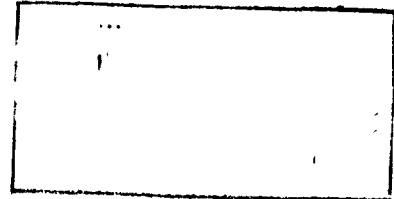
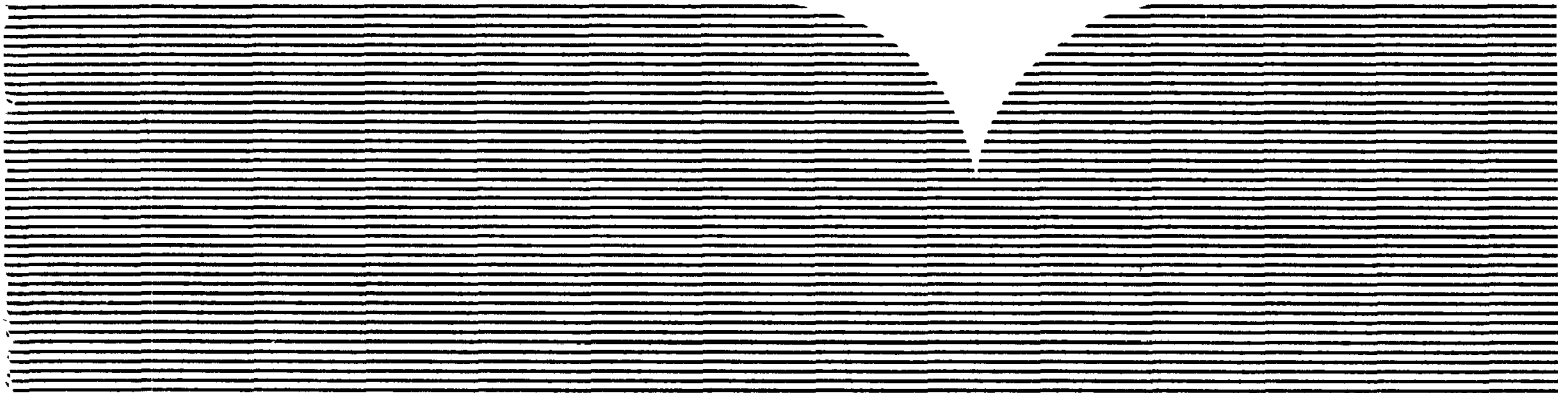


Fate of Toxic and Hazardous
Materials in the Air Environment

(U.S.) Environmental Sciences Research Lab.
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FATE OF TOXIC AND HAZARDOUS
MATERIALS IN THE AIR ENVIRONMENT

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ABSTRACT

Potential toxic/hazardous chemicals are currently undergoing Type I (preliminary) and Type II (detailed) assessment by the Office of Air Quality Planning and Standards. This report evaluates the atmospheric fate of these compounds, i.e., their probable lifetime in the troposphere. Emphasis has primarily been given to the volatile chemicals undergoing Type II Assessment, i.e., acrylonitrile, ethylene dichloride, perchloroethylene, vinylidene chloride and benzo(a)pyrene (as a representative polycyclic organic material).

Chemical and physical removal processes are discussed. Various parameters were considered that influence chemical removal processes involving photolytic transformations and reactions with hydroxyl radicals, ozone, and other tropospheric species. Mathematical descriptions of physical removal mechanisms were developed and applied to the volatile Type II Assessment chemicals. Estimates of physical removal by rainfall suggest half-lives of 300 days or longer for all volatile Type II compounds. Calculations based on reported photo-decomposition rates of halomethanes in contact with silica surfaces (e.g., desert sands) suggest half-lives on the order of 25 years for such halogenated chemicals, and dry deposition of the other compounds of interest is probably equally slow. Adsorption on aerosol particles is a reasonable removal mechanism only for benzo(a)pyrene and all physical removal processes are generally demonstrated to be rather inefficient.

Forty-six individual materials were evaluated relative to their probable fates and tropospheric lifetimes. Known or theoretical rate constants are listed for reaction with hydroxyl radicals and ozone. The probability of photolysis and of physical removal was assessed, and

residence lifetimes assigned. Probable products of tropospheric oxidation processes were also tabulated.

