

Atmospheric Availability as a Component of the Tropospheric Ozone-Forming Potential of Volatile Organic Compounds

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Summary

Modeling of ozone formation requires accurate emissions inventories and chemical mechanisms. Consideration of equilibrium vapor pressures and partition between gas phase and aerosols suggested that many low-vapor-pressure (LVP) VOC in consumer, commercial, and agricultural products would be present predominately in the gas phase. However, this conclusion may not be correct in view of studies indicating alternate fates for those VOCs. The tropospheric concentration of a VOC is 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 (e.g. photooxidation, deposition, horizontal and vertical transport, aerosol formation). 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 kinetic, mechanistic and smog chamber studies upon which calculations of MIRs are based do not include transport to water or soil, which are present in the natural environment. Not only the compound to be evaluated, but also its oxidation products, may not participate in ozone formation to the extent predicted if they have other environmental fates besides oxidation in air and advection in air.

Models need to be developed that can incorporate a chemical's entire tropospheric fate. Environmental fate modeling, used extensively to track persistent organic pollutants, may be applicable in assessing tropospheric ozone-forming potential of VOCs as well.

Introduction

Current EPA policy presumes the availability of low-vapor-pressure (LVP) VOCs in air¹. The assumption is based on equilibrium considerations for air-surface exchange and consideration that during performance of EPA Method 24 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 °C.¹

However, this conclusion may not be correct because there are alternative fates for those VOCs^{2,3}. Compounds of low volatility, especially those which are hydrophilic, have many competing ways (e.g., photooxidation, deposition, horizontal and vertical transport and aerosol formation) by which they may be prevented from entering the atmosphere or removed once they enter it, but quantitative assessments are rare.

Though some regional-scale predictive models for ozone formation incorporate information on fate and removal, others do not. Models need to be developed that can incorporate all that that is known about a chemical's tropospheric fate and removal. Environmental fate

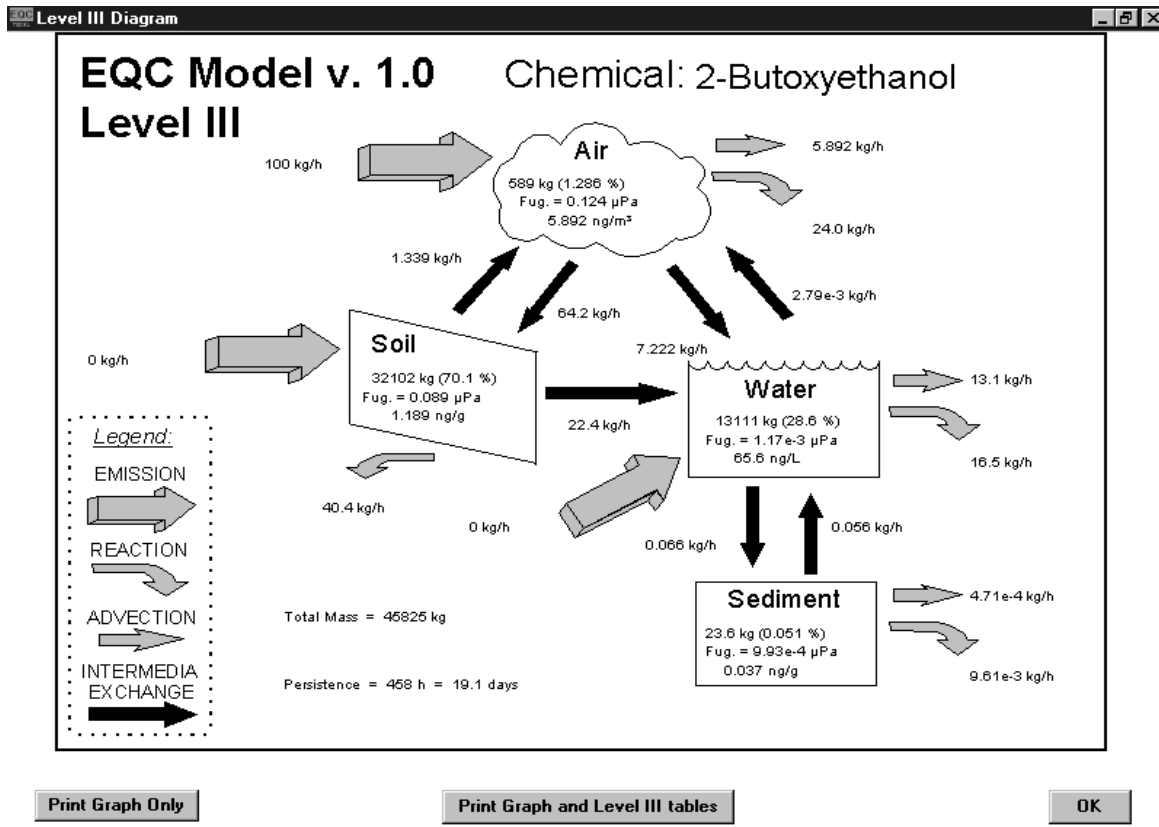
modeling has been used extensively to track persistent organic pollutants. Research is needed to see what modifications are required to make it a useful tool for assessing tropospheric ozone-forming potential of VOCs with short atmospheric lifetimes.

