4	146	3.2E-01	0.05[g]	9.9E+03
	Dipropylene glycol n-propyl ether	29911-27-1	176	2.0E-04[f]	0.04[f]	1.5E+05
	Diethylene glycol monobutyl ether	112-34-5	162	7.3E-04	0.02	1.0E+06
	Dipropylene glycol n-butyl ether	29911-28-2	190	2.7E-04[f]	0.004[f]	4.5E+04
	Triethylene glycol monobutyl ether	143-22-6	206	2.4E-06[f]	0.003	1.0E+06
Others (N = 6)	Dimethyl glutarate[i]	1119-40-0	160	6.5E-02[j]	0.05[h]	5.9E+04
	2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol)	25265-77-4	216	8.3E-03[f]	0.01	3.2E+02[f]
	Glyceryl triacetate	102-76-1	218	1.2E-03[j]	0.003	5.8E+04
	Benzyl alcohol[i]	100-51-6	108	3.4E-02	0.09	4.3E+04
	Glycerol	56-81-5	92	1.8E-03	1.7E-04	1.0E+06
	Triethanolamine	102-71-6	149	4.1E-08	3.6E-06	1.0E+06

Note.
[a] CAS #: chemical abstracts service registry number.
[b] MW: molecular weight from the U.S. EPA EPI Suite ™ (U.S. EPA, 2015b).
[c] H: Henry's law constant in Pa·m^3/mol at 25 °C from the U.S. EPA EPI Suite ™ (U.S. EPA, 2015b). The unitless Henry's law constant can be obtained by dividing ideal gas constant (8.314 Pa m^3/mol/K) and temperature (298 K).
[d] VP: vapor pressure in mm Hg at 25 °C from the U.S. EPA EPI Suite ™ (U.S. EPA, 2015b).
[e] Sw: Solubility in water in g/m^3 at 25 °C.
[f] Estimated values of H, VP, and S.
[g] Measured vapor pressure in mm Hg at 20 °C (http://www.dow.com).
[h] Measured vapor pressure in mm Hg at 20 °C (http://www.cleanersolutions.org/).
[i] Characterized as 'slightly volatile from water' based on the guide in the U.S. EPA document (U.S. EPA, 2013). Those that are not noted are characterized as 'nonvolatile'.
[j] Derived from experimental values of vapor pressure and water solubility (=VP/Sw).

emissions of organic compounds in consumer products (Guo and Roache, 2003; U.S. EPA, 2003; Guo et al., 2008; McCready and Fontaine, 2010; McCready et al., 2012; McCready, 2013; Liu et al., 2015). However, these models are reliant upon measured data which are lacking for most chemicals. The University of Texas Corsi research group (Shepherd et al., 1996; Howard and Corsi, 1998; Howard-Reed et al., 1999) developed models to estimate emissions of chemicals during the operation of residential dishwashers and clothes washing machines. We note that the goal of these models was to estimate emission rates of common disinfection byproducts (e.g., chloroform) or other volatile organic compounds (e.g., toluene) dissolved in drinking water. We selected these models to determine $f_{\text{volatilized}}$ and $f_{\text{down-the-drain}}$. We also note that there may be a small fraction of compounds in the wet clothes that is moved to the dryer and then subsequently volatilized to the outdoor air. However, we did not quantify emissions from this pathway in our study because we lacked sufficient data to develop a model. Similarly, although there may be chemical residues on dishes after the dishwasher operation, we assume that all of the compounds added to a dishwashing detergent are either volatilized or disposed down the drain. Below, we briefly describe the key characteristics of each model and the assumptions and modifications we made for emissions of LVP–VOCs used as dish or laundry detergents.

In the dishwasher and washing machine models, the Henry's law constant (H) and the overall mass transfer coefficient (K_L) are two key chemical properties needed to estimate emissions, which are dependent on the system's operating temperature. The typical water temperatures reported in both models are 35 °C for washing machines and 50 °C for dishwashers, respectively. We provide more details on how we estimated key chemical properties in the Appendix along with the values of chemical properties used for both models. To examine the effect of water temperature on emissions during clothes washing, we also ran the washing machine model for cold water (20 °C) and hot water (55 °C) cycles.