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SECTION 1

INTRODUCTION

The Office of Air Quality Planning and Standards (OAQPS) has recently distributed lists of potentially toxic/hazardous chemicals being assessed in regard to possible regulatory action. The list of "43 chemicals" under Type I (preliminary) Assessment, and a second list of chemicals under Type II (detailed) Assessment, contain a variety of species that may be found in the air environment. Because of the high probability of harmful effects resulting from exposure to these chemicals, this report attempted to evaluate the atmospheric fate of many of these compounds. Particular attention was paid to those chemicals currently under Type II Assessment that may possibly be found as gaseous emissions, specifically, acrylonitrile, ethylene dichloride, perchloroethylene, vinylidene chloride, and polycyclic organic materials. Because the phrase "polycyclic organic materials" includes an infinite variety of possible compounds, all of which cannot be addressed in any document, this report considered benzo(a)pyrene (BaP) a representative of the class.

Ambient concentrations of toxic/hazardous materials (T/H M's) represent a dynamic balance between emission rates, dilution, and physico-chemical removal rates. Sources may be either anthropogenic or natural, and sinks may involve chemical/physical processes. This paper did not address source strengths or localized dilution effects. Instead it surveys a variety of chemical/physical removal processes and assesses the likely fate of individual compounds.

SECTION 2

CONCLUSIONS

By taking experimental and theoretical parameters into consideration, reasonable values may be assigned to the rate of reaction of T/H M's with reactive species found in the lower troposphere. For the volatile chemicals currently undergoing Type II Assessment (i.e., acrylonitrile, vinylidene chloride, ethylene dichloride, perchloroethylene and benzo(a)pyrene), chemical removal residence times, based upon reaction with hydroxyl radicals and ozone, are estimated to range between approximately 3 to approximately 70 days.

Estimates can also be made of the physical removal rates for the volatile Type II chemicals. Removal by dissolution into rain droplets yields estimated half-lives of from 0.8 to greater than 100,000 years. Dry deposition rates imply half-lives of approximately 25 years, and adsorption on aerosols is demonstrated to be a reasonable removal mechanism only for materials with saturation vapor pressures of 10^{-7} torr or less. Only in the case of B(a)P, where adsorption on aerosol particles suggested a lifetime of about 8 days, was a physical removal mechanism significant.

Quantitative description of the atmospheric degradation or photolytic transformation of the T/H M must be on a chemical-by-chemical basis and requires a great deal of experimental evidence that may not yet be available. Nonetheless, estimates of reasonable residence times are feasible on the basis of the normally predominant chemical removal mechanisms. Based upon current knowledge of atmospheric oxidation mechanisms, possible tropospheric reaction products may be anticipated.

SECTION 3

CHEMICAL REMOVAL PROCESSES

INTRODUCTION

For a wide variety of molecules, the most important chemical removal process in the troposphere is reaction with hydroxyl (OH) radicals. For those organic chemicals containing isolated double bonds, ozonolysis is also available as a second reaction pathway. In addition, reactions with minor tropospheric species or with species known to exist in the stratosphere (e.g. $O(^3P)$, $O(^1D)$, HO_2 , RO_2 , NO_3 , $O_2(^1\Delta g)$, etc.) must be considered for chemicals that are relatively long-lived. Table 1 lists average tropospheric concentrations of some of these reactive species.¹⁻³

REACTION WITH HYDROXYL RADICALS

Despite the fact that the average concentration of OH radicals given in Table 1 is much lower than for many other reactive species, reaction with hydroxyl radicals is the predominant tropospheric removal mechanism for a wide variety of organic molecules. The reaction pathway with OH may proceed by abstraction, addition, or both.

Abstraction reactions occur when a hydrogen atom is available to be removed by the OH to form H_2O and an organic radical. The rate at which this reaction occurs depends upon the ease with which the organic molecule gives up the hydrogen atom. Since this process is controlled by the number of hydrogens and the nature of the molecular orbitals influencing both the

original carbon-hydrogen bond and the resulting radicals, substituent groups in the vicinity of the abstractable hydrogen influence the rate of abstraction. While the rate constant for many abstraction reactions is in the range of 1 to $10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, the actual rate constant is dependent upon the particular molecular composition.