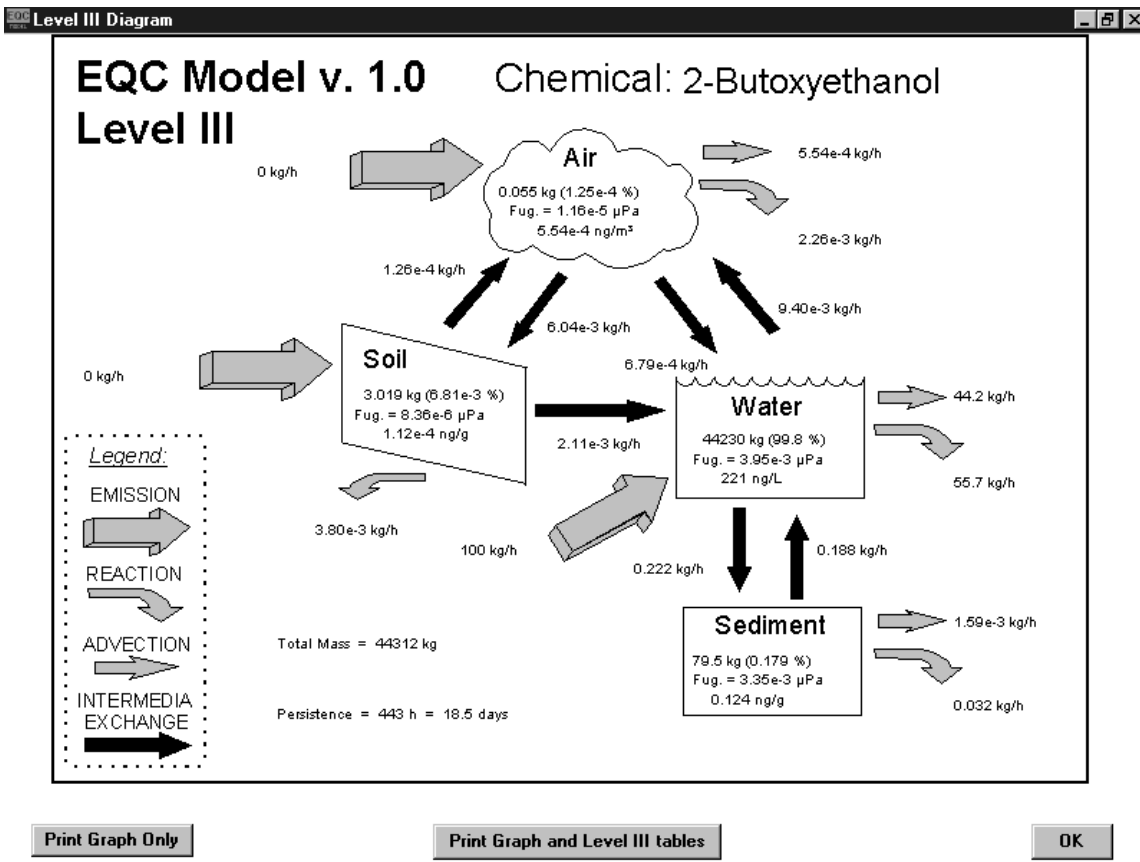
Environmental fate and transport models are available to examine how a chemical partitions among air, water, soil, and sediment⁴. These fate and transport models examine intermedia transport rates for various diffusive and nondiffusive processes and estimates the mass fraction of a chemical in each environmental 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.

We used a version of this modeling technique as a reality check for our hypotheses that the extent to which organics in consumer products and coatings enter and remain in the air, is a factor in ozone generating potential that may be as important as atmospheric reactivity. We have begun to explore whether the atmospheric availability of organic compounds in products can be determined using environmental fate modeling.

