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Atmospheric Persistence of Eight Air Toxics

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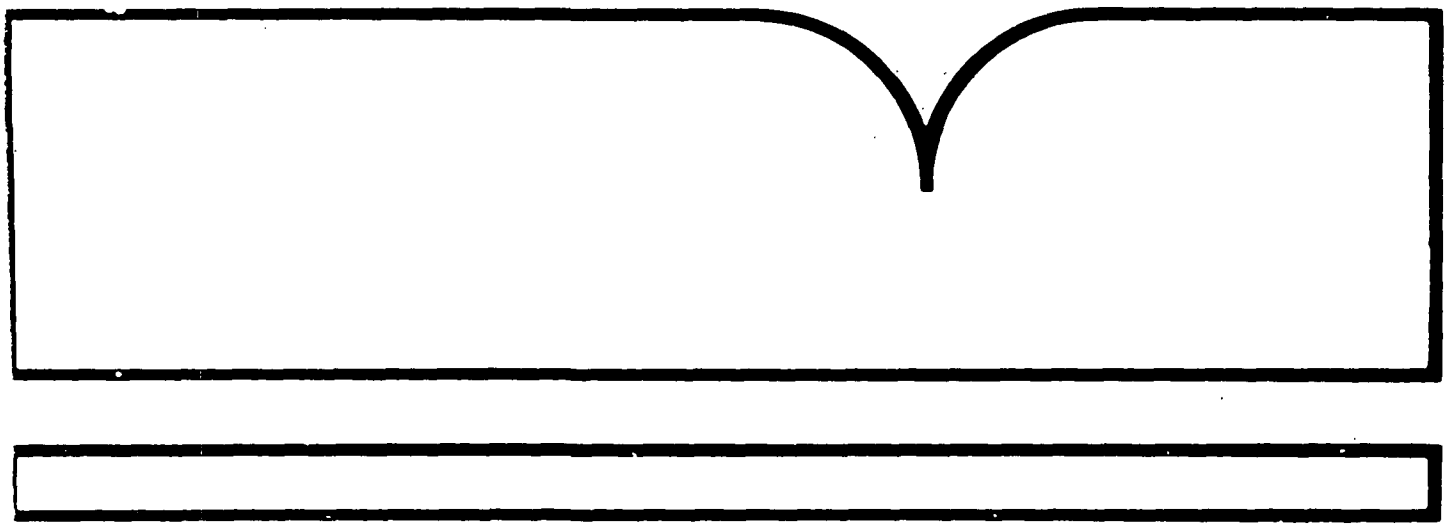

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ATMOSPHERIC PERSISTENCE OF EIGHT AIR TOXICS

by

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16. ABSTRACT

Atmospheric lifetimes were estimated for eight air toxic chemicals (i.e., methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, perchloroethylene, 1,3-butadiene, and ethylene oxide), which were designated in 1985 in "Intent-to-List" notices by EPA in the Federal Register. Seven of the eight chemicals were removed from the atmosphere primarily by reaction with OH radicals. Because of the importance of OH radical chemistry to the estimation of the atmospheric lifetimes of many air toxics, recommendations were made for the "average" conditions to use in estimating the lifetime of air toxics over the continental U.S. due to OH reactions. These conditions were then applied to the designated air toxics to derive estimates of the "average" atmospheric lifetimes. Lifetimes of the seven chemicals primarily removed by OH reaction ranged from around 4 hours to around 18 months. In the case of eighth chemical, carbon tetrachloride, the primary removal mechanism is unknown. Carbon tetrachloride has a very long atmospheric lifetime, estimated in the literature as around 50 years.

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ABSTRACT

The concept of the "atmospheric lifetime" of an air toxic chemical is defined, and methods are 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 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 four 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.

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SECTION 1

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). Since that time, the Agency has continued to develop data on each of these potentially hazardous air pollutants in order to assess better the exposure and risk that these species pose in the environment. During the regulatory decision making process, a large quantity of information is collected and evaluated to develop a comprehensive understanding of the environmental impact of such air toxics. Important aspects to be considered include human health effects, the concentration levels to which people are exposed, routes of exposure, the environmental distribution, removal processes and the fate of the chemical, the strengths and locations of the emission sources, and the global impacts of the air toxics.

The environmental concentrations to which humans may be exposed are the result of a dynamic balance between emissions of the air toxic chemical and the processes which remove or modify that chemical. Once a quantity of an air toxic is introduced into the environment, its lifetime, distribution, and ultimate fate is determined by a variety of factors which act to transport, remove, or redistribute the chemical. 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.

This report will focus on describing the probable range of ambient concentrations and the atmospheric processes which control the environmental lifetime and distribution of the eight air toxic chemicals named above.

SECTION 2

CONCLUSIONS

Relationships have been developed 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.

TABLE 1. 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

For all the chemicals except carbon tetrachloride, the dominant removal mechanism 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[1] 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.

SECTION 3

FACTORS AFFECTING THE ATMOSPHERIC LIFETIME

CHEMICALS INVOLVED

Eight potentially hazardous chemicals are under consideration by EPA for possible regulation under the Clean Air Act. Those chemicals, for which intent to list decisions have been published, are identified in Table 2 below. Also listed are the name and registry number used by Chemical Abstracts Service (CAS) to identify uniquely the specific chemicals.[2]

TABLE 2: ORGANIC CHEMICAL NAMED IN INTENT TO LIST NOTIFICATIONS

CHEMICAL	CAS INDEX NAME	REGISTRY NO.
Methylene Chloride	Dichloromethane	75-09-2
Chloroform	Trichloromethane	67-66-3
Carbon Tetrachloride	Tetrachloromethane	56-23-5
Ethylene Dichloride	1,2-Dichloroethane	107-06-2
Trichloroethylene	Trichloroethene	70-01-6
Perchloroethylene	Tetrachloroethene	127-18-4
Butadiene	1,3-Butadiene	106-99-0
Ethylene Oxide	Oxirane	75-21-8

ATMOSPHERIC LIFETIMES

Once a potentially hazardous air pollutant, like those under consideration in this report, 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.

Within any environmental compartment (e.g., a plume from an emission source, the troposphere, the total atmosphere, etc.), the total quantity (mass), Q, of an air toxic chemical can be accounted for. (In the preceding sentence, the term "environmental compartment" could be replaced by "atmospheric air parcel", "environmental reservoir", or "microenvironment": the concept is that of an identifiable region of the atmosphere or environment for which it is convenient to consider the fate of the air toxic.) The time rate of change for the total mass in the compartment, dQ/dt, is described by Equation (1).

$$dQ/dt = (P + I) - (R + O) = G - D \ , \qquad (1)$$

where P is the total mass production rate of the air toxic compound within the compartment, I is the total mass influx rate, R is the total mass removal rate, and O is the total mass outflow rate. G is the sum, P plus I, and represents the total growth rate. Similarly, D represents the total decay rate. All of the parameters on the right side of Equation (1) are expressed in units of mass time^{-1}.

The production rate term, P, would be important to consider in the case of a pollutant like formaldehyde, which is both directly emitted and is also formed in the troposphere by secondary photochemical reactions. The

influx rate term represents both additional source emissions and the inflow of material from other environmental compartments. Stratospheric intrusion of ozone into the troposphere is an example of the flux of a pollutant from one compartment into another. The removal rate and outflow terms include a variety of processes which bring about chemical reactions, photolytic decomposition, or the transport of the pollutant from one environmental compartment to another. The actual processes which should be included in these terms may vary considerably, depending upon the particular chemical involved and the environmental compartment being discussed. For air toxics, a wide variety of processes may need to be considered in describing the atmospheric fate, lifetime and distribution of these chemicals: the processes to be considered include dry deposition, washout and rainout, changes in phase distribution between aerosol-bound and gaseous pollutants, transport into and reaction within the stratosphere, etc.[3]

Equation (1) represents a dynamic situation in which the factors which cause the total mass loading of an air toxic to grow are counteracted by factors which cause the total mass to decay. The total quantity of a chemical in the compartment, and the resultant concentrations to which people may be exposed, can clearly be expected to change with time in response to variations in the growth and decay rates.

In describing the transit of an air toxic through the environment, it is useful to define several characteristic time parameters associated with Equation (1). The characteristic decay time may be defined as

$$\tau_D = Q/(R + O) = Q/D \quad . \tag{2}$$

Since Q has units of mass and D has units of mass time^{-1}, τ_D is expressed in units of time. Similarly, a characteristic growth time, τ_G, may be defined as Q/G.