TABLE 1. ESTIMATED CONCENTRATIONS OF REACTIVE SPECIES IN THE LOWER TROPOSPHERE

Specie	Concentration ^a	
	molecule cm^{-3}	ppm
OH	1×10^6	4×10^{-8}
O ₃	1×10^{12}	4×10^{-2}
O ₂ (¹ Δg)	5×10^8	2×10^{-5}
O ₂ (¹ Σ)	7×10^2	3×10^{-11}
O(³ P)	5×10^4	2×10^{-9}
O(¹ D)	2×10^{-1}	8×10^{-16}
HO ₂	5×10^9	2×10^{-4}
RO ₂	5×10^9	2×10^{-4}
NO ₃	1×10^5	4×10^{-9}

^aConcentrations are taken from References 1 to 3 and from sources therein. Conversion factors between concentration units assume 1 atmosphere pressure at 300°K.

In the addition reaction pathway, the electrophilic OH radicals will add to molecules having areas of high localized electron density. For alkenes, alkynes and aromatics, the OH adds across a multiple bond to form a β-hydroxyl organic radical. Substituents also affect the molecular orbitals of the parent, transition state, and product species, thereby influencing the reaction kinetics. Addition of OH to an organic molecule forms an adduct which may fall apart and revert back to the reactant species unless stabilized by collision or by energy transfer to other parts of the molecule. This

reversion means that OH addition reactions are subject to pressure effects, but the more complex the species the lower the "fall off" region between second-order and third-order kinetics.

Atmospheric reactions are a combination of abstraction and addition processes leading primarily to oxygenated organic compounds like aldehydes, ketones, and dicarbonyls. Halogenated organics tend to lose halogen atoms in the form of halo-oxy radicals. Hendry and Kenley¹ describe a systematic method for estimating reaction rates and reaction products resulting from the atmospheric oxidation of organic compounds.

REACTION WITH OZONE

Organic chemicals with isolated double bonds may have a significant atmospheric loss rate via reaction with ozone (O_3). While the rate constant for reaction of alkenes with O_3 is much less than the rate constant for OH reaction (approximately $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ compared to approximately $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$), ozone concentrations are so much larger than OH concentrations that the two loss processes are competitive for many alkenes. While aromatic compounds may react with O_3 , their ozonolysis removal mechanism is usually slow compared to reaction with OH.

Ozone is believed to add across the double bond, with subsequent cleavage to form a carbonyl compound (aldehyde or ketone) and a percarbonyl biradical. The biradical may rearrange or react to form a variety of products including organic acids, carbon dioxide and a host of organic radicals. Epoxides have also been suggested as minor products of ozonolysis reactions.

Reaction with Other Radicals

Thorough understanding of laboratory experiments involving ozonolysis processes is clouded by the formation, during reaction, of reactive radicals that may interact with the reagents, intermediates and products. A wide variety of such reactive species, including those produced during ozonolysis

and hydroxylation reactions, exists in the ambient atmosphere (Table 1). With the exception of OH and O₃, however, their concentrations are low, and their importance as reactants with T/H M's is small. For certain relatively unreactive chemicals, reaction with species other than OH and O₃ may provide the predominant (albeit, slow) removal process.⁴ Reactions with the minor species listed in Table 1 need not be considered unless all other chemical or physical removal processes are ineffective.

PHOTOLYTIC TRANSFORMATIONS

Solar radiation in the troposphere covers the region from 2900 to 8000 angstroms.⁵ Photochemical fragmentation or rearrangement processes are possible for those chemicals that absorb radiation of the appropriate wavelength. Estimates of the magnitude of photochemical processes are difficult to make because of uncertainties in light intensity, quantum yields, etc.¹ Photolysis can be an important removal process only for chemicals which absorb strongly within the solar radiation region, otherwise reaction with OH or O₃ is likely to predominate the removal process. This reaction removal pathway limits the compounds to be considered to those possessing a strongly absorbing chromophore, like carbonyl compounds, conjugated alkenes, nitro and other nitrogen-containing compounds and halides. Compounds which may form from photolysis of these absorbing groups can be suggested although predictions of efficiencies and specific yields are impractical.

SECTION 4

PHYSICAL REMOVAL PROCESSES

DISSOLUTION

Toxic hazardous materials in the gas-phase may be removed from the air environment by dissolving them into cloud or rain droplets to be subsequently removed by rainfall. An estimate of the efficacy of such a removal process can be obtained by calculating the partitioning of material between the aqueous and gas phases.

