

VOLATILITY AND FATE

J. J. Kurland¹, D. A. Morgott² and R. W. Hamilton³

¹ Union Carbide Corporation.

² Eastman Kodak Co., Health, Safety and Environment Laboratories

³ Amway Corporation

June 2, 1999

CONTENTS

SUMMARY	1
VOLATILIZATION	2
FATE ANALYSIS	4
EMISSION AND REMOVAL PROCESSES	4
Emission Attenuation Processes.....	4
Competitive Removal Processes	5
RESEARCH OPPORTUNITIES	7
REFERENCES.....	8

SUMMARY

The formation of tropospheric ozone from a volatile compound is a dynamic multi-step kinetic process that is highly dependent upon the relative concentrations of NO_x and the VOC¹. The tropospheric concentration of a VOC is likewise affected by both the rate and extent of release from an emission source and by the rate of removal through a variety of competing processes (photooxidation, deposition, horizontal and vertical transport, aerosol formation)².

Consideration of equilibrium vapor pressures and partition between gas phase and aerosols suggests that many low-vapor-pressure (LVP) VOC will be present predominately in the gas phase. However, this conclusion may not be entirely correct in view of those studies indicating alternate fates for the VOCs contained in consumer, commercial, and agricultural products^{3,4}. There are many ways that compounds of low volatility, especially those which are hydrophilic, may be prevented from entering the atmosphere or removed once they enter, but quantitative assessments are rare.

The rate of volatilization may dictate the overall rate of ozone formation for a particular VOC. Under some circumstances, the rate of release of a VOC to the

environment may be the rate-limiting step in ozone production, thereby restricting its relative importance and overall contribution. Although, research has shown that the rate of volatilization from wastewater's and agricultural lands can affect airborne exposures to VOCs, there has been no systematic study of the volatilization rates from complex mixtures such as coatings, composites, and consumer products^{5,6}. The overall impact of VOCs from these emission categories can be affected by the nature of matrix in which they are dissolved with lower rates of volatilization occurring when water soluble compounds are dissolved in an aqueous matrices⁷. Another important aspect of the volatilization issue is the role of competing removal processes. When volatilization rates are low, there is time for competing processes to remove the VOC by alternate routes⁸. New research is needed to examine the issue of volatilization rate and to develop models that can incorporate all that is known about a chemical's tropospheric fate and removal.

Because LVPs fall outside normal analytical methods, little is known about the ambient air concentration of semi-volatile compounds. Difficulties with source apportionment by chemical mass balance and analytical determination hinder any reliable estimation of the emissions rate for low volatility compounds. The total emissions of these compounds is not known with certainty, and the contribution from coatings and commercial products may be much lower than the proportions attributed to these sources in current emissions inventories⁸.

VOLATILIZATION

Current regulations presume the availability of low-vapor-pressure (LVP) VOCs in air⁹. The assumption is based on equilibrium considerations for air-surface exchange and consideration that during performance of EPA Method 24 to determine VOC emissions from paints and coatings certain compounds, such as diethylene glycol monobutyl ether, may be volatilized even though they have a vapor pressure of less than 0.1 mm Hg at 20 degrees C⁹. Source apportionment studies show that LVP VOCs emitted such as cholesterol and oleic acid from meat cooking are observed on aerosols¹⁰. Semi-volatile compounds (including heavy hydrocarbons, C10-C20) may exist as gases if they are emitted at high temperatures; however, there are alternative fates for these compounds when their evaporation rate is slow¹¹. These processes effectively modify the fraction of LVP VOC released into the air and consumed by photooxidation. Removal processes such as aerosol formation and dry deposition also need to be considered in any modeling exercise aimed at assessing the contribution of an LVP VOC on ozone yield.

Though some regional-scale predictive models for ozone formation incorporate information on fate and removal, others do not, and a systematic approach is necessary to ensure that all available information on the rates of release and removal of all VOCs has been incorporated and evaluated in future modeling exercises.