τ_D is not necessarily a constant, however, since it is clearly a function of Q, and according to Equation (1), Q may change. In addition, the decay terms, R, O, and D, may be arbitrary functions of Q, making τ_D even more complex. Once a release scenario is defined, τ_D may be determined if all of the factors comprising D are known. Since Q is a function of time, τ_D will also vary with time as the chemical is removed from the compartment.

The concept of a characteristic decay time would be most useful if it were really a constant. This can be accomplished if one constrains Q to be invariant. D, which is some arbitrary function of Q, also becomes invariant, and Equation (2) becomes constant. Since Q is constant, the time rate of change of Q as given in Equation (1) must equal zero. This implies that a "steady state" condition is achieved where the growth rate is exactly equal to the decay rate, and τ_D equals τ_G. It is only under these "steady state" conditions that various authors have defined the "residence time", τ.[4-7]

$$\tau \equiv \tau_D \equiv \tau_G \,. \qquad (3)$$

The requirement of a "steady state" condition is both very stringent and, probably, unrealistic. Sampling measurements at remote locations have shown that the concentrations of many trace air toxics are slowly increasing with time.[8,9] These chemicals are clearly not at a "steady state" condition, although, in some cases, their growth may be so slow as to approximate "steady state".

It is not practical to depend upon a definition which is applicable only under unrealistic conditions, especially when the requirement in Equation (3) that the growth rate equal the decay rate is not reasonable for many air toxics. The emission rate of many of the potentially hazardous air pollutants can be highly variable, depending on production volumes and market pressures, accidental releases, or even the imposition of regulations. From an exposure assessment perspective, EPA is often

primarily concerned with how long an air toxic chemical is likely to remain in the air, once it has been released into the environment. A reasonable question to ask in any exposure assessment is, "Does the chemical persist in the atmosphere long enough for it to constitute an exposure threat?" These concerns lead to a focus on the decay rate as the atmospheric lifetime.

The characteristic decay time, τ_D, will also be a constant whenever D can be represented as a linear function of Q. If $D = k_D Q$, then Equation (3) simplifies to

$$\tau_D = 1/k_D \ . \qquad (4)$$

The assumption that the decay rate can be expressed, or at least approximated, as a linear function of Q is reasonable for many of the processes which remove air toxics from the atmosphere. Neglecting the input terms, Equation (1) can be rewritten as a series of first order terms which represent the processes which remove or transform the chemical. The time rate of change in Q is given by the equation,

$$-dQ/dt = k_{rxn} Q + k_{phot} Q + \ldots + k_{drydep} Q + k_{trans} Q \ , \qquad (5)$$

where the k's represent first-order removal rate constants for the various processes involved. Equation (5) can be summarized as

$$-dQ/Q = k_D \, dt \ , \qquad (6)$$

where k_D is the combined removal rate constant defined above.

Integrating from time t=0 to t=t, one finds

$$\ln Q_0 - \ln Q = k_D \, t \ , \qquad (7)$$

where Q_0 is the total mass of Q in the compartment at time = 0. Rearranging Equation (7), one finds

$$t = (\ln Q_0 - \ln Q)/ k_D \quad . \tag{8}$$

Letting $(\ln Q_0 - \ln Q) = 1$, Equation (8) becomes identical to Equation (4),

$$t = 1 / k_D \equiv \tau_D \, . \tag{9}$$

Throughout the rest of this report, the characteristic decay time, τ_D, will be referred to as the "atmospheric lifetime", and the subscript, D, will be dropped for convenience.

Clearly, the discussion of atmospheric lifetimes in this report focuses on the removal processes and ignores any additional influx of material. In this sense, τ represents the decay time for the air toxic in the environment and differs from other discussions[4-7] in the literature where τ is used to represent the "atmospheric residence time" or the "turn-over time" or the "average transit time" through the environment.

From Equations (8) and (9), it is clear that τ is the time at which an initial injection of a chemical has decayed until $Q = Q_0/e$, 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, one may calculate the half-life of a chemical by setting the mass at time t equal to one-half the starting mass. The half-life, $t_{1/2}$, then is given by

$$t_{1/2} = \ln 2/k_D \approx 0.693/k_D \approx 0.693\ \tau \quad . \tag{10}$$

Note also that, by combining Equations (5) and (9), one concludes

$$1/\tau_D = k_D = k_{rxn} + k_{phot} + \ldots = 1/\tau_{rxn} + 1/\tau_{phot} + \ldots , \qquad (11)$$

where τ_{rxn}, etc. are defined analogously to τ_D. The characteristic time constants for the various decay processes combine in the same way that parallel resistances combine in an electrical circuit. And like an electrical circuit, the total resistance (atmospheric lifetime) is dominated by the paths of least resistance, i.e., the processes with the shortest lifetimes. This has practical significance in assessing the atmospheric lifetime of an air toxic, because one need only consider the processes which are most effective at removing the chemical. It is safe to ignore processes which can be shown to be relatively slow, without wasting valuable time and effort in measuring those processes precisely.

In any environmental compartment, the average concentration of chemical A in the compartment is simply determined by dividing the total mass, Q, by the total volume, V, of the compartment.

$$[A] = Q/V, \qquad (12)$$

If chemical A is well mixed in the compartment (that is, the atmospheric lifetime of A in the compartment is long compared to the mixing time in the compartment), then any individual observation of [A] will be very close to the average value. Indeed, Junge[4] has demonstrated that, for a wide variety of chemicals which at least approximate a "steady state" condition, there appears to be an inverse relationship between the tropospheric residence time and the relative standard deviation, σ, of at least one year's worth of measurements taken at enough sites to represent a tropospheric average. The estimated lifetime is given by the empirically-derived equation

$$\tau = 0.14/\sigma \quad \text{years} . \qquad (13)$$

Obviously, Equation (13) is not applicable for non-steady state conditions, since the chemical concentration is continually changing during the sampling period under consideration.

Localized sources or sinks may cause the observations of the concentration of A, [A], at any particular site to vary widely and make σ be large. Such inhomogeneities in concentration are to be expected for many chemicals. For example, air toxics adsorbed on atmospheric aerosols are likely to be removed effectively by rain out and washout.[5] Since rain events are often highly localized phenomena, they will introduce inhomogeneities in the concentration of the aerosol-bound species.

These inhomogeneities do not invalidate any of the equations above. However, it may be useful to give careful consideration to the data sets, the environmental compartment, and the averaging times involved. Equations (5) through (12) require only that the removal processes be represented as first-order functions of Q (or [A]), not that chemical A be well-mixed in the compartment. Practically, however, thorough mixing can make the estimation of the removal rates easier, even though it is not mathematically necessary. In the real atmosphere, inhomogeneities are likely to arise from non-uniform mixing effects or from significant differences in the removal rates. To avoid difficulties in estimating the removal rates because of inhomogeneities, it may become useful to consider the fate of an air toxic as it traverses through a series of distinctive compartments.

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. The estimated concentrations of these trace species in the troposphere are listed in Table 3.

TABLE 3. ESTIMATED CONCENTRATIONS OF REACTIVE SPECIES IN THE LOWER TROPOSPHERE*

CHEMICAL NAME	CONCENTRATION molecule cm^{-3}	ppm
OH	1×10^{6}	4×10^{-8}
O_3	1×10^{12}	4×10^{-2}
O_2 ($^1\Delta_g$)	5×10^{8}	2×10^{-5}
O_2 ($^3\Sigma$)	7×10^{2}	3×10^{-11}
O (^3P)	5×10^{4}	2×10^{-9}
O (^1D)	2×10^{-1}	8×10^{-16}
HO_2	5×10^{9}	2×10^{-4}
RO_2	5×10^{9}	2×10^{-4}
NO_3	2×10^{8}	8×10^{-6}

* Concentrations are taken from References 10-13 and from sources cited therein.

For many air pollutants, the predominant tropospheric reaction is with the hydroxyl radical, OH, despite its relatively low concentration.[3,10,13] Reactions with OH may occur via abstraction, addition, or both. For chemicals with isolated double bonds, a significant removal pathway may occur via reaction with ozone.[10,14] For a few chemicals, reaction with the NO_3 radical also appears to be significant.[13,15] The other reactive species do not play a major role in removing air pollutants from the troposphere, although in some cases the actual removal mechanism may be in doubt (e.g., carbon tetrachloride).