Henry's Law relates the equilibrium vapor phase and liquid phase concentrations of a dilute solution of material *i* via the equation

$$p_i = x_i K_i \quad (\text{Eq. 1})$$

where: p_i = the equilibrium vapor pressure of the solute above the dilute solution

x_i = the mole fraction of the solute, and

K_i = the Henry's Law constant.

For very dilute solutions ($x_i \ll x_{\text{water}}$), the concentration of solute, c_i (in g cm^{-3}) is proportional to x_i . Assuming ideal gas behavior at 298°K , the term p_i may also be converted to a gas-phase concentration term, c_{ig} , in units of g cm^{-3} . Equation 1 becomes

$$c_{ig} = c_i K_i \frac{(18)}{(22414)} \frac{(273)}{(298)(760)}$$

$$c_{ig} = 9.7 \times 10^{-7} K_i c_i \quad (\text{Eq. 2})$$

where the Henry's Law constant, K_i , has the units of torr.

The ratio at equilibrium of the concentration in the aqueous phase to the concentration in the gas phase is a dimensionless number, α , describing the partitioning of the material between the two phases. Rearranging Equation 2, one finds that

$$\alpha = \frac{c_i}{c_{ig}} = \frac{1.03 \times 10^6}{K_i} \quad (\text{Eq. 3})$$

For materials which are only slightly soluble in water, it is reasonable to assume that Henry's Law (Equation 1) holds for all concentrations of i from infinite dilution ($x_i \rightarrow 0$) to the saturation point ($x_i = x_{is}$). It is also reasonable to assume that, at saturation, bulk quantities of i are in equilibrium with the saturated solution and also in equilibrium with a saturated vapor phase. At saturation, therefore, Equation 1 becomes

$$p_{is} = x_{is} K_i \quad \text{and}$$

$$K_i = \frac{p_{is}}{x_{is}} \quad (\text{Eq. 4})$$

where: p_{is} = the saturation vapor pressure of the solute, and
 x_{is} = the saturation mole fraction of the solute

The value of the Henry's Law constant is now expressed in terms of two experimentally measurable values: the saturation vapor pressure, p_{is} , and the mole fraction of i at saturation, x_{is} . Expressing p_{is} in torr, Equation 4 may be substituted into Equation 3 to yield

$$\alpha = 1.03 \times 10^6 \frac{x_{is}}{P_{is}} \quad (\text{Eq. 5})$$

The fraction of material i removed each year as dissolved compound in rain is the product of α times the ratio of the volume of the average annual rainfall to the volume of the well-mixed troposphere. Assuming an annual rainfall of 0.75 meter⁶ and a height of 8 km for the homogeneous atmosphere⁷, one calculates

$$\frac{dc_i}{dt} = - \frac{\alpha \cdot 0.75 \cdot A \cdot (\text{yr}^{-1})}{8000 \cdot A} c_i$$

$$\int_{c_{i0}}^{0.5 c_{i0}} \frac{dc_i}{c_i} = \frac{- 9.375 \times 10^{-5}}{\text{yr}} \alpha \int_{t=0}^{t = \tau_{1/2}} dt$$

$$\tau_{1/2} = \frac{7.39 \times 10^3}{\alpha} \text{ yr} \quad (\text{Eq. 6})$$

where: A = the surface area of the earth,
 $\tau_{1/2}$ = the half-life of the species i ,
 t = time, and
 c_{i0} = the concentration of i in the troposphere at time zero.

Table 2 lists the relevant physical parameters and estimates $\tau_{1/2}$ for some of the compounds under Type II Assessment. The calculated half-lives are in general quite long.

The fate of the dissolved material is subject to question. Hydrolysis, oxidation by hydrogen peroxide or other species, adsorption on particulates in the rain drops or in contact with the ground water, etc., may all remove

or alter the toxic materials. The assumed equilibrium is perturbed if chemical interaction does occur within the suspended droplets. The more T/H M absorbed by the droplet, the lower the values of $\tau_{1/2}$ are reduced. Volatilization of the chemicals during evaporation of the rainfall run-off will re-introduce the T/H M into the atmosphere. Any subsequent return of the T/H M's to the air will lengthen the half-lives listed in Table 2.