Waste treatment, industrial and commercial operations, combustion, and product applications are all potential VOC emission sources that can result in the release of VOCs

to the environment¹². Under some circumstances, however, the rate of release to the environment will be sufficiently slow to limit the airborne concentration of a VOC and its ultimate contribution to ozone formation. This occurs if the rate of release of a VOC to the environment is less than its rate of reaction in the condensed phase with hydroxyl radicals or other species that convert it through one or more reactions to non volatile or photochemically unreactive material (such as carbon dioxide from waste treatment). Under these circumstances the rate of release or volatilization becomes the rate-limiting step in ozone formation, thereby restricting the relative importance and contribution of the VOC.

Although, research has shown that the rate of volatilization from wastewaters and agricultural lands can affect airborne exposures to VOCs, there has been no systematic study of the volatilization rates from complex mixtures such as coatings, composites, and consumer products.

The overall impact on ozone formation of VOCs from these emission categories may be affected by their volatilization rates from complex matrices. A low volatilization rate allows time for competing processes to consume the VOC. New research is needed to examine the issue of volatilization rate and to develop models that can incorporate all that is known about a chemicals tropospheric availability.

A source of concern from the standpoint of scientifically sound reactivity policy is the lack of established methodology for determining volatility-reactivity linkages for some classes of emissions. For example, current EPA policy exempts Consumer Product organic compounds with low volatility (vapor pressure < 0.1 mm Hg at 25 °C) in setting VOC content limits in the National Volatile Organic Emission Standards^{12a}. This was primarily due to a lack of an established test method for VOC content/volatility in consumer products¹³. In contrast, paints have an accepted test method - Reference Method 24 (ASTM D 2369) - which is used to compare VOC content and determine compliance, and an attempt was made to adapt it to use in consumer products¹⁴. The precision of the modified method was similar to that of EPA Method 24. The mean method reproducibility was found to be 4.8 weight percent VOC. The California Air Resources Board has recently adopted Method 310, "Determination of VOC in Consumer Products". Like method 24 it is an accelerated evaporation test under standard conditions with provisions for subtracting exempt volatile materials (e.g., water and acetone). A failing of both methods is that they are not calibrated to reflect emissions in the real world. Method 310 was tested with mixtures of VOC, water and glycerine. The method tended to give high values for VOC due to loss of glycerine, especially in the presence of large amounts of water. Glycerine has a vapor pressure at 20 °C of about 10^{-8} atm, so its loss is more likely to be an artifact of the test than a true indication that it would be released at ambient temperature. ASTM D 2369 was originally published in 1965. In 1978, as a result of a meeting of six people representing the California Air Resources Board, the paint industry, academia and the U. S. Environmental Protection Agency (EPA), the EPA selected D 2369 as the basis for its measure of air pollution resulting from the use of paints, inks and other coatings^{14a}. The precision of the method has been established but not its bias.

FATE ANALYSIS

Environmental fate and transport models are available to examine how a chemical partitions among air, water, soil, and sediment¹⁵. These fate and transport models examine intermedia transport rates for various diffusive and nondiffusive processes and estimates the mass fraction of a chemical in each environmental compartment. Four processes govern the transport of a chemical from air to water: diffusion (absorption), dissolution in rain, and wet and dry deposition of particle-associated chemical. The troposphere is treated as an air-aerosol mixture in these calculations with chemicals partitioning between the two phases. Calculations with 2-butoxyethanol have shown that once emitted to air most of the chemical is removed by deposition to soil, while about 24% is removed by reaction in air. If the compound is emitted into water, more than 99% of the chemical is found in water¹⁶. These data indicate that partitioning of organic compounds among different media is an important consideration that can directly impact the amount of VOC available in the atmosphere for hydroxyl radical reactions and ozone formation.

These processes may account for the large discrepancies sometimes found in VOC emissions inventory versus emissions monitoring. According to the South Coast Air Quality Management District emissions inventory, architectural coatings contribute approximately 4% of total VOC emissions (including biogenic VOC from trees and vegetation) within the South Coast Air Basin^{17a}. Recent monitoring and source apportionment studies found that the concentration of VOC attributable to architectural coatings in Los Angeles was 3.2%-5% at 3 Air Resources Board sites and 0.3-1.1% at 8 Coordinating Research Council sites⁸. Two source apportionment studies in Chicago showed contributions to non-methane organic compounds (NMOC) from solvents from architectural coatings of 1.5% and 3.1% compared to emissions inventories of 5.5%⁸. The agreement ranges from good to poor.