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. They are consistently present in the atmosphere during daylight hours, however, because their concentration results from the dynamic balance between the photochemical processes which produce them and the reactions which remove them.[16] 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[13] which may be applied to the problem of estimating atmospheric lifetimes. It should be relatively simple, therefore, to apply Equation (9) to chemical A and estimate the atmospheric lifetime via

$$\tau_A = 1/k_D = 1/(k_{OH}\,[OH]) \quad . \tag{14}$$

Unfortunately, it is not always simple to assign values to k_{OH} and the hydroxyl radical concentration, [OH]. The rate constant is a function of temperature, and the choice of the value to use can sometimes be difficult, since the temperature can change with the time of day, the season, the latitude, how high in the troposphere the reactions are taking place, etc. In addition, the [OH] depends upon a balance of competing chemical reactions. Some of the reactions are photochemical in nature, while others depend upon both the temperature and the concentrations of the many other chemicals involved. Profiles of [OH] in the troposphere can, therefore, be expected to vary as a function of light intensity, temperature, latitude, altitude, the presence of pollutants, whether the air mass is over land or water, etc.[16]

The difficulties in estimating k_{OH} and [OH] are not really so great as one may infer from the tone of the previous paragraph. As physical phenomena, both the temperature and the OH concentration can be described as continuous, albeit highly variable, functions of location across any environmental compartment, e.g. the troposphere. The temperature dependent function, k_{OH}, and the decay rate constant, $k_D = (k_{OH}\,[OH])$, are also

continuous functions. The mean value theorem of calculus[17] states that the integrated value of a continuous function across a finite region can be represented as the product of some average value of the function times the size of the finite region. This means that it is not necessary to describe k_{OH} and [OH] at all locations throughout the environmental compartment. Only reasonable estimates of the average values for k_{OH} and [OH] are necessary to calculate the decay rate and the subsequent atmospheric lifetime. As one attempts to determine the "mean values" to use in Equation (14), it is useful to consider the structure of the atmosphere and a pollutant's transport through it.

Atmospheric Mixing and OH Removal

The troposphere is that portion of the atmosphere nearest the earth. It contains about 75-80% of the mass of the atmosphere and extends from the surface to a height of about 8 to 18 km, depending upon the latitude and the season.[18] The name, troposphere, derives from the Greek word "tropos" which means "turning". The troposphere is a well-mixed region of continuous turbulence. Above the troposphere is the stratosphere. This portion of the atmosphere extends roughly from 11 km to 50 km. It is a region with little turbulence or mixing. The name derives from the Latin "stratum" meaning "layer". Most of the remaining 20-25% of the atmosphere's mass is in this zone. The characteristic feature which distinguishes these regions is the manner in which temperature varies with height. In the troposphere, the temperature normally decreases linearly with increasing altitude, while in the stratosphere, the temperature is essentially constant or increases with height. The boundary between these two zones is called the tropopause.

The troposphere itself is often described as being divided into layers. The planetary boundary layer extends from the surface to a few thousand meters altitude. Within this zone, frictional forces between the atmosphere and the earth's surface strongly influence mixing and transport.[19] Mixing within the boundary layer can be very efficient and

intense: under normal meteorological daytime conditions, the boundary layer can be considered to be well-mixed within a few hours. At the bottom of the planetary boundary layer is a layer of essentially constant shearing stress, called the surface layer. Frictional forces between wind fields and the earth are greatest in this layer. It extends roughly from 0 to 30-100 m[5,19]. During inversions, winds in this layer tend to die out because of frictional losses of energy to the earth's surface. Because man's activities and emissions of air pollutants occur primarily in the surface layer and boundary layer, it is important to understand the transport and fate of air toxics in these reservoirs.

The third layer in the troposphere is called the geostrophic layer, or the free troposphere.[19] It extends from from the top of the boundary layer to the top of the troposphere. Winds in this region are not strongly influenced by the earth's surface, and mixing in the free troposphere is, in general, less efficient than mixing within the boundary layer.[19] Exchange between the boundary layer and the free troposphere can also be somewhat restricted. Slinn[5] has estimated that the time constant for vertical mixing in the troposphere is about 1 week. Horizontal mixing (north-south mixing across latitudes) is estimated to have a period of about 1 year.[5] Exchange between the Northern and Southern Hemispheres has an estimated time constant of 1.2 years.[9]

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.[16] 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. As Altshuller[20] points out, "For compounds with lifetimes substantially less than one year, seasonal variability in OH concentration and temperature is important." It may be necessary, therefore, to consider the temperature and [OH] in each of the tropospheric layers as the chemical diffuses.

Under normal meteorological conditions, the surface layer exists as a distinctive atmospheric reservoir only during nocturnal inversions. Since the hydroxyl radical is formed from photochemical processes, its nighttime concentration effectively drops to zero, and no removal by hydroxyl radical takes place within the nocturnal surface layer. This means that a hazardous chemical, which may be rapidly removed by OH during the daytime, may persist all night long when trapped in this layer. Because the mixing height is so low and the resultant mixing volume is so small, emissions of air toxics into this layer often result in the highest observed concentration levels. Singh et al.[21,22] have documented numerous occasions when diurnal profiles of hazardous air pollutants reached a maximum at night and a minimum in the early afternoon.

After sunrise, heating of the air at the earth's surface begins to form convective currents which penetrate the nocturnal inversion and establish a well-mixed layer averaging about 1 km in depth[5] throughout the daytime period. Because sunlight must be present for thorough mixing to occur, conditions are also conducive for the photochemical formation of OH. Since decay of the air toxics by OH occurs only during the daytime, the appropriate temperature to use in determining the rate constant is the daytime average. Air toxics which mix into this layer during the day, remain at night and are transported and mixed by the normal meteorological processes. Once again, chemical removal by OH at night can be considered to be non-existent.

Stable chemicals injected into the boundary layer will subsequently mix into the free troposphere. Mixing is not uniform in all directions, however. Vertical mixing has a time constant of about 1 week.[5] Air toxics with lifetimes longer than a few weeks can therefore be considered to be thoroughly mixed throughout the troposphere in the vertical direction. Horizontal mixing, specifically north-south mixing across latitudes, has a time constant of about one year.[5] A similar time constant applies to the exchange of air in the troposphere between northern and southern hemispheres.[9] Air toxics with lifetimes longer than several years become distributed globally.

While the stratosphere is quite stable, with inefficient vertical mixing, there is some exchange of air between the troposphere and the lower stratosphere. This exchange can transport extremely stable air toxic chemicals into the stratosphere where a wide range of chemical processes, other than reaction with OH, may occur. Junge[23] estimates that the time constant for exchange from the troposphere to the stratosphere is 4 years, while exchange from the stratosphere to the troposphere has a time constant of 1 year. The difference in time constants arises from the fact that the troposphere contains roughly four times as much mass as does the stratosphere. For extremely long-lived air toxics, stratospheric removal processes may need to be characterized.

The previous discussions suggest that the atmosphere can be split into several distinctive reservoirs which should be considered when estimating chemical removal by OH. The first reservoir is the boundary layer. The [OH] is that for a polluted air mass at or near the surface, and the temperature of choice is a daytime average. The second reservoir is the vertically well-mixed troposphere. The choices for [OH] and temperature are dependent upon the latitude selected. The choice of temperature is once again influenced by the fact that OH removal occurs only during the daytime, but since the full troposphere is being considered the impact is much less. The third reservoir is the hemispheric or global troposphere. Here concentrations and temperatures should be

averaged over both altitudes and latitudes. Finally, transfer into the stratosphere may need to be included for very stable pollutants.

Selection of Temperatures

The choice of temperature to use in each of the domains to be considered depends upon many factors. Obviously, temperatures vary with time of day, from day to day, from location to location, from season to season. Any choice of any single temperature to represent an average in the various reservoirs will require some compromises. For specific chemicals or release scenarios, the fate may need to be determined on a case-by-case basis. This paper will attempt to establish some starting values which may reasonably represent annual averages across the United States. Because Alaska and Hawaii may represent significantly different climates, the following discussion will focus only on the contiguous forty-eight states.

The average temperature is strongly influenced by the latitude which is selected to represent the nation. A variety of approaches can be used to estimate the appropriate latitude. The middle of the latitudes for the northernmost and southernmost locations[24] in the contiguous forty-eight states is around 37° N. The center of the total U. S. population in the 1980 census was found to be at 38° 8' N.[25] Since it is reasonable to expect that the location of air toxics emissions may roughly correlate with the location of the population, a choice between the 37th and 38th parallels seems reasonable.