Evaporative losses from a solution should be directly proportional to the concentration of the materials in the gas-phase above the bulk solution. The ratio of the equilibrium vapor-phase concentration of i , c_{ig} , to that of water, c_{wg} , divided by the similar ratio for the aqueous phase can be considered as the "relative volatility" of the compound.

$$\text{Relative volatility} = \frac{c_{ig}/c_{wg}}{c_i/c_w} = \frac{\alpha_w}{\alpha_i} \quad (\text{Eq. 7})$$

For water at 25°C, $\alpha_w = 4.34 \times 10^4$. Values of α_w/α_i have also been listed in Table 2 and indicate that evaporation of even small amounts of rain water are likely to reintroduce the T/H M into the air.

Estimation of actual evaporation rates from physico-chemical parameters is very complex^{8,9} and depends in large part upon the model system selected.¹⁰ Even in simple systems, laboratory experiments have shown that the actual evaporation rate is diffusion limited in the liquid phase for species with high relative volatilities.¹¹ This result implies that, while the evaporative losses are still fast, they are not so fast as equilibrium considerations would indicate.

Nonetheless, the data in Table 2 suggest that for those chemicals of concern, dissolution into and removal by raindrops is not a significant removal mechanism.

TABLE 2. PHYSICAL AND CALCULATED PARAMETERS INFLUENCING REMOVAL OF SOME ATMOSPHERIC POLLUTANTS BY RAIN DROPLETS

Compound ^a	P_{is} torr	x_{is}	α_i^c	$\tau^{1/2}$ yr	α_w/α_i
Acrylonitrile ^b (12)	1.14×10^2	<1.0	$<9.05 \times 10^3$	> 0.8	4.8
B(a)P (13,14)	5.46×10^{-9}	2.8×10^{-11}	5.4×10^3	1.4	8.0
Ethylene di- chloride (12, 15)	8.4×10^1	1.6×10^{-3}	1.9×10^1	390	2,300
Tetrachloro- ethylene (12, 16)	1.85×10^1	1.1×10^{-5}	6.1×10^{-1}	12,000	71,000
Vinylidene chloride (12, 17)	6.17×10^2	3.9×10^{-5}	6.5×10^{-2}	110,000	670,000

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^a Numbers in parentheses next to the compounds' names refer to the references from which the data was obtained.

^b The theory developed above does not directly apply to soluble chemicals like acrylonitrile; however, substitution of Raoult's Law for Henry's Law leads to an equivalent derivation, but with slightly different assumptions.

^c Equation 5 defines x as $1.03 \times 10^6 (x_i/p_{is})$. Since x_{is} and P_{is} are both temperature dependent, is also temperature dependent. The values quoted in the table assume a temperature of 25°C, whereas the average tropospheric temperature may be substantially different. This means that all half-lives calculated from this data should be considered approximations.

ADSORPTION ON AEROSOL PARTICLES

Toxic chemicals in the vapor phase may be adsorbed on aerosol particulates and removed from the atmosphere with the aerosol. Since the average tropospheric lifetime of aerosol particles is approximately seven days,¹⁸ adsorption on natural aerosols may establish a limit for the gas-phase lifetime of various toxic compounds. If ϕ is the fraction of a compound attached to aerosol particles, then the atmospheric lifetime of that compound is $7/\phi$ days.

Unfortunately, ϕ has not been measured for many compounds. Those measurements which have been made are subject to questions about sampling artifacts and often lack adequate characterization of the ambient aerosols.

Using adsorption theory ϕ can be estimated, but such theoretical calculations are severely limited because of approximations and assumptions involved in deriving useable equations. They should be considered "order of magnitude" estimates only.

Brunauer, Emmett, and Teller (BET)¹⁹ modified Langmuir adsorption theory to overcome the problems of multilayer adsorption and heterogeneous surfaces. Their results take the form

$$\frac{V}{V_m} = \frac{Cp}{(p_0 - p) (1 + (C - 1) p/p_0)} \quad (\text{Eq. 8})$$

where: V = the volume of gas adsorbed,
 V_m = the volume of gas adsorbed when one complete monolayer has been formed,
 p = the pressure of the gas,
 p_0 = the saturation pressure of the gas, and
 C = a constant.