EMISSION AND REMOVAL PROCESSES

The following emission and removal processes have been identified as potentially important contributors to the atmospheric availability of a VOC. Although data exist to support the inclusion of these processes in reactivity models under specific sets of circumstances and conditions of use, it is difficult to judge *a priori* their overall importance on model-predicted ozone formation. Research is needed to further evaluate the impact of these processes for specific classes of chemicals and environmental conditions. The physico-chemical and kinetic data needed to conduct this research are generally available, either through direct measurement or predictive models.

Emission Attenuation Processes

Down-the-drain preference. A large percentage of the hydrophilic VOCs found in commercial products may never reach the atmosphere, but will remain instead in aqueous

solution. Environmental removal of these compounds will then occur by chemical and biological degradation after the chemical goes down-the-drain. This process may be important in limiting VOC emissions from consumer products and has been shown to be important for ethanol and eleven other VOCs in laundry and dish washing products^{18,19}. At present, the California Air Resources Board applies an adjustment factor to ethanol emissions from liquid laundry detergent to account for the “down-the-drain” effect.

Indoor atmospheric chemistry. Research in the field of indoor atmospheric chemistry has begun producing results that may be particularly relevant to emissions modeling. Data are beginning to emerge which show an appreciable generation of hydroxyl radicals concentrations indoors²⁰. The generation of hydroxyl radicals indoors may have a profound effect upon VOC emissions by oxidizing a portion of the VOCs emitted from consumer products and limiting the amount available for ozone formation outdoors. A recent study has in fact shown that the total VOC concentration in the supply air of some buildings can be higher than the total VOC concentration inside the room²¹.

Adsorption onto inert materials. Although the emission of VOCs from consumer products and building materials has received considerable attention by both indoor air scientists and material manufacturers, the dynamics of VOC emissions from commercial products is not completely understood. Research has shown that materials in the vicinity of a product’s use can quickly adsorb an emitted VOC and then slowly re-release the chemical over time. This rapid adsorption-slow desorption phenomenon has been shown to occur with latex paint on gypsum board and the adhesives used for carpet laying²². Environmental conditions such as temperature control and air flow may also enhance or diminish VOC emissions indoors.

Competitive Removal Processes

Sorption onto vegetation. Recent studies have shown that the sorption of chemicals in the cuticles covering the leaves of plants may be an important removal process for many VOCs²³. The process of plant sorption may occur by direct partitioning from air or by dry deposition from the particle phase²⁴. Methods are currently available to independently assess the impact of both processes on VOC concentrations in the environment, through model experiments with isolated cuticular membranes²³ and studies of the temperature dependence of partition coefficients^{23a,24}.

Welke et al.²³ estimated that 1.6 g of 12 volatile compounds would be sorbed by the cuticles of vegetation growing on 1 km² and concluded that the high affinities of cuticular material for organic substances and the extensive leaf areas present in most types of vegetation suggest that substantial amounts of VOCs will be removed from the atmosphere by this mechanism. This estimate of deposition assumes a leaf index of ~23, which is very high. Using a value between 6-14 would be more reasonable^{23a}, and would lower the deposition rate by 40-70 percent. In an absolute sense, the sorption of hydrocarbons to plant surfaces is likely to be minor, and stomatal uptake of vapor-phase organics is not a well established removal process. However semivolatile persistent hydrophobic compounds are rapidly absorbed with a good correlation of the leaf/air

partition coefficient with the octanol/air partition coefficient^{23b}. The deposition of gas-phase organic compounds to plant surface is likely to be dependent primarily upon atmospheric concentration and ambient temperature and for particle, aerodynamic diameter as well.

The most important factors leading to deviations from equilibrium air-to-cuticle partitioning are slow equilibrium kinetics for highly lipophilic compounds as well as metabolism and translocation within the plant²³. Compounds other than hydrocarbons, especially water -soluble compounds, may be more effectively scavenged from the atmosphere due to translocation and metabolism. As with other work on environmental fate modeling,. most of the work has not been concerned with how vegetation (or some other compartment) purifies the atmosphere, but with how the atmosphere deposits persistent pollutants (polycyclic aromatic hydrocarbons (PAH) and polychlorinated compounds) into these compartments. Thus, the majority of compounds studied have not been those that are photochemically reactive.