The U.S. Standard Atmosphere Supplements, 1966[26] uses long-term averages of temperature and pressure observations to describe profiles for the atmosphere at 30° N and 45° N during the months of January and July. January and July normally represent the extremes in temperature at any location. Averaging those two monthly periods and interpolating across latitudes, one can derive a reasonable, observation-based approximation of the annual average tropospheric conditions for the contiguous

United States. The definitions of standard atmospheres suggest an average sea-level temperature of 289 K at the mid-latitude of 37.5° N, and an average lapse rate of about -4.6 K per kilometer of height. If one assumes that the continental land mass has approximately an altitude of 500 meters above sea level, then an annual mean temperature of about 286.7 K is estimated. This value is very close to the mean temperature of 286.9 K estimated for the same latitude from a regression fit of thirty-year averages of the annual mean temperature[25] for 58 continental U. S. cities located between 30° N and 45° N latitude. The estimate is also very close to the average temperature derived for the U. S. of 287.0 K, which is obtained by weighting the ambient temperature by the number of vehicular miles traveled at that temperature.[27] If vehicular use is indicative of human activity and, therefore, of air toxic emissions, then it is reasonable that the estimates should agree.

For use with estimates of OH removal, one is not interested in the mean temperature at the surface, but rather in the average daytime temperature across the mixing layer. A regression fit of the thirty-year averages of the normal daily high temperatures for the same 58 cities mentioned above suggests that the annual average high temperature is 5.9 K higher than the mean at this latitude. If the average daytime temperature is taken to be mid-way between the annual mean and the annual high temperature, then the estimated temperature must be increased by about 2.9° to account for the effect of daylight. But the mixing layer is about 1 km thick and the descriptions of the standard atmospheres suggest an average lapse rate of about -4.6° per kilometer, so the estimated temperature must also be decreased by about 2.3 K. The net result is that the estimated mixing layer temperature for the contiguous forty-eight States is approximately 287.5 K. This is somewhat lower than the values of 291-293 K suggested by Heicklen.[28,29]

The second domain of interest is the vertically mixed troposphere at the same latitude. To estimate this value, the temperature profiles from the four standard atmospheres (two seasons at two latitudes) were

weighted at each altitude by the density of the air and averaged. The temperature values were weighted by density to account for the fact that, as altitude increases both the temperature and the mass of gas at that temperature decrease. The four calculated temperatures were averaged to yield a value at 37.5° N of 263 K.

The third reservoir of interest is the global troposphere. Altshuller[20] states that a temperature of 265 K is very close to the average annual tropospheric temperature weighted for distribution of species with altitude, and that it corresponds within a few degrees to the annual 600-mb, 4-km altitude value derived by two methods, involving averaging 600-mb temperatures over latitudes or over the monthly average temperature. The density-weighted temperature profiles for the standard atmospheres[26] at 45° N, mid-way between the equator and the pole, yield an average tropospheric temperature of 260 K. The density-weighted standard atmosphere based on traditional definitions also yields an average tropospheric temperature of 260 K.[30]

Activation energies for many OH reactions seem to fall within the range of -1000 cal $mole^{-1}$ to +4000 cal $mole^{-1}$ (cf. Reference 13). With this range of activation energies, the rate constant is not likely to vary more than a factor of 3 across the range from room temperature to 260 K. Across an even smaller temperature range, the difference in rate constant is proportionately small, e.g., from 287.5 K to 293 K, the rate constant will vary not more than 15%.

Selection of Hydroxyl Radical Concentrations.

Over the years, a wide variety of attempts have been made to characterize the hydroxyl radical concentration in the troposphere. Unfortunately, the modeling efforts have often disagreed and direct experimental measurement is still difficult. The various modeling approaches have predicted average [OH] in the troposphere across a widely divergent range.[16,31] The instrumental measurements are not yet sufficiently

sensitive to measure the ambient OH concentration routinely and accurately, although values in excess of several million radicals per cubic centimeter have been reported in some polluted situations.[32]

The concentration of OH in the boundary layer has been estimated experimentally by using both direct and indirect measurements. The reported values by direct measurement of [OH] vary widely, ranging from 0.3 to 150 x 10^6 molecules cm^{-3}. Problems with sensitivity, calibration, and interferences pose serious questions about the accuracy of the experimental observations, especially the very large values determined using laser induced fluorescence (LIF). A set of measurements does seem to be emerging, however, which is consistent within itself and which also agrees with the most comprehensive of current tropospheric models. Perner et al. used a long path optical absorbtion technique to measure OH in the boundary layer at about 51° N in Germany. Their early measurements[33] usually remained below their detection limit of 4 x 10^6, with occasional excursions up to 7 x 10^6 molecules cm^{-3}. More recent measurements with an improved instrument[32] have yielded values of 0.8 to 4 x 10^6, with a simple average of 1.9 x 10^6 molecules cm^{-3}. The measurements by Perner et al. have been made between April and October in different years. Given the scatter in the data, there is no discernable effect of season upon the OH concentration. Campbell et al. monitor the oxidation of isotopically labeled CO to deduce the concentration of OH.[34] They report four values (2.0, 3.3, 3.4, 3.4 x 10^6) for [OH] in non-pristine air over the North American continent. Campbell's data from New Zealand show lower [OH], which is to be expected in a comparatively unpolluted site dominated by a marine environment.[16] D. Davis et al.[35,36] have reported [OH] using an LIF technique. Most of their measurements have been made from an aircraft at high altitudes, but one report[36] from an airplane at the top of the boundary layer gave [OH] of 8 to 11 x 10^6. Wang and L. I. Davis, who first reported using LIF techniques to measure atmospheric concentrations of OH,[37] have recently made considerable advances in overcoming the problems inherent in the method. Their latest measurements at ground level in Dearborn, MI show an average [OH] of

1.9×10^6 for two days, almost a year apart.[38] Hjorth et al.[39] estimated [OH] by collecting bag samples of ambient air at a semi-rural site in Italy, then adding isotopically labeled CO, and irradiating the bags with natural sunlight. They monitored the oxidation rate using Fourier transform infrared spectroscopy and, based upon thirteen experiments from May to July, deduced an average OH concentration of 2×10^6 molecules cm^{-3}.

There have been several estimates of [OH] using measurements of other species, from which the [OH] can be deduced. Calvert[40] used the rate of disappearance of a variety of alkanes and alkenes relative to acetylene to estimate the OH concentration in the morning hours of November 5, 1973, in Los Angeles as $2.5 \pm 2.0 \times 10^6$ molecules cm^{-3}. Singh et al.[41] used the same technique on more recent data from the Los Angeles area to estimate a mean OH daytime concentration of $2.9 \pm 1.9 \times 10^6$ molecules cm^{-3} during the months of June through September. In a subsequent study, Singh and coworkers[22,42] applied the technique to a series of aromatic species to estimate a lower limit for the OH concentration in the Los Angeles area in February. The calculated values of [OH] represented an average for the time period from 7:30 a.m. to 1:30 p.m. and resulted in a postulated OH concentration of $2.6 \pm 0.6 \times 10^6$ molecules cm^{-3}. Similarly, Anderson[43] used the rate of disappearance of a light alkene relative to acetylene to deduce the OH concentrations present during an experiment in November and December in Denver. The estimated OH concentrations ranged from 0.6 to 6×10^6 molecules cm^{-3}, with an average of 1.8×10^6.

Several modeling efforts have also attempted to predict OH concentrations throughout the troposphere. Two of the more comprehensive models are those by Logan et al.[16] and by Crutzen and Fishman.[44] The Logan et al. model predicts that diurnally-averaged (24 hr.) concentrations of OH at the continental land surface, in the Northern Hemisphere across the latitudes of the continental U.S., should be about $0.8\text{-}0.9 \times 10^6$ molecules cm^{-3} annually. (See Figures 18, 27a, and 27b of the paper, Reference 16.) Summertime diurnally-averaged concentrations at the

surface are probably near 1.3×10^6. The Crutzen and Fishman model suggests an annual average surface concentration of about $0.5\text{-}0.6 \times 10^6$ across the same latitudes. Crutzen and Fishman predict summertime average concentrations of about 1.4×10^6 molecules cm^{-3}.

Assuming equal periods of daylight and darkness, and diurnal concentration profiles similar to those predicted by Logan, one finds that the average concentration for a 24-hour day should be a factor of 2 to 4 less than the daytime maximum values. The experimentally measured (or derived) concentrations suggest that the average daytime [OH] in the boundary layer should be about 2 to 3×10^6 molecules cm^{-3}. The daytime maximum in concentration can be even larger. A reasonable 24-hr. average for [OH] in the boundary layer, based upon experimental data, therefore, is 1×10^6 molecules cm^{-3}. This estimate is consistent with current models in that it exceeds, only slightly, the model predictions of Logan et al. and of Crutzen and Fishman for an annual average concentration at the earth's surface over the continental U.S.