2.3.1. Dishwashing

For compounds categorized as components of a dishwashing detergent (see Table A1), we used the model developed by Howard-Reed et al. (1999) to calculate $f_{\text{volatilized}}$ during the operation of residential dishwashers. Dishwashing machines or “dishwashers” described in the Howard-Reed et al. (1999) study operate through a series of cycles, including first fill, pre-rinse, first drain, second fill, wash, second drain, third fill, first rinse, third drain, fourth fill, final rinse, and final drain. To estimate emissions of chemicals dissolved in drinking water, Howard-Reed et al. (1999) simulated all cycles. However, in our study, the first fill, pre-rinse, and the first drain cycles are not modeled, because detergents are only added to the system (i.e., dishwasher) after the first drain. Also, all fill cycles are not included as a model run for estimating emissions, because the mass transfer between liquid and gas phases is expected to be much smaller than that during wash and rinse cycles (Howard-Reed et al., 1999). We note that the mass transfer coefficients during the fill cycle are not reported in Howard-Reed et al. (1999). In the Appendix, we presented a brief description of the dishwasher model developed by Howard-Reed et al. (1999). Also, we provided the solutions for the time-dependent gas- and liquid-phase concentrations (C_g and C_l) which are derived from Howard-Reed et al. (1999) and the equation to estimate emission rates during the operation of the dishwasher. Selected input parameters for the dishwasher model (Howard-Reed et al., 1999) are listed in Table A3.

2.3.2. Clothes washing

To predict emissions during the operation of clothes washing machine (or “washing machine”), we selected a model developed by the Corsi research group (Howard and Corsi, 1998; Shepherd et al., 1996). Similar to the dishwasher model, mass balance equations were derived for the wash and rinse cycles and were solved for time-dependent C_g and C_l of chemicals dissolved in tap water during the operation of the washing machine. For the wash and rinse cycles, the format of the mass balance is the same for both washing machine and dishwasher models, with different values of input parameters used in each model. Because our interest is to estimate volatilization of chemicals formulated in laundry detergents instead of chemicals in the contaminated water supply, we assumed that volatilization during the fill cycle can be ignored. Shepherd et al. (1996) also assumed that volatilization during a spin cycle is negligible because of the low volume of water and a rather short contact time between the liquid and gas phases. Therefore, we assumed that the washing machine has wash, first drain, rinse, and second drain cycles and that 90 percent of water used for wash and rinse is drained from the washing machine during a period of drain. Selected input parameters for the washing machine model (Howard and Corsi, 1998; Howard-Reed and Corsi, 2000) are listed in Table A3.

2.3.3. Surface cleaning

There have been efforts to derive simple correlations between vapor pressure and the evaporation rate of pesticides from plant and/or soil surfaces (Woodrow et al., 1997, 2001; Guth et al., 2004; van Wesenbeeck et al., 2008; Davie-Martin et al., 2013). In addition, for the pure fluid substance on quiescent liquid pools, a simple correlation (Equation (1)) was derived between the evaporation rate (ER, μg/m^2/hour) and a product of vapor pressure (VP, Pa) and molecular weight (MW, g/mol) (Mackay and van Wesenbeeck, 2014).

$$\mathrm{ER} = 1464 \times \mathrm{VP} \times \mathrm{MW} \quad \left(\mathrm{R}^2 = 0.95\right) \tag{1}$$

where the slope coefficient of 1464 has units of mol/(Pa·m^2·hour) and is modified by a factor of 10^6 (μg/g).

