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Project Summary

Atmospheric Persistence of Eight Air Toxics

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The concept of the "atmospheric lifetime" of an air toxic chemical was defined, and methods were described for estimating the lifetimes of such chemicals in the atmosphere. For many air toxics, the primary removal mechanism in the air is its reaction with hydroxyl radicals. Because hydroxyl radical chemistry is so important in determining the atmospheric lifetime of many chemicals, recommendations are made for the "average" conditions to use in estimating the lifetime of air toxics over the continental U.S. These methods and conditions are applied to, and estimates of the "average" atmospheric lifetimes are derived for eight volatile air toxic chemicals which EPA had identified in "Intent-to-List" notifications during 1985. The eight chemicals for which lifetimes are derived are methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, perchloroethylene, 1,3-butadiene, and ethylene oxide. Seven of the eight chemicals are removed from the atmosphere primarily by reaction with OH radicals. The lifetimes of the seven chemicals primarily removed by OH reaction ranged from around 4 hours to around 18 months. The eighth chemical, carbon tetrachloride, has such a long atmospheric lifetime (ca. 50 years) that the primary removal mechanism is not identifiable.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering Information at back).

Introduction

During 1985, the Environmental Protection Agency (EPA) published intent to list decisions for eight organic chemicals (i.e., methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, perchloroethylene, and ethylene oxide). The atmospheric lifetime, distribution, and ultimate fate of these air toxics is determined by a variety of factors which act to transport, remove, or redistribute the chemicals. These factors control the magnitude and nature of any potential exposure to the air toxic chemical. A wide range of processes may be involved: they may be chemical in nature, like reactions with ozone or hydroxyl radicals, or physicochemical processes like photolytic decomposition, or physical mechanisms like washout, dry deposition, transport to the stratosphere, etc.

Factors Affecting the Atmospheric Lifetime

Atmospheric Lifetimes

Once a potentially hazardous air pollutant, like those named above, is released into the atmosphere, its concentration and fate is determined by a variety of chemical or physical processes. The emitted material immediately begins to mix in the atmosphere and to dilute, reducing the exposure levels and the associated risk. The total mass of the chemical in the environment is not reduced, however, until some process acts to remove or transform the chemical. The rate at which physical or chemical processes remove or transform the target compound determines the atmospheric lifetime of the chemical.

The persistence of the air toxic chemicals in the atmosphere can be described by the characteristic decay time, τ_D. If the decay rate in the air can be expressed as a linear function of Q, one finds that τ_D is the time at which an initial injection of a chemical has decayed until $Q = Q_o/e$, where e is the natural number 2.718.... After one lifetime, about 37% of the starting concentration is still present. After a second lifetime, only 13.5% of the chemical remains. After three lifetimes, less than 5% of the starting material remains. Similarly, the half-life, $t_{1/2}$, then is given by $t_{1/2} = \ln 2/k_D \approx 0.693/k_D \approx 0.693\,\tau$.

Chemical Reaction Processes

A wide range of reactive species are known to be present in both the troposphere and the stratosphere which may react with the emitted air toxics to transform them into other compounds. For many air pollutants, however, the predominant tropospheric reaction is with the hydroxyl radical, OH, despite the fact that its concentration is relatively low.

Reactions With Hydroxyl Radicals

Hydroxyl radicals are ubiquitously present throughout the troposphere, being formed from the normal photochemical processes which occur even in "clean" air. The radicals are so reactive that their own atmospheric lifetime is very short, and their concentration never becomes very large. Because of their importance to atmospheric and combustion chemistry, the reaction rates for OH and many organic species have been measured. A large data base of kinetic information is already available which may be applied to the problem of estimating atmospheric lifetimes.

The choice of values to assign to k_{OH} and to the hydroxyl radical concentration, [OH], is complicated by the fact that the rate constant is a function of temperature, and the [OH] depends upon a balance of competing chemical reactions involving temperature, light intensity and the concentrations of many other pollutants.