The average OH concentration in the vertically-mixed troposphere at about 38° N is less clear. While the models of Logan et al. and Crutzen and Fishman predict roughly the same surface level concentrations of OH, the vertical profiles differ remarkably. In general, the Logan model predicts an [OH] maximum at an altitude of 2 to 6 km, while the Crutzen and Fishman model indicates a maximum concentration at the surface, dropping off to an average concentration of around 0.1×10^6 at altitudes of 6 to 10 km. The choice of which vertical profile to use could be made easier by inspection of the measured values of [OH] at altitude. The experimental data on [OH] at various altitudes are highly variable, probably because of instrumental difficulties. A variety of tropospheric measurements, taken between 30° N and 45° N, are listed in Table 4.

TABLE 4. EXPERIMENTALLY MEASURED OH CONCENTRATIONS IN THE FREE TROPOSPHERE

Latitude °N	Altitude km	[OH] 10^6 molec cm^{-3}	Analytical Method	Reference
37	6	1.9	Spin Trap	Watanabe[45]
37	6	2.1	Spin Trap	Watanabe[45]
37	6	1.5	Spin Trap	Watanabe[45]
37	6	3.5	Spin Trap	Watanabe[45]
~ 37	6.9	3.3	LIF	Davis[36]
32	7	< 2	LIF	Davis[35]
32	7	3.5 ± 2.3	LIF	Davis[35]
~ 37	10	0 ± 5	LIF	Wang[46]
~ 37	10	1 ± 3	LIF	Wang[46]
34	10	20 ± 6	LIF	Wang[46]
37	10	< .5	Spin Trap	Watanabe[45]
37	10	< .5	Spin Trap	Watanabe[45]
37	10	0.8	Spin Trap	Watanabe[45]
37	10	1.9	Spin Trap	Watanabe[45]
34	10.7	10 ± 4	LIF	Wang[46]
34	11.9	2 ± .5	LIF	Wang[46]

The experimental data of Watanabe et al.[45] are self-consistent, suggesting a value of 2 to 3 x 10^6 at 6 km and a somewhat lower value at 10 km. The results obtained by laser-induced fluorescence[35,36,46] are more scattered, but they do suggest that concentrations in excess of 1 x 10^6 are present. Clearly, the experimental data agree better with the model predictions of Logan et al. than with those of Crutzen and Fishman. From the vertical profiles of OH concentration in the Logan paper, one may estimate a diurnally averaged [OH] of around 1 x 10^6 molecules cm^{-3} for the continental U. S.

The annual average [OH] for the global troposphere and/or for the Northern and Southern Hemispheres has been estimated by several authors. Crutzen and Fishman estimate an average [OH] in the Northern Hemisphere (NH) of 0.25×10^6. Logan et al. estimate a value of 1×10^6 for the Northern Hemisphere. Other researchers have attempted to use atmospheric distributions of man-made pollutants to estimate the global concentration of OH through a tropospheric budget model. Because production quantities of synthetic organic pollutants are often reasonably well known, their emissions can be balanced against the observed tropospheric distributions to estimate their tropospheric lifetime. Since the primary removal mechanism for many of these chemicals is from reaction with OH, the lifetime calculated from source strengths may be used to deduce an average tropospheric OH concentration.

Several authors have deduced average global and hemispheric OH concentrations from the distribution of methyl chloroform (1,1,1-trichloroethane). Singh[47,48] was the first to apply a global budget estimate to methyl chloroform. He calculated Northern Hemispheric and global values of OH concentration as $0.21 - 0.31 \times 10^6$ and $0.33 - 0.51 \times 10^6$, respectively. Neely and Plonka[49], from Dow Chemical Co., used a smaller emissions budget in a similar tropospheric model to estimate NH and global OH concentrations of 0.48 and 1.1×10^6. Unfortunately, these investigators used a rate constant which was subsequently found to be in error.[50,51] Use of the correct rate constant requires that all the estimates of [OH] be increased by a factor of 1.3 to 2.[16] Singh has subsequently reapplied the model with the correct rate constant[9] and has deduced a global average [OH] of 0.6×10^6 molecules cm^{-3} Using four other man-made chemicals, Singh estimates the global average [OH] of 0.25, 0.37, 0.51 and 0.52×10^6. Logan et al.[16] also applied their calculated OH profiles to the atmospheric accumulation of methyl chloroform. They concluded that the data in both hemispheres fit their profiles to within a factor of two. In the NH, the best fit appeared to be at the lower limit value, implying an average [OH] of 0.5×10^6. Also, Volz et al.[51] recently deduced an average tropospheric OH concentration

of 0.65×10^6 molecule cm^{-3} from consideration of the oxidation of ^{14}CO. A reasonable estimate of the hemispheric or global [OH], therefore, seems to be around 0.5×10^6 molecules cm^{-3}.

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 in each compartment for continental air at around 37.5° N latitude are shown in Table 5. 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.

TABLE 5. SELECTED AVERAGE VALUES OF TEMPERATURE AND [OH] IN THREE REGIMES OF THE TROPOSPHERE AT 37.5° N LATITUDE

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

REACTION WITH OTHER SPECIES

Air toxic pollutants may also react with other chemical species in the atmosphere, primarily O_3 and NO_3. Ozone reactions are an important atmospheric removal pathway for alkenes. The kinetics and mechanisms of ozone reactions under atmospheric conditions have recently been reviewed by Atkinson and Carter.[14] NO_3 radicals may react with a variety of compounds.[13,15] Data on individual chemicals must be consulted to determine the relative importance of these removal processes. In some cases, reaction with other pollutants, like nitric acid, or stratospheric reactants may need to be considered.

OTHER REMOVAL PROCESSES

Air toxics may also be removed from the atmosphere by a variety of other processes. Previous papers[3,23] have discussed these processes in detail, so they will only be described briefly here.

Solar radiation in the troposphere may be absorbed by specific air toxics, causing them to degrade. This process of photolytic degradation is likely to be important only for those chemicals which absorb strongly within the solar radiation region. This limits the applicable compounds to those possessing a strongly absorbing chromophore, like carbonyl compounds, conjugated alkenes, alkyl nitrites, nitro compounds, etc.

Air toxics may also interact with objects at the earth's surface and be adsorbed and removed through a process called dry deposition. The deposition velocity, which is expressed as the speed (length $time^{-1}$) at which chemicals deposit, has been determined for only a few gases. Except for a few reactive gases, the available data[53] suggest that this removal route is not very effective for gas-phase chemicals. Two of the chemicals under consideration, carbon tetrachloride and tetrachloroethene, have had dry deposition velocities measured or estimated.[3,54] In both cases, the deposition rate was so slow that lifetimes in excess of

25 years are estimated from this removal mechanism. Dry deposition is an important process for other pollutants, like polychlorinated biphenyls, and can constitute a major input source for such pollutants into lakes and streams.[55]

Toxic pollutants which are emitted as gases may adsorb on small airborne particles, or aerosols, in the atmosphere. Adsorption does not immediately transform an air toxic or remove it from the air medium. The interaction of the air toxic with the surface of the particle may, however, change the nature of the chemical and photolytic removal processes which affect the pollutant. Consideration of the phase distribution, i.e., the quantity of the air toxic in the vapor phase compared to the aerosol-bound phase, can be important in risk assessment, however, since the route of exposure and possible uptake of the pollutant by plants and animals may be considerably different for the two phases. In addition, the average tropospheric lifetime of an ambient aerosol particle is approximately seven days.[23] Any air toxic adsorbed on aerosol particles will then have only a short lifetime in the atmosphere before it enters the soil or water media.

Finally, gases which are water soluble may dissolve into water droplets present in the atmosphere in the form of rain, snow, fog, or aqueous aerosols. Deposition of these droplets may remove the pollutant from the air environment. While the processes of rainout and washout are effective for removing atmospheric particles, they are not generally considered to be effective for gaseous pollutants[23,56] because of subsequent evaporation and revolatilization of the pollutant.[3] This process could be important, however, if transformations occurred rapidly enough in the aqueous phase for the droplets to constitute a sink for the air toxic.