Rain-out and wash-out. Rain-out and wash-out are important for both vapors and aerosols. Aerosols with radii $<0.01 \mu\text{m}$ may act as condensation nuclei which are subject to wet removal with a lifetime of 3-30 days²⁵. The amount of removal of a vapor may be calculated from the air-to-water partition coefficient (i.e., Henry's law constant). A significant fraction of VOC will only reside in the aqueous phase if its Henry's law constant exceeds $5,000 \text{ M atm}^{-1}$, which suggests that VOCs with Henry's law coefficients between 1000 and $10,000 \text{ M atm}^{-1}$ can be classified as moderately soluble²⁷. Since many oxygenated solvents and VOC intermediates with low volatilities tend to have high Henry's law coefficients, this process may be particularly important for LVP VOCs. Overall, wash-out is a rather minor removal process for vapor-phase chemicals, since the majority are quite volatile and/or are hydrocarbons, which have low Henry's law coefficients.

Gas to aerosol conversion. Photochemical oxidation of organic molecules containing seven or more carbon atoms can generate semi-volatile secondary organic aerosol (SOAs)²⁷. In addition, SOAs may also be formed by both physical absorption and chemical adsorption onto urban particulate material, which is composed mostly of amorphous organic carbon²⁸. Semivolatile organic compounds (SOCs), substances with vapor pressures roughly between 10^{-4} and 10^{-11} atm at ambient temperature exist in air distribute between gas and particle phases. The vapor-to-particle ratio is controlled by the SOC vapor pressure and the total suspended particle concentration. Airborne SOCs are almost entirely gaseous or particulate at the high and low ends of the above vapor pressure range, but both phases are important to their atmospheric chemistry at intermediate volatilities.^{28a}. The gas/particle partitioning of SOCs to urban particulate matter containing a significant fraction of secondary organic carbon will be dominated by absorptive partitioning^{28b} so it will sensitive to polarity of both the SOC and the organic component of the aerosol. SOA formation thus represents a sink for the removal of many emitted LVP VOCs.

RESEARCH OPPORTUNITIES

Validation. Fate and transport models (such as those described above in the Fate Analysis section) have been applied mainly to long-term disposition of persistent pollutants. The results are not readily subject to validation because the emissions are usually not known. Some validation data ~~is~~ are available for chlorinated solvents; however, more data are needed²⁹.

Applicability to Ozone-forming Potential. The applicability of such modeling to the relatively short times and small areas involved in non-attainment of ozone standards is unknown. A method is needed to 1) incorporate alternative fates into EKMA calculations of MIR or 2) incorporate EKMA modeling or some of its outputs into environmental fate models. Work needs to be done to see if there is a practical means to obtain an ozone yield. One difficulty is that the EKMA model used to obtain MIR values begins with a single charge of VOC, while the availability models use continuous input and loss.

Physico-Chemical Data. The principal physicochemical properties used in environmental fate analysis include Henry's law constant³⁰, octanol-water partition coefficient³¹, air-octanol partition coefficient, and vapor pressure at 25 °C. These parameters are generally available for common volatile compounds, but the values for low-vapor-pressure compounds are often undetermined and must be estimated³².

Analytical Techniques. Methodologies for the ambient air measurement of carbonyl compounds is much more advanced than for other VOC classes such as alcohols and glycol ethers. The list of commonly measured substances in ambient air does not include semi-volatile oxygenated compounds⁹. The standard methods: non-methane hydrocarbons by TO-14 canister sampling and GC-FID analysis; heavy hydrocarbons by Tenax/GC-FID, aldehydes by DNPH/HPLC; and a variety of compounds in the gas and solid phase by PUF-XAD/GC-MS, do not detect many oxygenated and LVP VOCs. More research on VOC monitoring methods is needed to ensure data reliability.