Results of Environmental Fate Modeling

To get a rough estimate of the potential removal of compounds from the atmosphere we have used Mackay's EQC Model version 1.0, Level III⁵, which uses the environment of southern Ontario, Canada as the "landscape."





If 2-butoxyethanol is emitted to air, most of it is removed by deposition to soil, while about 24% is removed by reaction in air. If it is emitted into water, more than 99% stays in water, where it is readily biodegraded⁶. These data indicate that partitioning of organic compounds among different media can directly impact the amount of VOC available in the atmosphere for hydroxyl radical reactions and ozone formation. The results of three cases are summarized below.

	Air	Water	Soil	Sediment
Emission to Air				
Reaction	24.0%	16.5%	40.4%	0.0%
Advection	5.9%	13.1%		0.0%
Emission to Water				
Reaction	0.0%	55.7%	0.0%	0.0%
Advection	0.0%	44.2%		0.0%
Emission to Soil				
Reaction	0.5%	19.8%	63.8%	0.0%
Advection	0.1%	15.7%		0.0%

To roughly quantify the potential removal of compounds from the atmosphere we have used the Level III EQC model and calculated the fraction of material either reacted in air or advected in air, as a conservative estimate of the amount that can contribute to ozone formation. We refer to this as the emission inventory factor (EIF) in the following tables, since consumer product sales would have to be multiplied by this factor to get the emissions for use in airshed models that do not incorporate environmental fate.

Calculated % VOC Contributing to Ozone Formation from Oxygenated Chemicals by the EQC Model

Chemical	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)	EIF _{air} % VOC	EIF _{soil} % VOC	EIF _{aq} % VOC
Acetone	56	185	96	27	12
Propylene Glycol Methyl Ether	120	8	27	1	0
Ethylene Glycol Methyl Ether	124	6	93	8	1
Ethylene Glycol Ethyl Ether	135	4	93	8	1
Propylene Glycol Butyl Ether	170	0.6	97	7	1
Ethylene Glycol Butyl Ether	171	0.6	30	1	0
Dipropylene Glycol Methyl Ether	188	0.2	1	0	0
Dipropylene Glycol Butyl Ether	229	0.03	90	4	0
Diethylene Glycol Butyl Ether	231	0.01	9	0	0
Ethoxytriglycol	256	0.01	0	0	0
Butoxytriglycol	281	0.00002	0	0	0

Assumptions:

- Environment is representation of southern Ontario, Canada
- EIF_{air} = % reaction + advection in air for 100% emission into air
- EIF_{soil} = % reaction + advection in air for 100% emission into soil
- EIF_{aq} = % reaction + advection in air for 100% emission into water

Same mass transfer coefficients for all chemicals

Calculated % VOC Contributing to Ozone Formation from Common Chemicals by the EQC Model

Chemical	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)	EIF _{air} % VOC	EIF _{soil} % VOC	EIF _{aq} % VOC
Methanol	64.5	97	92	10	1
Ethanol	78.3	44	94	9	0
Butanol	117.7	5	97	11	2
Hexanol	157.0	0.5	97	6	3
Methyl Ethyl Ketone	80	74	96	30	8
2-Pentanone	102	27	98	40	12
2-Heptanone	152	2	99	23	13
Methyl Isobutyl Ketone	116	43	100	47	16
Methyl Acetate	57	173	97	48	14
Ethyl Acetate	77	75	98	54	16
Butyl Acetate	126	8	99	46	21
Hexane	69	120	100	98	52
Decane	174	0.9	100	96	48
Dodecane	216	0.1	100	65	24
Hexadecane	287	0.001	100	0	0

Assumptions:

Environment is representation of southern Ontario, Canada

EIF_{air} = % reaction + advection in air for 100% emission into air

EIF_{soil} = % reaction + advection in air for 100% emission into soil

EIF_{aq} = % reaction + advection in air for 100% emission into water

Same mass transfer coefficients for all chemicals

We took the worst case, emission entirely to air, and calculated an ozone-forming potential by multiplying the maximum incremental reactivity (MIR) by the emission inventory factor (EIF).