For the chemicals formulated in cleaning products, Singer et al. (2006) conducted chamber experiments to quantify air concentrations and emissions of glycol ethers and terpenoids during the use of surface cleaning products under various cleaning activity scenarios. We selected one of the general purpose cleaners (i.e., GPC-1) used in their study because this product was applied under different cleaning activity scenarios and both product composition results and measured emission factors (i.e., mg of chemical emitted per g of product used) are available for each scenario. Identified analytes ($n = 15$) in this product accounted for approximately 15% of the product mass (Singer et al., 2006). We fitted emission factors (EF) against VP, MW, and the fraction of chemical concentrations in the product (f_c) as independent variables. The regression results with all three independent variables (i.e., VP, MW, and f_c) are very similar to those with only VP and f_c as independent variables. All fitted results and raw data from Singer et al. (2006) along with a range of applicable vapor pressure are provided in the Appendix. The best fitted results for the three surface cleaning experiments are as follows:

$$\mathrm{Counter\,cleaning\,'A'}: \mathrm{EF} = 0.1807 \times (\mathrm{VP} \times \mathrm{f_c}) - 0.0959 \quad \left(\mathrm{R}^2 = 0.95\right) \tag{2}$$

$$\mathrm{Counter\,cleaning\,'B'}: \mathrm{EF} = 0.2875 \times (\mathrm{VP} \times \mathrm{f_c}) + 0.0726 \quad \left(\mathrm{R}^2 = 0.90\right) \tag{3}$$

$$\mathrm{Floor\ cleaning}: \mathrm{EF} = 0.0462 \times (\mathrm{VP} \times \mathrm{f_c}) + 0.0352 \quad \left(\mathrm{R}^2 = 0.86\right) \tag{4}$$

where the slope coefficients of 0.1807, 0.2875, and 0.0462 have units of Pa^{-1}. In both counter cleaning experiments ‘A’ and ‘B’, Singer et al. applied 10 g of a product at full-strength to a 0.56 m^2 area of a laminate tabletop for 1 min. Then, the surface was scrubbed with a wetted sponge. After scrubbing, the tabletop was dried with paper towels. The difference between counter cleaning experiments ‘A’ and ‘B’ is that the towels were removed after cleaning in experiment ‘A’ and were retained throughout and after cleaning in the experiment ‘B’. In typical use, the sponge is rinsed, disposing of some of the chemical down the drain. In a floor cleaning experiment, Singer et al. diluted a product with 4 L of warm water and spread diluted solution with a sponge mop to the floor. Evaporation of LVP–VOCs may occur both in a bucket while preparing the solution and on the floor while spreading the solution and mopping the floor. We used the fitted results above as a first estimate to predict $f_{\text{volatilized}}$ during surface cleaning activities. For all cleaning activity scenarios, we assumed that the fraction of chemical concentrations in the product (f_c) is equal to 1 for the purpose of providing a plausible upper bound estimate.

Because the product in the counter cleaning experiment ‘A’ was applied undisturbed for 1 min on the laminate tabletop, which was then immediately removed from the chamber, the regression results from that experiment ‘A’ with *VP*, *MW*, and *fc* (i.e., $EF = 0.0013 \times (VP \times MW \times f_c) - 0.1061$) can be directly compared with a linear relationship derived from quiescent pure liquid pools (Equation (1)). When considering the pure liquid substance in the product (i.e., $f_c = 1$), the unit of *ER* (μg/m^2/hour) in Equation (1) can be converted to that of *EF* (unitless) above by multiplying 1 min of volatilization time, 0.56 m^2 of applied area, and 10 g of the product applied. Then Equation (1) becomes $EF = 0.0014 \times (VP \times MW \times f_c)$, showing a very close relationship to that from the Singer et al.'s counter cleaning experiment ‘A’.

2.4. Model integration and uncertainty analysis

To illustrate the overall impact of the two modes of releases (i.e., direct release to outdoor air and down-the-drain disposal) on the overall fraction available for ozone formation, f_{O3}, we integrated the results from two volatilization models and surface cleaning product regression analyses and those from the multimedia and WWTP fate models (Shin et al., 2015). Thus, we multiplied $f_{\text{volatilized}}$ estimated from this present study by the fraction of reaction in air from the multimedia fate model ($f_{O3|\text{volatilized}}$) presented in our previous study (see Table A5 in the Appendix). In addition, we also multiplied $f_{\text{down-the-drain}}$ estimated from this present study and the fraction of reaction in air following emissions from a WWTP ($f_{O3|\text{down-the-drain}}$) presented in our previous study (see Table A5 in the Appendix).