SECTION 4

ATMOSPHERIC PERSISTENCE OF EIGHT AIR TOXICS

METHYLENE CHLORIDE

Methylene chloride (dichloromethane) is a high volume, commonly used solvent which is a mutagen and suspect carcinogen.[22] It is used as a degreaser, cleaner, paint solvent, aerosol propellant, laboratory solvent, etc. Most of its uses result in large and rapid losses to the atmosphere.[20] The chemical is of anthropogenic origin, with no known natural sources.[22] Its background concentration at 40° N is about 50 parts per trillion (ppt).[22] The global average background concentration is 29 ppt, with the concentration in the Southern Hemisphere being only about one-half that in the Northern Hemisphere.[9] Its concentration in urban areas of the U. S. is highly variable,[57] 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.[57]

Methylene chloride reacts with OH radicals in the atmosphere at a moderate rate. Atkinson[13] has recently reviewed the literature on the reaction of OH and methylene chloride. The rates have been measured by at least five different investigators and are in reasonably good agreement. Atkinson recommends the modified Arrhenius expression

$$k(CH_2Cl_2) = 8.54 \times 10^{-18}\ T^2 \exp(-500/T)\ cm^3\ molecule^{-1}\ s^{-1} \qquad (15)$$

for estimating the hydroxyl radical rate constant. Recommended values of the rate constant at various relevant temperatures are tabulated below, together with estimates of the atmospheric lifetime due to OH reactions.

TABLE 6. METHYLENE CHLORIDE REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	OH Reaction Rate Constant 10^{-14} cm^3 $molec^{-1}$ s^{-1}	Assumed [OH] 10^6 molec cm^{-3}	Lifetime days
288	12.5	1.0	93
263	8.8	1.0	131
260	8.4	0.5	274

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. Table 6 lists three choices of atmospheric lifetime based upon hydroxyl radical, however. The three choices reflect the three domains described previously. (See Table 5.) The first line, with the temperature of 288 K, represents an average boundary layer condition. The second line lists conditions in the representative, vertically well-mixed troposphere. The last estimate is for the hemispheric or global troposphere. Since the first estimate of 93 days exceeds the applicable range for the boundary layer domain, that value must be neglected. The estimate of 131 days, however, is within the applicable range for the vertically well-mixed troposphere (i.e., 3 weeks to 5 months) so that value is the one selected as the estimate of the atmospheric lifetime. This means that, on average, a quantity of

methylene chloride emitted into the atmosphere above the continental U.S. will persist in the troposphere for several months. Even after four months, 37% of the emitted material will still remain in the atmosphere. The estimated half life is about 69% of the lifetime quoted above, or about 91 days.

Singh et al.[9] recently used a two-box model to estimate the global lifetime of methylene chloride. The model uses the background concentration, the distribution of the chemical between the Northern and Southern Hemispheres, and estimates of production and release to calculate a global lifetime. His data suggested a lifetime of 0.9 ± 0.3 years, a value two and one-half times as large as that calculated above. Considering the uncertainties in the emission strength, contributions from Europe and elsewhere, and the scatter in the experimental data, the agreement is not bad. It is reassuring that the global model lifetime exceeds the estimate from hydroxyl removal alone, since that fact suggests that no major loss mechanism has been overlooked. It seems, therefore, that the estimate of 131 days is reasonable.

CHLOROFORM

Chloroform (trichloromethane) is a mutagen and suspect carcinogen which is ubiquitously present in the atmosphere. It has received much attention recently because of its high concentrations in chlorinated drinking water.[22] Unit risk numbers, which estimate the probability of death due to cancer arising from a lifetime of exposure to the chemical, have been developed for chloroform.[20]

The chemical is manufactured for use as a solvent, a cleaning agent,[58] and as an intermediate in the manufacture of chlorofluorocarbon-22.[22] Geochemical background concentrations are around 16 ppt, with slightly higher values in the Northern Hemisphere.[9] Data on chloroform reported between 1970 and 1980 were recently critically evaluated.[57]

While the results were highly variable and much of the data taken with Tenax had to be rejected because it consistently reported concentrations below the known geochemical background levels, an interesting concentration pattern did emerge. Rural and remote areas of the U.S. had concentrations near 40 ppt; urban and suburban areas had concentrations around 270 ppt; and source dominated areas had still larger concentrations. More recent measurements[22] have reported average urban concentrations of 60 to 250 ppt, with maximum values being many times higher. World wide emissions of chloroform do not seem to account for the levels observed: the sources of chloroform, both in urban and remote areas, appear to be ill defined.[22]

The reaction rate constant for chloroform with OH has been reported by at least three investigators, and the data are in excellent agreement.[13] Recommended values of the OH rate constant are given in Table 7.

TABLE 7. CHLOROFORM REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	OH Reaction Rate Constant 10^{-14} cm^3 $molec^{-1}$ s^{-1}	Assumed [OH] 10^6 molec cm^{-3}	Lifetime days
288	9.08	1.0	127
263	6.41	1.0	181
260	6.13	0.5	378

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. None of the estimated lifetimes listed in Table 7 fall within the applicable periods for the three domains. It is best, therefore, to express the lifetime as a range. Because the lifetime appears to fall most appropriately between the applicable periods for the vertically-mixed troposphere and the hemispheric or global troposphere,

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 a suspect carcinogen[20] which is nearly uniformly distributed around the globe.[1] 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.

Carbon tetrachloride has seen wide usage as a solvent and as an intermediate in the production of other compounds.[58] Large natural sources of carbon tetrachloride have been postulated, but none have been found.[22] Indeed, the most comprehensive analyses of the carbon tetrachloride budget have concluded that all of the ambient concentrations can easily be accounted for from man-made production and emissions.[22]

The measurement of carbon tetrachloride in the ambient atmosphere has proven difficult over the years, with investigators reporting significantly different values.[57] Since the detailed efforts of the Atmospheric Lifetime Experiment,[1,59] however, a consistent set of data on carbon tetrachloride has begun to emerge. Many of the data currently in the literature involved the use of Tenax, which seems to have severe problems in collecting this chemical. Since there are no known large sinks for this chemical, any data set which consistently reports concentrations significantly below the geochemical background concentrations must be considered suspect.[57] The Atmospheric Lifetime Experiment[1] established the geochemical background concentrations in 1978-1981 to be around 118 ppt. Concentrations of the chemical were found to be increasing at about 2 ppt per year. Urban measurements, reported by investigators whose data are consistent with the geochemical background, show that urban concentrations are a factor of two to three higher than background.

Maximum excursions in urban areas can be in excess of 1000 ppt.[57] A lifetime cancer risk number for carbon tetrachloride has been published.[20]

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.[3,13] In the troposphere, photolytic decomposition and other chemical removal processes seem to be equally slow. An inferred dry deposition velocity has been used to suggest a lifetime in excess of 25 years.[3] With such a long tropospheric lifetime, stratospheric removal processes must be considered. In addition to possible chemical reactions and photolysis in the stratosphere, a number of removal processes have been postulated including 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.[1] There are no known removal processes which can be used to estimate a lifetime of carbon tetrachloride reliably.

Two modeling approaches were applied to the carbon tetrachloride data set of the Atmospheric Lifetime Experiment.[1] 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. The material is a mutagen and suspected carcinogen, and a lifetime unit risk

number has been developed. Ethylene dichloride (EDC) is primarily used as an intermediate in the production of other chemicals, particularly vinyl chloride monomer. Other minor uses include use as a gasoline additive and as a solvent.[20,22,58]

Singh et al.[9] report a global background concentration of EDC of 25 ppt in December 1981. The Northern Hemisphere average was 37 ppt, very close to the value of 40 ppt calculated by Altshuller from production values. A critical assessment and compilation of data on EDC for values reported from 1970-1980 gave a median urban/suburban concentration of 120 ppt.[57] Those data were strongly influenced, however, by a large data set from a single investigator in which all of the values, except two, were below the detection limit. Actual urban concentrations may be even higher, and are likely strongly influenced by local users.

The reaction rate of EDC with OH radicals has not been so thoroughly investigated as the reactions of many other chlorinated alkanes. In fact, Atkinson[13] lists only one rate constant, by Howard and Evenson[60], and does not give an activation energy. There is, however, one additional literature value for the rate constant which Atkinson does not mention. Snelson et al.[61] have also reported a value for the rate constant which is a factor of 3 below the value of Howard and Evenson. Both research groups measured the rate constant at room temperature (about 298 K), and no measurement of the activation energy of the reaction was made. The measurement by Howard and Evenson was made in a relatively simple, or "clean", kinetic system, while Snelson et al. used a much more complex photochemical arrangement. Snelson et al. argue that their method, with oxygen and nitrogen also present in the reactor, was more representative of actual tropospheric conditions than bimolecular reaction studies. That is not true in this case. The reaction proceeds via abstraction, and there will not be a significant "pressure effect", as there is for an addition reaction. (See, for example, References 13 and 62.) The addition of other reactive gases, in this instance, only makes the reaction scheme more complex and makes extraction of kinetic

rate data more difficult. Indeed, Snelson et al. had to assume a reaction mechanism and deduce an effective chain length without comprehensive product analysis. Such an assumption is always precarious, but it is especially precarious when it involves photolysis of chlorinated species. In any case, a pressure effect should increase the reaction rate (by making any addition mechanism more effective), but the rate constant calculated by Snelson et al. is actually lower than that measured at low pressure by Howard and Evenson. Snelson et al. report that they had difficulty separating the EDC effects from the background reactivity, and they actually estimated an upper limit to the rate constant which was almost a factor of 4.5 larger than their "most probable" value. Snelson et al. demonstrate little confidence in their own value of 6.5×10^{-14} cm^3 $molecule^{-1}$ sec^{-1} since they selected a value of 19.1×10^{-14} cm^3 $molecule^{-1}$ sec^{-1} as the 298 K rate constant for use in calculating the tropospheric residence time of EDC. They arrived at that value by averaging their value of 6.5×10^{-14} cm^3 $molecule^{-1}$ sec^{-1} with that of Howard and Evenson, weighting each by its probable accuracy. Obviously, the Howard and Evenson value of 22×10^{-14} cm^3 $molecule^{-1}$ sec^{-1} is relatively unchanged.