The volume terms in Equation 8 represent a specific mass for a defined compound, pressure and temperature. Letting η represent a "surface density"

term (in units of g/cm^2), the equation becomes

$$\frac{\eta}{\eta_m} = \frac{Cp}{(p_o - p) (1 + (C - 1) p/p_o)} \quad (\text{Eq. 9})$$

where: η = the number of grams of gas adsorbed per square centimeter of surface area of adsorbing material, and
 η_m = the similar surface area density term when a complete monolayer exists on the adsorbing surface.

In the environment, aerosol particles are characterized by their number count, surface area, and volume (or mass) characteristics. If θ is the surface area density of the aerosol particles in the atmosphere, then the ambient concentration of the T/H M adsorbed on aerosol particles is given by:

$$\rho_a = \eta \theta \quad (\text{Eq. 10})$$

where: θ = the number of cm^2 of aerosol surface per cm^3 of ambient air, and
 ρ_a = the number of grams of T/H M adsorbed on aerosol particles per cm^3 of air.

From ideal gas laws, the gas-phase density is:

$$\rho_g = \frac{Mp}{RT} \quad (\text{Eq. 11})$$

where: ρ_g = gas phase density, and
 M = the gram molecular weight

Combining Equations 9, 10, and 11 yields:

$$\frac{\rho_a}{\rho_g} = \frac{C \eta_m \theta RT}{M (p_o - p) (1 + (C - 1) p/p_o)} = \frac{\kappa \theta}{(p_o - p) (1 + (C - 1) p/p_o)} \quad (\text{Eq. 12})$$

where: κ = a combination of constants.

Equation 12 can be greatly simplified via two assumptions ($p_0 \gg p$ and $p_0 > C_p$) to become

$$\frac{\rho_a}{\rho_g} = \frac{\kappa \theta}{P_0} \quad (\text{Eq. 13})$$

Since C usually has a value of 5 to 25, both assumptions above are valid only when $p < 0.04 p_0$. For most pollutants, the requirement that the ambient pressure be less than 4% of the saturation pressure is easily met, especially on the global scale.

Phi is related to the expression in Equation 13 via

$$\phi^{-1} = \frac{\rho_g + \rho_a}{\rho_a} = \frac{\rho_g}{\rho_a} + 1 = \frac{p_0}{\kappa \theta} + 1 = \frac{\kappa \theta + P_0}{\kappa \theta} \quad (\text{Eq. 14})$$

$$\phi = \frac{\kappa \theta}{\kappa \theta + P_0} \quad (\text{Eq. 15})$$

Evaluation of κ will permit calculation of ϕ as a function of θ and p_0 . From Equation 12

$$\kappa = \frac{\eta_m C RT}{M} \quad (\text{Eq. 16})$$

η_m is in units of g/cm^2 and is the surface density when a complete monolayer exists on the particle surface. It is estimated by determining the number of molecules adsorbed per unit area and multiplying by the mass of each adsorbed molecule. Emmett and Brunauer²⁰ calculate the surface area covered by each molecule, S, as

$$S = (4) (0.866) (M/4\sqrt{2} N_0 D)^{2/3} \quad (\text{Eq. 17})$$

where: N_0 = Avogadro's number, and

D = the bulk density of the adsorbed chemical in g/cm^3 .

η_m is therefore given by

$$\eta_m = \frac{1}{S} \left(\frac{M}{N_o} \right) = \frac{(4 \sqrt{2})^{2/3}}{(4)(0.966)} \left(\frac{D N_o}{M} \right)^{2/3} \left(\frac{M}{N_o} \right)$$

$$\eta_m = 0.917 \left(\frac{D^2 M}{N_o} \right)^{1/3} \quad (\text{Eq. 18})$$

The value of C is generally significantly greater than 1. Values of C reported by BET¹⁹ range from 3 to 26 at 298°K, with the larger value given for butane and the smaller values given for inorganic gases like nitrogen and argon. Assuming a value of 25 and a temperature of 298°K, κ is evaluated as

$$\kappa = \frac{0.917}{M} \left(\frac{D^2 M}{N_o} \right)^{1/3} \quad (25) \quad \frac{(22414) (760) (298)}{(273)}$$

$$\kappa = 5.05 \left(\frac{D}{M} \right)^{2/3} \frac{\text{torr-cm}^3}{\text{cm}^2} \quad (\text{Eq. 19})$$

Table 3 lists values of M , D , κ , p_o , ϕ and lifetime for several chemicals currently undergoing Type II evaluation.