For both dishwasher and washing machine volatilization models, we performed a Monte Carlo uncertainty analysis for each study compound to determine the relative contribution of input parameter variation to the output uncertainty (i.e., the overall fraction available for ozone formation). The details of the uncertainty analysis are provided in the Appendix. We note that we did not conduct an uncertainty analysis for the surface cleaning product regression analyses because f_{O3} from surface cleaning follows a simple linear relationship with vapor pressure, $f_{O3|\text{volatilized}}$, and $f_{O3|\text{down-the-drain}}$.

3. Results

3.1. Concentration profile during the dishwasher and washing machine operation

In order to understand volatilization of the selected LVP–VOCs during three cleaning-product-associated activities in indoor residential environments, we explored volatilization models developed for a dishwasher and a washing machine as well as a regression model we fit to the results of experimental studies that measured emission rates from the use of surface cleaning products. In Figs. A1 and A2, we present the estimated liquid- and gas-phase concentrations (C_g and C_l) of polyethylene glycol and ethylene glycol hexyl ether which show different concentration profiles during the operation of a dishwasher and washing machine, respectively. Among the studied compounds, polyethylene glycol has the smallest effective mass transfer coefficient (K_LA) (e.g., 1.0×10^{-8} for a wash cycle in a dishwasher), resulting in low C_g. In contrast, ethylene glycol hexyl ether has the largest K_LA (e.g., 4.2 for a wash cycle in a dishwasher), resulting in high C_g. Given that the same operating conditions were applied to all chemicals, C_g and C_l are largely influenced by the magnitude of K_LA.

3.2. Fraction volatilized from dishwasher and washing machine operation

Table 2 shows the estimated emission factors (=mg of chemical emitted per mg of product used) or volatilization fractions ($f_{\text{volatilized}}$) of the LVP–VOCs from the dishwasher and washing machine volatilization models as well as from the surface cleaning product regression analyses. Overall, the emission factors from a dishwasher are approximately a factor of two greater than those from a washing machine because of the large K_LA value resulting from the higher water temperature in a dishwasher (50 °C) than that in a washing machine (35 °C). From the cold water (20 °C) and hot water (55 °C) cycles, we found that the estimated $f_{\text{volatilized}}$ for the cold and hot water cycles is approximately a factor of two smaller and larger than those for the typical water-temperature cycle (results are not shown), indicating that operating water temperature largely influences $f_{\text{volatilized}}$. Overall, less than 0.6% of LVP–VOCs are volatilized from the use of dishwashing detergents and laundry detergents. For chemicals that are added to water, *H* is an effective measure for volatilization from water (U.S. EPA, 2013). For example, the guide in the U.S. EPA document (U.S. EPA, 2013) characterizes four of our study chemicals (hexylene glycol, ethylene glycol hexyl ether, dimethyl glutarate, and benzyl alcohol) into ‘slightly volatile from water’ and the rest into ‘nonvolatile’. For those four ‘slightly volatile from water’ chemicals, the estimated volatilized fractions from dishwasher and washing machines are higher than other fourteen ‘nonvolatile’ chemicals. For compounds with less than 0.32 Pa-m^3/mol of *H* value at 25 °C, less than 0.6% and 0.4% is expected to be released during the operation of dishwasher and washing machine, respectively.