The work by Howard and Evenson, on the other hand, is more straightforward, and their measured value of $22.0 \pm 5.0 \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1} is much more consistent with the reaction rates of similar chlorinated ethanes than is the value of Snelson et al.. Table 8 below shows the reported room temperature rate constants for ethane and a number of chlorinated ethanes, including EDC. It seems clear that a value of 22.0×10^{-14} cm^3 $molecule^{-1}$ sec^{-1} is much more consistent with the other measured values than is a value of 6.5×10^{-14} cm^3 $molecule^{-1}$ sec^{-1}.

Once a room temperature rate constant is selected from the experimental data, one still needs to estimate the rate constant at cooler temperatures in order to estimate the lifetime. In estimating the lifetime of EDC, Altshuller[20] chose a temperature of 265 K, stating that it is very close to the average annual tropospheric temperature weighted

for distribution of species with altitude. He then uses rates at this temperature to represent an average tropospheric reaction rate. When the rate constant at 265 K is not known, Altshuller estimates it by dividing

TABLE 8. HYDROXYL RADICAL RATE CONSTANTS FOR ETHANE AND SEVERAL CHLORINATED ETHANES

Chemical Name	Rate Constant Units of 10^{-14} cm^3 $molecule^{-1}$ sec^{-1}
CH_3CH_3	27[13]
CH_3CH_2Cl	39[60], 39[63], 44[61]
CH_3CHCl_2	26[60]
CH_2ClCH_2Cl (EDC)	22[60], 6.5[61]
$CH_2ClCHCl_2$	33[13], 33[60]

the 298 K rate constant by 1.75. This is equivalent to an activation energy of 2.66 kcal mol^{-1}. This relationship is strictly empirical and is applied only to saturated organics. He estimates the EDC rate constant as 22/1.75= 12.6 X 10^{-14} cm^3 $molecule^{-1}$ sec^{-1}. Snelson et al.[61] calculate a rate of 12.5 X 10^{-14} cm^3 $molecule^{-1}$ sec^{-1} at 265 K and use that value to estimate the tropospheric lifetime of EDC. They calculate the 265 K rate constant by using an assumed activation energy of 2.07 kcal mol^{-1}, which they calculated by averaging seven values for the activation energy of chlorinated methanes and ethanes taken from the literature. (In two instances, E/R values were used. The actual average of the activation energies is 2.49 kcal mol^{-1}.) Atkinson has apparently recommended to Singh[9] that the best activation energy to assume is that of methylene chloride. Atkinson's recommended expression for the temperature dependence of methylene chloride, given previously, is equivalent to an activation energy of 2.1 kcal mol^{-1}. In light of the small number of activation energies which have been measured for analogous species, Atkinson's recommendation to use the activation energy of

methylene chloride seems most appropriate for EDC. An activation energy of 2.1 kcal mol^{-1} is assumed for the lifetime calculations in Table 9.

TABLE 9. ETHYLENE DICHLORIDE REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	OH Reaction Rate Constant 10^{-14} cm^3 $molec^{-1}$ s^{-1}	Assumed [OH] 10^6 molec cm^{-3}	Lifetime days
288	19.0	1.0	61
263	12.6	1.0	92
260	11.9	0.5	195

Other removal processes are, once again, not likely to be effective in removing this air toxic. For example, the atmospheric lifetime resulting from rain out processes has been estimated to be around 400 years.[3] From Table 9, one would select the value of 92 days as the lifetime, since this falls within the appropriate range for the vertically well-mixed troposphere. Given the uncertainty in the activation energy however, the value of 92 days should only be viewed as the most probable value. If one selects a factor of two as a margin of safety, then one estimates that the EDC 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 Singh et al.[9] from ambient concentration measurements and a global budget model. Singh's calculated residence time does not depend upon an assumed [OH]: it is based, however, on a sparse set of ambient data. There are only 16 measurements, 8 in each hemisphere (based upon a preprint copy of reference 9 kindly supplied by Dr. Singh). All samples were collected over the eastern Pacific Ocean in December 1981. Variations in the release rate for EDC may have a substantial effect on the calculated residence time.

TRICHLOROETHYLENE

Trichloroethylene (trichloroethene) is a chlorinated alkene which has found use as a degreaser and solvent.[58] It, too, is a mutagen and a suspect carcinogen.[21] The Northern Hemispheric background concentrations in the Eastern Pacific Ocean were reported as 12 ppt.[9] Brodzinsky and Singh[57] reported median urban concentrations of 150 ppt for measurements reported between 1970 and 1980. A two-hour average concentration of 900 ppt was recently reported for stagnant conditions in San Jose.[22]

The available rate data for reactions with OH radicals are in reasonable agreement. Atkinson[13] recommends calculating the temperature dependent rate constants using the Arrhenius expression:

$$k(CHClCCl_2) = 5.63 \times 10^{-13} \exp(427/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} . \qquad (16)$$

Notice that the exponential function in Equation (16) is raised to a positive power. This means that the activation energy is actually negative and that the rate constant for this chemical will increase as the temperature cools. A negative activation energy is consistent with an addition reaction, as is often seen in alkenes.[13] One of the anticipated products from this chemicals decomposition in the atmosphere is phosgene.[3,64] The recommended rate constants for reaction with OH radicals are given in Table 10.

TABLE 10. TRICHLOROETHYLENE REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	OH Reaction Rate Constant 10^{-14} cm^3 molec^{-1} s^{-1}	Assumed [OH] 10^6 molec cm^{-3}	Lifetime days
288	248	1.0	4.7
263	286	1.0	4.1
260	291	0.5	8.0

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.[14] Ozonolysis, therefore, plays no significant role in the removal of this compound. Other removal mechanisms are also expected to be ineffective. The lifetime, then, is computed solely from the hydroxyl removal rate. The lifetime for the boundary layer of 4.7 days is at the upper end of the applicable range. The lifetime computed for the vertically mixed troposphere is even shorter, due to the negative activation energy exhibited by this compound. The lifetime of trichloroethylene is estimated as slightly over four days.

PERCHLOROETHYLENE

Perchloroethylene (tetrachloroethene) is a suspect carcinogen[21] for which lifetime risk estimate for carcinogenesis has been published.[20] The chemical is quite volatile and is commonly used as a degreaser and solvent.[58] It is emitted in significant amounts from dry cleaning operations.[20] The chemical is consistently found in urban areas of the U.S. The data compilation of Brodzinsky and Singh[57] 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.[22]

The smog chamber data for perchloroethylene was recently reviewed by Dimitriades et al.[65] They concluded that much of the data reported in the literature on mechanisms and product distribution in smog chamber irradiations was influenced by chlorine atom chain reactions. Atkinson recently reviewed the data on reactions between OH radicals and perchloroethylene.[13] From a consistent set of kinetic rates, he derived the following Arrhenius expression for the rate constant:

$$k(CCl_2CCl_2) = 9.64 \times 10^{-12} \exp(-1209/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} . \quad (17)$$

Unlike the case of the other chlorinated alkene, trichloroethylene, above, the rate constant for perchloroethylene decreases as the temperature cools. The recommended rate constants are tabulated below. One of the reaction products which results from the atmospheric photooxidation of this compound is phosgene.[3]

TABLE 11. PERCHLOROETHYLENE REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	OH Reaction Rate Constant 10^{-14} cm^3 molec^{-1} s^{-1}	Assumed [OH] 10^6 molec cm^{-3}	Lifetime days
288	14.5	1.0	80
263	9.7	1.0	119
260	9.2	0.5	251

The only reported value for the rate constant of the reaction of perchloroethylene and ozone[14] 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.[56] 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, taken from Table 11, should be expressed as ranging from 119 to 251 days. This value is completely consistent with the estimate of Singh et al.[9] of 146 to 292 days, based upon a two-box model.