An average value of $\kappa = 0.25$ was used, together with Equation 15 to calculate ϕ as a function of particle surface area, θ , for a variety of p_o values. The results are shown in Table 4. On the global scale, θ should range between 10^{-7} and 10^{-6} cm^2/cm^3 .¹⁸ For a reasonable value of $\theta = 3 \times 10^{-7}$ cm^2/cm^3 , ϕ is small for any chemical with a saturation vapor pressure greater than 10^{-7} torr.

Of the five compounds listed in Table 3, only B(a)P has a vapor pressure which is sufficiently low to suggest a reasonable value of ϕ . Cautreels and Van Cauwenberghe²¹ measured a particulate-to-gaseous ratio of 7.47 for B(a)P in a urban sample. The resulting value of $\phi = 0.88$ is in reasonable agreement

TABLE 3. PARAMETERS INFLUENCING ADSORPTION OF SOME AIR POLLUTANTS ON AEROSOL PARTICLES

Compound ^a	M g mole ⁻¹	D g cm ⁻³	κ cm-torr	P ₀ torr	φ ^b	Lifetime ^c days
Acrylonitrile (12)	53	0.8	0.31	114.	8.2 x 10 ⁻¹⁰	8.6 x 10 ⁹
Vinylidene chloride (12)	97	1.213	0.27	617.	1.3 x 10 ⁻¹⁰	5.3 x 10 ¹⁰
Ethylene dichloride (12)	99	1.26	0.28	84.	1.0 x 10 ⁻⁹	7.0 x 10 ⁹
Perchloroethylene (12)	166	1.6	0.23	18.	3.8 x 10 ⁻⁹	1.8 x 10 ⁹
B(a)P (13)	252	~ 1.3 ^d	0.15	5.5 x 10 ⁻⁹	0.89	7.9

^a The numbers in parentheses following the chemical name refer to the references from which the data was obtained.

^b φ is calculated from Equation 15, assuming a value for θ of 3 x 10⁻⁷ cm²/cm³.

^c The lifetime is calculated as 7/φ days.

^d Estimated from densities of similar compounds. See Reference 34.

with the value of 0.99 predicted by Equation 15 when $\kappa = 0.151$ and $p_o = 5.5 \times 10^{-9}$ torr (see Table 3) for a reasonable urban θ value of $5 \times 10^{-6} \text{ cm}^2/\text{cm}^3$.

TABLE 4. FRACTION (ϕ) OF MATERIAL ADSORBED ON AEROSOLS FOR VARIOUS VALUES OF AEROSOL SURFACE AREA (θ) AND CHEMICAL SATURATION VAPOR PRESSURE (p_o) $\kappa = 0.25$

p_o (torr)	$\theta \text{ (cm}^2/\text{cm}^3\text{)}$			
	1×10^{-7}	3×10^{-7}	1×10^{-6}	1×10^{-5}
10^{-8}	0.714	0.882	0.962	0.996
10^{-7}	0.200	0.429	0.714	0.962
10^{-6}	0.024	0.070	0.200	0.714
10^{-5}	0.002	0.007	0.024	0.200

These results of Table 4 indicate that the theoretical calculations, while filled with approximations and assumptions, can provide at least "order of magnitude" estimates of the adsorption of toxic chemicals on atmospheric aerosols. The results further suggest that adsorption will be a reasonable vapor-phase removal mechanism only for materials with saturation vapor pressures of 10^{-7} torr or less.

DRY DEPOSITION

Gaseous toxic/hazardous materials will come in contact with soil and water at the earth's surface and may be removed by adsorption or absorption. The ratio of the deposition flux divided by the airborne concentration is defined as the deposition velocity, v_d . The values of v_d are highly variable, depending upon the type of surface, meteorology, and composition of the material settling out. Values of v_d have been reported for a few gases, and they range from 0.01 to 3 cm/sec, implying residence times of 3 to 900 days.²²

The deposition velocity of only one of the 43 chemicals on the Type I Assessment list, methyl iodide, has been measured. Its v_d was reported as 10^{-4} to 10^{-2} cm/sec. From reports of photodecomposition of carbon tetrachloride absorbed on silica surfaces²³, one may estimate $v_d < 10^{-4}$ cm/sec.