3.3. Fraction volatilized from surface cleaning

For the chemicals associated with surface cleaning activities, the estimated $f_{\text{volatilized}}$ is greater for compounds with large *VP* values (see Table 2). The maximum emission factor is estimated for diethylene glycol monoethyl ether (0.37%). We note that the *VP* values at 25 °C for the LVP–VOCs considered here range from 4.0×10^{-5} to 12.7 Pa ($=3.0 \times 10^{-7}$ to 0.095 mm Hg) and those in the experimental study of surface cleaning (Singer et al., 2006) range from 2.6 to 633 Pa. Noting that the maximum possible *VP* value for LVP–VOCs is less than 13.3 Pa (=0.1 mmHg), we found that all LVP–VOCs typically end up with less than 0.4% of emissions during surface cleaning.

3.4. Ozone formation potential of LVP–VOCs from cleaning product use

Table 3 shows the overall fraction of LVP–VOCs available for ozone forming reactions (f_{O3}) combined from both direct releases to the outdoor air and volatilization of down-the-drain disposal from a WWTP. When the LVP–VOC in a consumer product is volatilized from the surface to which it has been applied, all of the compounds have a significant fraction of ozone formation potential (mean = 94%) based on the multimedia fate model analysis (see results in Table A5), except for glycerol (67%). However, since $f_{\text{volatilized}}$ at the end of the consumer product use is less than 0.6%, the portion available for ozone formation is less than 0.6% during each of three cleaning product-associated activities (i.e., clothes washing, dish washing, and surface cleaning). We note that for the compounds that are disposed down the drain during a use phase, the portion available for ozone formation is less than 0.2% from the WWTP fate model (see results in Table A5). Thus, as almost all compounds are disposed of down the drain (greater than 99.4%), the portion available for ozone formation is less than 0.2% from the down-the-drain disposal.

The percent contribution towards ozone formation from the direct releases to the outdoor air during a use phase is shown in Table A7 in the Appendix. Overall, the direct releases to the

Table 2
Estimated volatilization fractions of LVP–VOCs from the dishwashing and washing machine volatilization models and surface cleaning product regression analyses.

Chemical class	Compounds	Dish-washer	Washing machine	Surface cleaning		
				Counter[a]	Counter[b]	Floor
Glycols (N = 6)	Ethylene glycol	8.4E-05	5.7E-05	2.1E-03	3.6E-03	6.0E-04
	Propylene glycol	2.2E-05	1.3E-05	1.8E-03	3.1E-03	5.3E-04
	Dipropylene glycol	6.1E-06	3.7E-06	6.7E-04	1.3E-03	2.3E-04
	Hexylene glycol	7.0E-04	4.2E-04	2.2E-04	5.7E-04	1.2E-04
	Diethylene glycol	3.5E-06	2.1E-06	4.1E-05	2.9E-04	7.0E-05
	Polyethylene glycol	1.3E-11	7.8E-12	<1.0E-06	7.3E-05	3.5E-05
Glycol Ethers (N = 6)	Diethylene glycol monoethyl ether	3.8E-05	2.3E-05	2.2E-03	3.7E-03	6.2E-04
	Ethylene glycol hexyl ether	5.3E-03	3.2E-03	1.1E-03	2.0E-03	3.4E-04
	Dipropylene glycol n-propyl ether	3.5E-06	2.1E-06	7.6E-04	1.4E-03	2.5E-04
	Diethylene glycol monobutyl ether	1.7E-05	1.1E-05	4.3E-04	9.1E-04	1.7E-04
	Dipropylene glycol n-butyl ether	4.6E-06	2.8E-06	<1.0E-06	2.1E-04	5.7E-05
	Triethylene glycol monobutyl ether	4.0E-08	2.4E-08	<1.0E-06	1.7E-04	5.1E-05
Others (N = 6)	Dimethyl glutarate	9.6E-04	6.3E-04	1.1E-03	2.0E-03	3.4E-04
	2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol)	1.4E-04	8.5E-05	<1.0E-06	1.0E-04	4.0E-05
	Glyceryl triacetate	1.8E-05	1.2E-05	<1.0E-06	1.7E-04	5.0E-05
	Benzyl alcohol	7.1E-04	3.8E-04	2.2E-03	3.7E-03	6.1E-04
	Glycerol	5.0E-05	2.2E-05	<1.0E-06	7.9E-05	3.6E-05
	Triethanolamine	1.2E-09	7.3E-10	<1.0E-06	7.3E-05	3.5E-05

[a] Towels were removed after cleaning.
[b] Towels were retained throughout after cleaning.