Field Studies. In order to test any modeled hypothesis regarding atmospheric fate of emitted species, field studies designed to measure the emitted species are required. These are a necessary last step in determining the accuracy of both the emissions profiles and the assumptions made with regards to the relationship among usage, emissions and ambient air concentrations. Experimental costs may require the generalization of a limited number of measurements to a larger class of compounds or emissions types.

Sensitivity Analysis. Studies are needed to examine how the ozone yield from VOCs can be affected by factors affecting the VOC volatilization and removal from the troposphere. These studies are needed using urban, regional, and global models which include state-of-the-art chemical mechanisms for VOC photooxidation.

ACKNOWLEDGEMENTS

We thank Andrew Chew, Erik Kwok, Eileen McCauley and Carla Takemoto of the California Air Resources Board for reviewing our original manuscript and for their helpful comments and suggestions.

REFERENCES

- ¹ R. Atkinson (1998). Atmospheric chemistry of VOCs and NO_x. 1998 Ozone Assessment - Critical Review Paper, North Atlantic Research Strategy for Tropospheric Ozone, Pasco, WA.
- ² D. Mackay, A. Di Guardo, S. Paterson, G. Kicsi, and CE. Cowan. (1996). Assessing the fate of new and existing chemicals: A five-stage process. *Environ. Toxicol. Chem.* **15**, 1618.
- ³ R.A. Rapaport (1988). Prediction of consumer product chemical concentrations as a function of publicly owned treatment works treatment type and riverine dilution. *Environ. Toxicol. Chem.* **7**, 107.
- ⁴ D.H. Bennett, T.E. McKone, M. Matthies, and W.E. Kastenbergl (1998). General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment. *Environ. Sci. Technol.* **32**, 4023.
- ⁵ A.P. Bianchi and M.S. Varney (1997). Volatilization processes in wastewater treatment plants as a source of potential exposure to VOCs *Ann. Occup.Hyg.* **41**, 437.
- ⁶ M. Sharma and T.J. Overcamp (1996). Air emissions of volatile liquids spilled on sands. *Environ. Prog.* **15**, 229.
- ⁷ D. Lyons (1990). Computer modelling of solvent blends. *J. Oil Colour Chemists Assoc.* **73**, 82.
- ⁸ J.G. Watson, J.C. Chow, and E.M. Fujita (1998). Review of volatile organic compound source apportionment by chemical mass balance. 1998 Ozone Assessment - Critical Review Paper, North Atlantic Research Strategy for Tropospheric Ozone, Pasco, WA.
- ⁹ G.T. Helms (1989). Definition of VOC: Rationale. Memorandum from USEPA Office of Air Quality planning and Standards. Research triangle Park, NC.
- ¹⁰ J. J. Schauer, W. F. Rogge, L. M. Hildemann, M. A. Mazurek, G. R. Cass and B. R. T. Simoneit (1996). Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers, *Atm. Environment*, **30** (22), 3837.