Atmospheric Mixing and OH Removal

The eight air toxics under consideration in this paper are man-made pollutants. Their release, therefore, is most likely to occur where man inhabits the earth, namely near the surface, in temperate zones, and into polluted air over the continental land masses. These factors suggest that such a released pollutant will initially encounter an environment which is likely to be warmer, and more reactive, than the average troposphere. As the pollutant is mixed, first within the boundary layer, then vertically in the troposphere, and finally horizontally throughout the troposphere, it encounters continually changing "average" temperatures and reactant species. If it persists long enough, it becomes well-mixed throughout the atmosphere, and the "average" conditions no longer change. Clearly, average tropospheric values for temperature and [OH] are actually only applicable for species which are sufficiently long-lived to become evenly dispersed throughout the troposphere. It may be necessary, therefore, to consider the temperature and [OH] in each of several tropospheric layers as the chemical diffuses.

Estimation of Atmospheric Lifetimes and Removal by OH

In order to estimate the removal rate of air toxics due to reaction with OH radicals, it is convenient to divide the troposphere into three compartments: the boundary layer, the vertically-mixed troposphere at a specific latitude, and the horizontally-mixed global or hemispheric troposphere. The average temperature and [OH] in the appropriate compartments can then be used to estimate the lifetime of an air toxic. Average values for [OH] and temperature in each compartment (for continental air at about 37.5° N latitude) are estimated, based upon current modeling and measurement efforts. The recommended values are shown in Table 1. The actual choice of the compartment to use depends upon the estimated lifetime of the chemical and the mixing times between reservoirs. For species with lifetimes of less than 2 or 3 days, the estimates for the boundary layer should be used. For chemicals with lifetimes of about 3 weeks to 5 months, the values for the vertically-mixed troposphere should be used. For very stable chemicals with lifetimes in excess of 3 years, the global values should be used. For species with lifetimes intermediate to the times described above, lifetimes should be estimated for the two bracketing regimes, and the lifetime expressed as a range.

Atmospheric Persistence of Eight Air Toxics

Methylene Chloride

Methylene chloride (dichloromethane) is a high volume, commonly used solvent. Its background concentration at 40° N is about 50 parts per trillion (ppt). Its concentration in urban areas of the U. S. is highly variable, probably due in part to the many sources resulting from its frequent use. Average urban concentrations are often ten to one hundred times as large as the geochemical background concentration.

Methylene chloride reacts with OH radicals in the atmosphere at a moderate rate. Reactions are not expected to occur with ozone or other common atmospheric pollutants. Dry deposition and rainout are also expected to be very slow. Since other removal mechanisms are not likely to be effective, they can be ignored in estimating the total removal rate. The atmospheric lifetime of methylene chloride is, therefore, simply that predicted from hydroxyl radical removal, around 130 days. The estimated half life is about 69% of the lifetime, or about 91 days. The estimate of 130 days agrees reasonably well with values derived by other researchers using a two-box model to estimate the global lifetime of methylene chloride from its distribution throughout the atmosphere.

Chloroform

Chloroform (trichloromethane) is another chemical which is ubiquitously present in the atmosphere. The chemical is manufactured for use as a solvent, a cleaning agent, and as an intermediate in the manufacture of other chemicals. Geochemical background concentrations are around 16 ppt.

The reaction rate constant for chloroform with OH has been reported by at least three investigators, and the data are in excellent agreement. For chloroform, reaction with other tropospheric pollutants and removal by physicochemical processes is not expected to be very large. The atmospheric lifetime is equated with the lifetime due to hydroxyl radical reaction. It is appropriate to assign chloroform an atmospheric lifetime of between 181 and 378 days (or 0.5 to 1.0 years).

Carbon Tetrachloride

Carbon tetrachloride (tetrachloromethane) is nearly uniformly distributed around the globe. This uniform distribution means that the chemical is well mixed in the troposphere and suggests that it has a very long lifetime compared to the atmospheric mixing processes.