Chemical	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)	MIR	EIF _{air} (fraction VOC)	MIR*EIF
Acetone	56	185	0.48	0.96	0.46
C ₇ Alkyl Ketone	152	2	2.65	0.99	2.62
2-Butoxyethanol	171	0.6	3.23	0.30	0.97
Dodecane	216	0.1	0.72	1.00	0.72
Diethylene Glycol Butyl Ether	231	0.01	3.36	0.09	0.30

MIRs (g of O₃/g of VOC) are from W. P. L. Carter, Updated Maximum Incremental Reactivity Scale for Regulatory Applications, Preliminary Report to California Air Resources Board, Contract No. 95-308, August 6, 1998

Note that the modeling shows striking differences in atmospheric availability among chemical classes. Vapor pressure alone is not adequate to estimate atmospheric availability. Volatility correlates better with Henry's Law constants and kOW. A remarkable result is that, on this scale, the ozone-forming potential of diethylene glycol butyl ether is less than that of acetone, which is exempted from consideration as a VOC due to "negligible reactivity". Is this real?

There are difficulties in employing existing environmental fate modeling to atmospheric availability for estimation of tropospheric ozone-forming potential. Most fugacity-based environmental fate modeling has dealt with persistent organic pollutants, especially PAHs and chlorinated hydrocarbons, which are hydrophobic and unreactive with hydroxyl radicals. The time scale has been years. To examine the fate of hydrophilic compounds with low vapor pressures and relatively high rates of photochemical oxidation one needs to work with much shorter times and a limited "landscape." The assumption of equilibrium within compartments needs to be tested. It does appear that transport rates between compartments is fast. As discussed below application of existing environmental fate modeling to urban ozone episodes is complicated by the existence in urban areas of processes which are not considered in the EQC model, but may be important. Regional modeling for estimates of ozone-forming potential related to an 80 ppb ozone standard will be easier than modeling urban areas that are in noncompliance with the 120 ppb standard, since the landscape will more closely approximate that used in current modeling. Daytime versus nighttime transport and reaction may need to be separated in the environmental fate modeling if we are looking at multi-day scenarios.

The following 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.

A significant percentage of the hydrophilic VOCs found in consumer products may never reach the atmosphere, but will go “down-the-drain” in aqueous solution and undergo biological degradation^{7,8}. Indoor atmospheric chemistry initiated by hydroxyl radicals generated indoors may have a profound effect upon VOC emissions by oxidizing a portion of the VOCs emitted from consumer products used indoors⁹ and limiting the amount available for ozone formation outdoors. Adsorption onto inert materials has been established as important in indoor air studies¹⁰. The absorption of SOC on vegetation has been studied mainly to determine whether our food is being contaminated by air-borne persistent organic pollutants. How vegetation cleanses the atmosphere has received less attention. Rain-out and wash-out are important for both vapors and aerosols. 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. Photochemical oxidation of organic molecules containing seven or more carbon atoms can generate semi-volatile secondary organic aerosol (SOAs)¹¹. SOA formation represents a sink for the removal of many emitted LVP VOCs.