- ¹¹ F. Wania, J.-E. Haugen, Y.D. Lei, D. Mackay (1998). Temperature dependence of atmospheric concentrations of semivolatile organic compounds. *Environ. Sci. Technol.* **32**, 1013.
- ¹² W.H. Schroeder and D.A. Lane (1988). The fate of toxic airborne pollutants. *Environ. Sci. Technol.* **22**, 240.
- ^{12a} 40CFR59.203(f)(1) published in the Federal Register, Vol 63, No. 176, September 11, 1998, pp. 48834-5.
- ¹³ National Volatile Organic Compound Emission Standards for Consumer Products -- Background for the Promulgated Standards, EPA-453/R-98-008b, page 2-6
- ¹⁴ E. E. Rickman, Jr., G. B. Howe, and R. K. M. Jayanty, Interlaboratory Study of a Test Method for Measuring Total Volatile Organic Compound Content of Consumer Products, EPA/600/SR-95/163 December 1995 (Order No. PB96-121652 from NTIS).
- ^{14a} J. Berry, ASTM *Standardization News*, February 1999, p26.
- ¹⁵ E. Webster, D. Mackay, and F. Wania (1998). Evaluating environmental persistence. *Environ. Toxicol. Chem.* **17**, 2148
- ¹⁶ Pathways Analysis Using Fugacity Modelling of 2-Butoxyethanol for the Second Priority Substances List (1996). Prepared for Chemicals Evaluation Division, Commercial Chemicals Evaluation Branch, Environment Canada, by DMER and Angus Environmental Limited.
- ^{17a} Staff Report, Proposed Modifications to the Appendices of the Draft 1997 Air Quality Management Plan, South Coast Air Quality Management District, October 1996.
- ^{17b} E. M. Fujita, Z. Lu, L. Sheetz, G. Harshfield and B. Zielinska, Desert Research Institute, July 23, 1997, "Determination of Mobile Source Emission Fraction Using Ambient Field Measurements," Coordinating Research Council Project No. E-5-1.
- ¹⁸ J. Wooley, W. W. Nazaroff and A. T. Hodgson (1990). Release of ethanol to the atmosphere during use of consumer cleaning products. *J. Air Waste Manage. Assoc.* **40**, 1114.
- ¹⁹ Emissions of Selected VOC Compounds from the Use of Laundry and Dishwashing Products Prepared for the Soap and Detergent Association by CH2M HILL May 1994
- ²⁰ C.J. Weschler and H.C. Shields (1996). Production of the hydroxyl radical in indoor air. *Environ. Sci. Technol.* **30**, 3250; Weschler C.J. and Shields, H.C. (1997) Measurements of the Hydroxyl Radical in a Manipulated but Realistic Indoor Environment. *Environ. Sci. Technol.* **31**, 3719-3722.
- ²¹ J. Sundell, B. Andersson, K. Andersson, and T. Lindvall (1993). *Indoor Air* **3**, 82.

- ²² Inside IAQ, Spring/Summer 1997, pp 1-4, EPA/600/N-97/003.
- ²³ B. Welke, K. Ettinger, and Riederer (1998). Sorption of volatile organic chemicals in plant surfaces. *Environ. Sci. Technol.* **32**, 1099.
- ^{23a} Simonich, S.L. and R.A. Hites (1994) Vegetation-atmosphere partitioning of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **28**, 939-943.
- ^{23b} J. Tolls and M. S. McLachian (1994) Partitioning of Semivolatile Organic Compounds between Air and Lolium multiflorum (Welsh Rye Grass). *Environ. Sci. Technol.* **28**, 159-166.
- ²⁴ D. M. Wagrowski and R. A. Hites (1998). Partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans between the atmosphere and corn. *Environ. Sci. Technol.* **32**, 2389.
- ²⁵ H. G. Wagner and R. Zellner (1979). Rates of reactive removal of anthropogenic emissions in the atmosphere. *Angew. Chem. Int. Ed. Engl.* **18**, 663.
- ²⁶ C. Liang, J.F. Pankow, J.R. Odum, and J.H. Seinfeld (1997). Gas/particle partitioning of semivolatile organic compounds to model inorganic, organic, and ambient smog aerosols. *Environ. Sci. Technol.* **31**, 3086.
- ²⁷ J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics*, John Wiley & Sons, Inc. 1998, pp 343-4
- ²⁸ Z. Meng, D. Dabdub, and J. H. Seinfeld (1997). Chemical coupling between atmospheric ozone and particulate matter. *Science* **277**, 116.
- ^{28a} Bidleman T.F. (1988) Atmospheric processes. *Environ. Sci. Technol.* **22**, 361.
- ^{28b} C. Liang, J. F. Pankow, J. R. Odum and J. H. Seinfeld (1997). Gas/Particle Partitioning of Semivolatile Organic Compounds to Model Inorganic, Organic, and Smog Aerosols. *Environ. Sci. Technol.* **22**, 361
- ²⁹ Y. Cohen and P. A. Ryan (1985). Multimedia modeling of environmental transport: Trichloroethylene test case. *Environ. Sci. Technol.* **19**, 412.
- ³⁰ R. Sander 1996,. Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (version 2). Available online: <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>
- ³¹ Experimental Kow values and information on available estimation techniques. Available online: <http://esc.syrres.com/~ESC/kowint.htm>.
- ³² J. Hine and P.K. Mookerjee (1975). Estimation of Henry's law constants. *J. Org. Chem.* **40**, 292.