Table 3
Overall fraction of LVP–VOCs available for ozone forming reactions combined from both direct releases to the outdoor air and volatilization of down-the-drain disposal from a WWTP. The fractions in bold indicate that majority (greater than 50%) is driven by down-the-drain disposal.

Chemical class	Compounds	Dish-washer	Washing machine	Surface cleaning		
				Counter[a]	Counter[b]	Floor
Glycols (N = 6)	Ethylene glycol	<0.01%	<0.01%	0.19%	0.33%	0.05%
	Propylene glycol	<0.01%	<0.01%	0.17%	0.30%	0.05%
	Dipropylene glycol	<0.01%	<0.01%	0.07%	0.13%	0.02%
	Hexylene glycol	0.06%	0.04%	0.02%	0.05%	0.01%
	Diethylene glycol	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
	Polyethylene glycol	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
Glycol Ethers (N = 6)	Diethylene glycol monoethyl ether	<0.01%	<0.01%	0.22%	0.37%	0.06%
	Ethylene glycol hexyl ether	0.52%	0.32%	0.11%	0.2%	<0.01%
	Dipropylene glycol n-propyl ether			0.08%	0.1%	<0.01%
	Diethylene glycol monobutyl ether	<0.01%	<0.01%	0.04%	0.09%	0.02%
	Dipropylene glycol n-butyl ether	<0.01%	<0.01%	**<0.01**%	0.02%	0.01%
	Triethylene glycol monobutyl ether			<0.01%	0.02%	<0.01%
Others (N = 6)	Dimethyl glutarate	0.09%	0.06%	0.10%	0.19%	0.03%
	2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol)	**0.18**%	**0.17**%	**0.18**%	**0.21**%	**0.17**%
	Glyceryl triacetate	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
	Benzyl alcohol	0.07%	0.04%	0.21%	0.36%	0.06%
	Glycerol	<0.01%	<0.01%	<0.01%	0.01%	<0.01%
	Triethanolamine	<0.01%	<0.01%	<0.01%	0.01%	<0.01%

[a] Towels were removed after cleaning.
[b] Towels were retained throughout after cleaning.

outdoor air during a use phase primarily contribute to ozone formation for the studied LVP–VOCs. But for one compound (taxanol) with relatively large $f_{O3|\text{down-the-drain}}$ presented in our previous study (see Table A5 in the Appendix) (Shin et al., 2015), the majority of ozone formation potential results from the down-the-drain disposal. To examine how much the mass volatilized indoors is transported outdoors ($f_{\text{ventilated}}$), we ran our indoor fate and transport model (Bennett and Furtaw, 2004; Shin et al., 2012) and explored the impact of indoor chemistry (e.g., sorption to indoor surfaces, gas-particle partitioning, and reaction with OH radical) and various transport and removal processes (e.g., removal via vacuum cleaning, deposition, and resuspension) on the magnitude of $f_{\text{ventilated}}$. As seen in Table A8 in the Appendix, once volatilized during the use phase, for 15 out of 18 compounds the entire quantity is ventilated outdoors (i.e., $f_{\text{ventilated}} > 0.91$). Exceptions are three compounds with vapor pressure values less than 3.0×10^{-7} mmHg: glycerol ($f_{\text{ventilated}} = 0.69$), polyethylene glycol ($f_{\text{ventilated}} = 0.61$), and triethanolamine ($f_{\text{ventilated}} = 0.58$). From this finding, for those chemicals with vapor pressure values larger than 3.0×10^{-7} mmHg, the assumption that all the mass volatilized indoors is transported outdoors ($f_{\text{ventilated}} = 1$) could simplify our model framework.