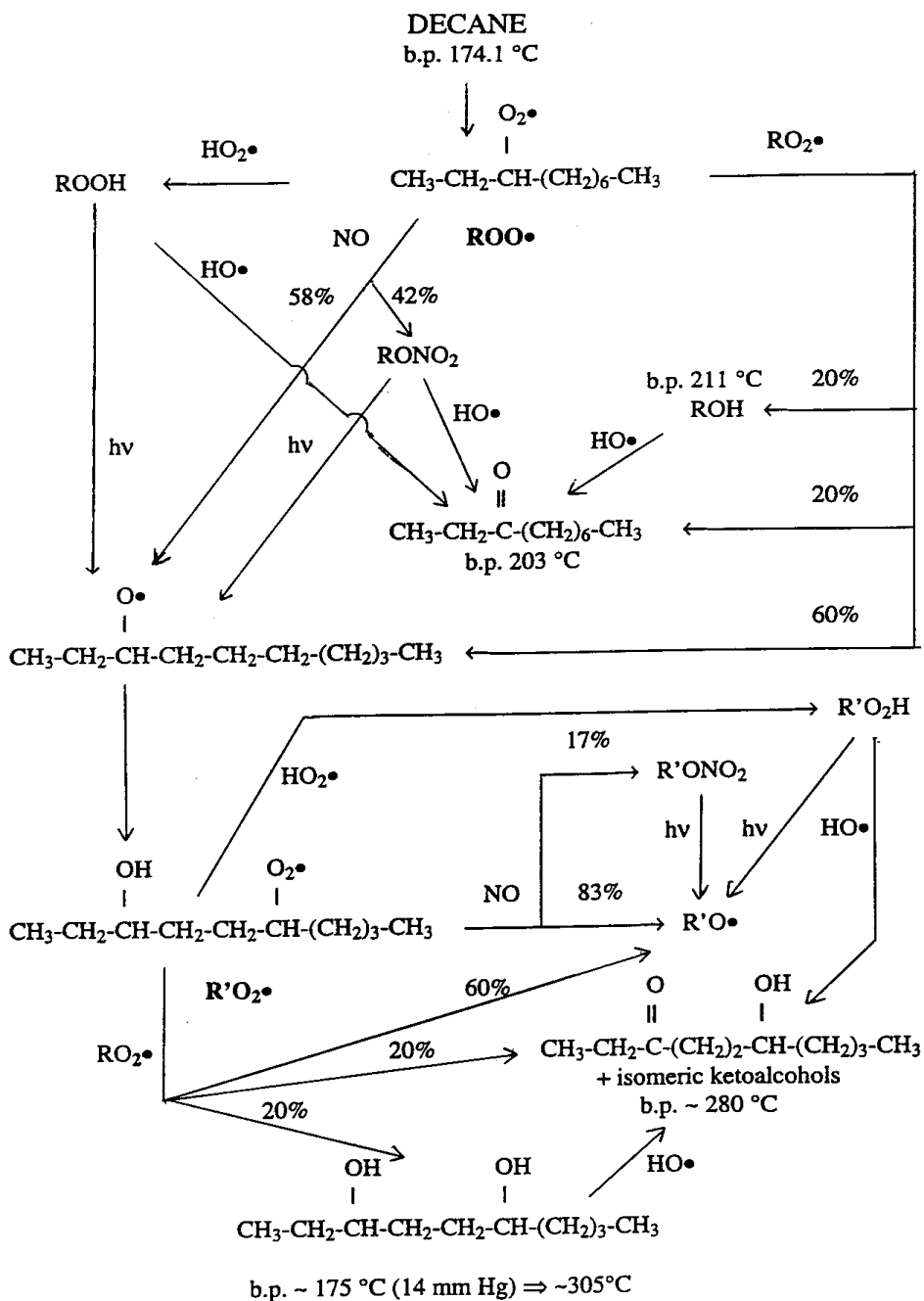
Potential Effects on MIR Estimation

The kinetic, mechanistic and smog chamber studies upon which calculations of MIRs are based do not include transport to water or soil, which are present in the natural environment. Not only the compound to be evaluated, but also its oxidation products, may not participate in ozone formation to the extent predicted if they have other environmental fates besides oxidation in air and advection in air.

The mechanism for n-decane has several pathways for the reaction of decylperoxy radicals, but they all lead mainly to or through decanol, decanone and (by intramolecular hydrogen abstraction [rearrangement] of alkoxy radicals) hydroxydecanones. These compounds have vapor pressures much lower than decane and much greater polarity.

As an example, we ran the EQC Model v. 1.0 Level III calculation on 6-hydroxy-3-decanone emitted into air (since it is formed in air from decane). Most of it is transported rapidly to soil. That which reaches water from air or soil is rapidly degraded so very little reaches sediment. Accumulation is in soil.

	Air	Water	Soil	Sediment
Emission to Air				
Reaction in	12.6%	22.6%	60.1%	0.0%
Advection in	2.9%	1.8%		0.0%



An oxidation product of ethylene glycol is glycolaldehyde. The estimated MIR of ethylene glycol, based on experiments at low relative humidity, may not reflect its true ozone-forming potential, since both ethylene glycol and glycolaldehyde have low volatility and high water solubility and may be removed from the atmosphere by processes other than gas-phase oxidation.

CONCLUSIONS

- Reactivity (MIR) alone is an insufficient indication of the ozone-forming potential of volatile organic compounds (VOC). Atmospheric availability is also important.
- Vapor pressure alone is not adequate to estimate atmospheric availability. Volatility correlates better with Henry's law constants and k_{ow} .
- Environmental fate modeling, used extensively to track persistent organic pollutants, may be applicable in assessing tropospheric ozone-forming potential of VOCs as well.
- Such modeling shows striking differences in atmospheric availability among chemical classes.
- The challenge is to extend environmental fate modeling to smaller areas and shorter times than normally assessed.
- The urban "landscape" may be quite different from that in larger areas. Relatively little is known about indoor "sinks" for VOC, exchange of indoor and outdoor air, adsorption or absorption on urban surfaces and vegetation and other aspects peculiar to an urban environment.
- The MIR of a VOC may be lower than indicated by simple models if the products of its oxidation have other environmental fates than oxidation in air.

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