The measurement of carbon tetrachloride in the ambient atmosphere has proven difficult over the years, with investigators reporting significantly dif-

Regime	Temperature K	[OH] 10^6 molec cm^{-3}	Applicable Lifetimes
Boundary Layer	288	1.0	< 3 days
Vertically-Mixed Troposphere	263	1.0	3 wk to 5 mo
Hemispheric/Global Troposphere	260	0.5	> 3 yrs

ferent values. Recently, however, a consistent set of data on carbon tetrachloride has begun to emerge. The geochemical background concentration in 1978-1981 was found to be around 118 ppt. Concentrations of the chemical were found to be increasing at about 2 ppt per year.

The reaction of carbon tetrachloride with OH radical is so slow that the rate constant has not been measured. Upper limits for the rate constant have been determined, and they suggest that the atmospheric lifetime due to hydroxyl radical reaction is longer than 50 years. In addition, a number of removal processes have been postulated including chemical reactions and photolysis in the stratosphere, hydrolysis in the ocean, ion-molecule reactions, and photolysis on sand. None of these processes has a very large effect, however. Most of them result in lifetime estimates of around 50 years.

Two modeling approaches have been applied to estimate the atmospheric lifetime of carbon tetrachloride. A trend analysis technique and an inventory analysis method yielded most probable lifetimes of 50 to 57 years, respectively. While these modeling approaches did produce lifetime estimates with substantial uncertainties, they are consistent with the known chemical and physical processes involving carbon tetrachloride. A lifetime estimate of around 50 years is the best that can currently be done.

Ethylene Dichloride

Ethylene dichloride (1,2-dichloroethane) is another high-volume man-made pollutant which has become ubiquitous in the atmosphere. A global background concentration of ethylene dichloride of 25 ppt was reported for December 1981. The reaction rate of ethylene dichloride with OH radicals has not been so thoroughly investigated as the reactions of many other chlorinated alkanes. A critical review of the available OH kinetics data for ethylene dichloride suggests that an estimated lifetime of 92 days is reasonable. Other removal processes are, once again, not likely to be effective in removing this air toxic. Given uncertainties in the kinetic estimates, however,

the value of 92 days should only be viewed as the most probable value. Allowing a factor of two as a margin of safety, the estimated ethylene dichloride residence time is between 0.13 and 0.50 years. The upper limit value is close to the residence time of 0.6 ± 0.2 years recently estimated by other researchers from ambient concentration measurements and a global budget model.

Trichloroethylene

Trichloroethylene (trichloroethene) is a chlorinated alkene which has found use as a degreaser and solvent. The Northern Hemispheric background concentrations in the Eastern Pacific Ocean were reported as 12 ppt. A critical review of the literature data reported median urban concentrations of 150 ppt.

The available rate data for reactions with OH radicals are in reasonable agreement. The activation energy for the reaction with OH is negative: the rate constant for this chemical will increase as the temperature cools. Although trichloroethylene is an alkene, with a double bond which may be subject to attack by ozone, the only reported rate constant for reaction with ozone is very low. Ozonolysis, therefore, plays no significant role in the removal of this compound. Other removal mechanisms are also expected to be ineffective. The lifetime computed for the vertically mixed troposphere is even shorter than the lifetime in the boundary layer, due to the negative activation energy exhibited by this compound. The lifetime of trichloroethylene is estimated as slightly over 4 days.

Perchloroethylene

Perchloroethylene (tetrachloroethene) is a volatile compound commonly used as a degreaser and solvent. It is emitted in significant amounts from dry cleaning operations. The chemical is consistently found in urban areas of the U.S. The recent data compilation reported a median concentration of 340 ppt in urban and suburban areas of the U.S. During a stagnant period in San Jose in December 1985, a two-hour integrated sample yielded a value of 6639 ppt.

The only reported value for the rate constant of the reaction of perchloroethylene and ozone is very small, implying that ozone will not effectively remove the chemical from the atmosphere. Dry deposition rates of perchloroethylene to some common surface materials found in urban areas were recently measured. The rates were so slow that they were often indistinguishable from zero. Dry deposition, therefore, does not appear to be a significant removal pathway. The lifetime estimated from hydroxyl removal rates is estimated to range from 119 to 251 days.

1,3-Butadiene

1,3-butadiene is a very reactive alkene with two double bonds. It is commonly used as a component in the synthesis of rubber and many other diverse compounds.