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.[58] Data on its occurrence in urban areas is not very extensive, but a median value of 1500 ppt was reported by Brodzinsky and Singh.[57] Most of the reported data points were from only one city, however.

Atkinson has recently reviewed the reactions of butadiene with both hydroxyl radicals and ozone.[13,14] Much of the data on hydroxyl reactions is in excellent agreement. There was only one reported temperature dependence with an Arrhenius activation energy of -0.93 kcal mol^{-1}. The negative activation energy implies that the rate should increase as the temperature decreases. The recommended OH reaction rate constant is given by the expression:

$$k(CH_2{=}CHCH{=}CH_2) = 6.68 \times 10^{-11} \exp(468/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} . \quad (18)$$

The recommended ozonolysis rate constant at room temperature is 8.1 x 10^{-18} cm^3 $molecule^{-1}$ s^{-1}.[14] The reaction with ozone has an activation energy of around 5.5 kcal mol^{-1}. The resultant rate constant at 288 K is 5.9 x 10^{-18} cm^3 $molecule^{-1}$ s^{-1}. The recommended rate constants and the computed lifetimes are shown in Table 12. Unlike the similar previous tables, the lifetimes in Table 12 are given in minutes. In calculating the ozone removal rate, an estimated concentration of 40 ppt (1 x 10^{12} molecules cm^{-3}) was assumed.[10,20]

TABLE 12. 1,3-BUTADIENE REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	Reaction Rate Constant 10^{-14} cm^3 $molec^{-1}$ s^{-1}	Assumed Conc. 10^6 molec cm^{-3}	Lifetime mins
288	7060	1.0	236
263	8240	1.0	202
260	8410	0.5	396
-	—	—	—
288	Ozone: 0.00059	Ozone: 1,000,000	Ozone: 2800

The estimated lifetime of butadiene is very short. The tabulated lifetimes were calculated for "average" conditions as were described above. Obviously, the actual lifetime of such a reactive compound will depend upon the specific conditions at the time of release. 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.[66] Ethylene oxide finds its use as an intermediate in the synthesis of ethylene glycol and as a sterilant or pesticide.[58] The chemical is a mutagen and suspect carcinogen, having been classified as being probably carcinogenic to humans by EPA's Carcinogen Assessment Group.[67]

While ethylene oxide has been monitored in the workplace, data on ambient concentrations of ethylene oxide is very sparse. Brodzinsky and Singh[57] did not report finding any measurements published during the period 1970-80. At this point, no ambient measurements are known.

Two investigators have recently measured the reaction rate constant for ethylene oxide with OH radicals.[13,66] The experimentally determined room temperature rate constants were 5.3 and 8.0 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1}. An activation energy of 2.9 kcal mol^{-1} was measured by one of the

investigators across the temperature range 297 K to 435 K. While one should be careful in extrapolating the temperature dependency outside the measured range, it is still reasonable to assume a similar activation energy across the small range to 260 K. Such an assumption does cause greater uncertainty in any lifetime estimates, however. The larger rate constant and the reported activation energy were used to estimate the rate constants shown in Table 13. The choice of the larger rate constant means that the estimated lifetimes are actually on the low side of the possible values.

TABLE 13. ETHYLENE OXIDE REACTION RATE CONSTANTS AND LIFETIMES

Temperature K	OH Reaction Rate Constant 10^{-14} cm^3 $molec^{-1}$ s^{-1}	Assumed [OH] 10^6 molec cm^{-3}	Lifetime days
288	6.9	1.0	167
263	4.3	1.0	217
260	4.0	0.5	578

Of the eight chemicals named in "Intent to List" notifications, ethylene oxide is the most soluble in water. When the concentrations of a chemical in water and air are expressed in the same units (e.g., moles $liter^{-1}$), the ratio of the aqueous phase concentration to the vapor phase concentration is defined as the dimensionless solubility parameter, α. This value has recently been measured at 288 K and found to be 6.2.[56] This means that ethylene oxide does distribute preferentially into the aqueous phase. Even without considering revolatilization of the chemical, however, rain out will still not be effective in removing the chemical from the environment: the estimated lifetime due to rain out is hundreds of years. Experimental measurements and theoretical modeling of rain out effects have demonstrated little impact from rain out for gases which are even far more soluble than ethylene oxide.[56]

Nor should the chemical distribute into the aqueous phase on ambient aerosols and be removed by deposition of the aerosol. Even a worst case condition of 150 $\mu g\ m^{-3}$ of aerosol, all of it being water, will reduce the gas phase concentration by only one part in one billion. If rapid hydrolysis reactions were to occur to the ethylene oxide dissolved in the aqueous aerosol, that chemical process could increase significantly the loss by this mechanism. Half lives of ethylene oxide in the aqueous phase have been reported[68] to fall between 200 and 400 hours for a wide variety of types of water (e.g., sterile distilled water, sea water, fresh water, sterile and non-sterile river water). Such long lifetimes suggest that hydrolysis reactions in aqueous aerosols are also not likely to be fast.

No other removal process are known which can rapidly deplete the ethylene oxide from the air. Results from smog chamber irradiations[69,70] in both natural sunlight and artificial illumination (private communication, Dr. E. Edney, Northrop Services, Inc., Research Triangle Park, North Carolina) are consistent with a slowly reacting organic chemical: they suggest that there is not some overlooked chemical or photolytic process occurring to remove ethylene oxide. The estimated lifetime, therefore, can be calculated simply from the OH radical removal rate. From Table 13, one estimates the lifetime as 217 to 578 days.

This estimate of lifetime is in disagreement with a previous EPA report by Bogyo et al.[71] and a monograph[72] by SRI International for the National Cancer Institute. Those references conclude that "ethylene oxide is highly reactive and does not persist in the environment" and that epoxides like ethylene oxide are "expected to degrade rapidly" in the environment. The SRI conclusion is based upon an extrapolation of the work by Bogyo et al. Bogyo's conclusions are based upon a few liquid phase experiments which may not be applicable and upon a single 1976 publication by Darnall et al.[73] in which the "reactivity" of various organics was ranked according to their reactivity with OH radicals. Citing the Darnall reference, Bogyo et al. state "ethers as a class

(epoxides are a type of ether) have been classified among the most reactive hydrocarbons." That sentence implies that the conclusion of "rapid" removal is based upon a doubtful analogy with unstrained ethers. Darnall et al. do not rank any ethers at all! The only reference to ethers is found in a table copied from an earlier publication[74] which concluded that ethers were capable of producing significant quantities of ozone. It also illustrates a misinterpretation of the literature: the word "reactivity" used in the paper cited by Darnall et al. referred to the ozone forming potential, and not necessarily the rate of removal. The conclusion that ethylene oxide "does not persist" is not warranted, in light of the recent kinetic data.

It is interesting that ethylene oxide, with an estimated lifetime as long as 1.5 years, has not been observed in the ambient atmosphere.[57] A study[75] of breakthrough volumes in Tenax concluded that there was no safe sampling volume for ethylene oxide when using Tenax. It is not surprising, therefore, that previous data from Tenax measurements did not include ethylene oxide. Although Singh et al.[21,22] have carried out a great deal of ambient measurements using a different technique, ethylene oxide was never one of the chemicals which they attempted to measure. In a recent EPA field study using samples collected in polished stainless steel canisters, all attempts to measure ethylene oxide were confounded by an interference from the water peak (private communication, T. A. Hartlage, U.S. EPA, Research Triangle Park, NC). A variety of other methods have been reported in the literature for use in analyzing for ethylene oxide.[67,76-79] These methods all have reported sensitivities from 0.05 parts per million to greater than 3 parts per million. The 1982 estimate[80] for production in the U.S. was 5000 million pounds, or 2270 million kilograms. Assuming that the total Northern Hemispheric production is twice that of the U.S. and that one-fourth of all the material produced is vented to the atmosphere, one calculates an annual input to the Northern Hemisphere of 1.14×10^{12} grams. If the OH radical decay rate is taken as $1/1.5\ year^{-1}$ and the transfer rate to the Southern Hemisphere is assumed[9] to be $1/1.2\ year^{-1}$, 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. Even if excursions of factors of 10 to 100 above geochemical background were to occur in urban areas (analogous to some of the observations of Singh et al.[21,22] for other pollutants), the concentrations would still likely be below the detection limit.

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.

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