Figs. A3 and A4 in the Appendix illustrate the relative contribution of each input parameter variation to the output uncertainty (i.e., f_{O3}) from the Monte Carlo uncertainty analysis for the washing machine and dishwasher volatilization models, respectively. For all compounds, the gas flow rate through the appliance and H are influential parameters on f_{O3} and have similar contribution to the output uncertainty. Depending on the magnitude of $f_{O3|\text{down-the-drain}}$ and $f_{O3|\text{volatilized}}$ of the studied LVP–VOCs, either $f_{O3|\text{down-the-drain}}$ or $f_{O3|\text{volatilized}}$ is shown to be an important parameter determining f_{O3}. For taxanol, almost 80% of output uncertainty results from the variation of $f_{O3|\text{down-the-drain}}$. The contribution of input parameter variation to uncertainty of $f_{O3|\text{volatilized}}$ is further discussed in Shin et al. (2015) where the same Monte Carlo uncertainty analysis was performed.

4. Discussion

Limitations on the findings of this study arise from the uncertainty and variability of model input parameters. For example, the effective mass transfer coefficients (K_LA) of all LVP—VOCs and H of most LVP—VOCs used in this study are not measured, but estimated. The functions and operating conditions of the dishwasher and washing machine used in the late 1990s might be different from those in current use. In addition, only one type of washing machine and dishwasher was tested in volatilization model studies (Shepherd et al., 1996; Howard-Reed et al., 1999). Volatilization from the dryer that was not quantified in this study might not be negligible. Thus, there is a potential that we over- or underestimated emission factors. We also acknowledge that the results of this study had not been evaluated with experimental studies for all modeled cleaning products, which suggests experimental work in future research. This study did not determine the amount of ozone formed. More complex atmospheric photochemical models such as the U.S. EPA Community Multi-scale Air Quality (CMAQ) Model need to be used in conjunction with our results to simulate how much ozone will be formed in the atmosphere.

To improve the reliability of estimating the relative contribution of these two modes of release (i.e., direct release to outdoor air and down-the-drain disposal) to ozone formation as a result of consumer product use, two key information gaps should be addressed in future research. First, because the total contribution to ozone formation is sensitive to the mass distributed among relevant use categories, detailed information regarding the distribution of total production volumes to each use category is necessary to predict the overall fraction volatilized per unit of use. Second, more accurate information about the usage of cleaning products and the chemical mass fraction in a product is needed to determine the overall volatilization fraction resulting from cleaning activities. For example, for chemicals used for countertop cleaning, paper towels are commonly used for cleaning and then they are usually placed into a trash can, where a portion may volatilize and a portion may be disposed of to a landfill. Thus, depending on the time the towel sits uncovered in the trash can, the fraction volatilized to air varies.

5. Conclusions

This study provides preliminary results of modeled volatilization of the selected LVP—VOCs mixed in laundry detergents, dishwashing detergents, and surface cleaning agents and subsequently evaluates the impact on ozone formation from direct releases to air and from the down the drain disposal. The results from this study indicate that the impact on ozone formation is very sensitive to what occurs during the use phase. Thus, we suggest the need for more experimental work so that the results of this study can be evaluated with measured values for all modeled cleaning products.

In addition to laundry detergents, dishwashing detergents, and surface cleaners, other common uses of the studied LVP—VOCs include hand cleaners, stain removers, personal care products (e.g., shampoos, facial cleansers, hair products, moisturizers, lotions, etc.) and other products that may be disposed down the drain as part of normal use (U.S. EPA, 2015c). For a product added to water, a simple approach based on the mass of product applied and the evaporation time is available to estimate the emission rate of a specific product (U.S. EPA, 2015d), but chemical properties are not parameterized as input parameters in the approach. This highlights the need of development and evaluation of volatilization models that parameterize key chemical properties for individual compounds and the need for experiments regarding various human activities in future research.

Acknowledgments

We thank Brett Singer, who generously provided details of his chamber experimental work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.02.131.

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