Butadiene reacts quickly with both OH and ozone. The hydroxyl radical reaction has a negative activation energy, indicating that the rate constant will increase as the temperature decreases. The estimated lifetime, based on reaction with OH radicals, is 240 minutes. Assuming an ozone concentration of around 40 ppt, the lifetime computed for removal by ozone is around 2800 minutes.

Obviously, the actual lifetime of such a reactive compound will depend upon the specific conditions at the time of release. The quoted lifetimes were calculated for "average" conditions. Because the estimated lifetime is so short, the actual degradation of any real emissions is very dependent upon time of day, sunlight intensity, actual temperature, etc. While the lifetime during the middle of the day in the summer under polluted conditions could be much shorter than the estimated 4 hours, the lifetime of emissions at night could be essentially infinite. After sunset, there will be no hydroxyl radicals generated and the small amounts of residual ozone present in the evening will have little effect on the butadiene concentrations. On average then, 1,3-butadiene has an estimated lifetime of around 4 hours.

Ethylene Oxide

Ethylene oxide (oxirane) is the smallest possible organic epoxide. The nature of the chemical structure induces a high strain energy in the three-membered ring, and this strain energy influences the reaction kinetics and products.

Two investigators have recently measured the reaction rate constant for

ethylene oxide with OH radicals. The experimentally determined room temperature rate constants were in very good agreement, and they suggest an atmospheric lifetime of from 217 to 578 days.

Of the eight chemicals named in "Intent to List" notifications, ethylene oxide is the most soluble in water. The solubility of ethylene oxide in water has recently been quantified at ambient temperatures: the data suggest that neither rain out nor adsorption into aqueous aerosol particles in the air should remove very much of the compound.

No other removal processes are known which can rapidly deplete the ethylene oxide from the air. Results from smog chamber irradiations in both natural sunlight and artificial illumination are also consistent with a slowly reacting organic chemical. The estimated lifetime, therefore, can be calculated simply from the OH radical removal rate.

It is interesting that ethylene oxide, with an estimated lifetime as long as 1.5 years, has not been observed in the ambient atmosphere. A variety of other methods have been reported for use in analyzing for ethylene oxide, but these methods all have reported sensitivities from 0.05 parts per million to greater than 3 parts per million. Using the 1982 estimate for production of ethylene oxide in the U.S., and making reasonable estimates for other production and release rates, one estimates a background concentration in the Northern Hemisphere to be around 240 ppt. This value is a factor of 200 to 12,000 below the quoted analytical detection limits. It is not surprising then, that no ambient data on ethylene oxide have been reported. Nor does the lack of ambient data argue that there must be some rapid, but unknown, removal mechanism. Until additional data

arrive to modify these conclusions, it is appropriate to assign ethylene oxide an atmospheric lifetime of from 0.6 to 1.5 years.

Conclusions

Relationships have been developed in the full report which describe the atmospheric lifetimes of potentially hazardous chemicals in terms of their probable removal mechanisms. These relationships have been applied to eight air toxic chemicals identified by EPA in Intent to List notifications. The eight chemicals and their estimated atmospheric lifetimes are tabulated below.

For all the chemicals except carbon tetrachloride, the dominant removal mechanism from the atmosphere was reaction with hydroxyl (OH) radicals. Removal rates for carbon tetrachloride were so slow that the dominant removal mechanism could not be determined, and

the lifetime given is one, reported elsewhere, based upon modeling. Average tropospheric conditions for OH reactions were defined and utilized as the basis of the predicted atmospheric lifetimes for the other chemicals. In the case of ethylene oxide, questions regarding the atmospheric stability of the chemical and the lack of ambient data were addressed and resolved.

Table 2. *Estimated Atmospheric Lifetimes of Eight Air Toxics*

Chemical Name	Atmospheric Lifetime
Methylene chloride	131 days
Chloroform	181 to 378 days
Carbon tetrachloride	50 years
Ethylene dichloride	46 to 184 days
Trichloroethylene	4 days
Perchloroethylene	119 to 251 days
1,3-butadiene	4 hours
Ethylene oxide	217 to 578 days

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