Many of toxic and hazardous materials of concern (e.g., perchloroethylene, dichloroethylene, vinylidene chloride) can be expected to have deposition velocities comparable to those for CH_3I and CCl_4 . Assuming a mid-range value of 10^{-3} cm/sec, an estimated half-life of 25 years is predicted.

Considering the variability of the data and the likely ineffectiveness ($\tau_{1/2} \approx 25$ years) of dry deposition for removing or transforming many of the toxic or hazardous chemicals, this removal mechanism should be considered significant only under unusual circumstances.

SECTION 5

FATE OF CHEMICALS UNDER ASSESSMENT

The atmospheric chemical and physical removal processes are evaluated in Table 5 for 46 individual chemicals currently under assessment regarding regulatory action.

For each chemical listed, the following items are evaluated:

- (1) Hydroxyl radical reaction rate constant - Experimentally measured or theoretically-estimated gas-phase rate constants for the initial reaction between OH radicals and the volatile chemical are given in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.
- (2) Ozone reaction rate constant - The reaction rate constant is given in units of $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for those species whose rate has been measured and for all other species likely to react with O_3 . The theoretically-estimated rate constants in Table 5 (denoted by a superscript b) are subject to substantial uncertainty and should be used cautiously. In some cases, the estimates are for chemicals in structural classes far removed from those used to develop the estimation techniques in Reference 1. Caution is especially warranted in the case of ozonolysis of alkenes with strong electron withdrawing substituents and for OH reaction with substituted aromatics.
- (3) Photolysis probability - Any chemical possessing a chromophore likely to absorb light within the solar spectral region was given at least a "possible" rating. If photolysis of the specific compound, or of several structurally similar compounds, had been reported, then the chemical was given a "probable" rating. Quantitative values for photolytic decomposition are extremely difficult to predict, and accurate numbers require experimental determination. Because experimental

data are not available for many of the subject compounds, photolysis was largely ignored in the calculation of the species' lifetimes.

- (4) Physical removal probability - The ratio of the aqueous solubility density of the material to its saturation vapor density, α , (defined in Section 4), was determined. If the value exceeded 2×10^4 , implying a rainout lifetime of about 0.5 years, the chemical was rated as "possible." Because revolatilization of the materials is likely, removal by dissolution could be rated no higher than "possible." Materials with saturation vapor pressures of less than 10^{-7} torr are likely to be adsorbed on atmospheric aerosols, and they were given a "probable" rating. Species, like bis(chloromethyl)ether, which have been reported to decompose rather quickly in the environment,²⁴ were also rated as "probable." A priori prediction of decomposition is difficult, and it was considered as a physical removal mechanism only in cases where decomposition had been reported.
- (5) Atmospheric residence time - This number represents the estimated time, in days, required for a quantity of the individual chemical to be reduced to 1/e of its original value. As it is not a concentration lifetime it does not include a dilution term. For species with likely photolysis or physical removal mechanisms, the residence time was expressed as a range, and a comment about the smaller lifetime value was included in the footnotes to the table. In calculating the numbers listed in the table, two major assumptions were made:
- (a) The room temperature rate constants for OH and O₃ are valid for the ambient atmosphere. Since rate constants are temperature dependent, the actual removal rates will depend on time of day, season of the year, altitude, and any other parameter affecting the temperature. In addition, some OH reactions show positive temperature dependencies while others show negative effects. Because the temperature dependencies of so many of the species are unknown, room temperature values were used throughout.
- (b) Background concentrations of OH and O₃ were assumed to be constant, with values of 1×10^6 and 1×10^{12} molecules cm⁻³, respectively.

Obviously, the OH and O₃ concentrations depend on a complex set of chemical and physical conditions (light intensity, pollutant concentrations, temperature, altitude) and are not actually constant. The choices of concentrations used are reasonable averages for the lower troposphere.^{1,2,25} (Some data obtained in a private communication from H.B. Singh 1980).

- (6) Anticipated Products - The last column lists some of the products likely to result from the photochemical oxidation of dilute quantities of the specific compound in the atmosphere. The product list is not intended to be all-inclusive but is suggestive of the kinds of materials likely to be produced. Many of the products can be expected to react further, producing still other chemical species. Often reactive species like radicals are listed as products in order to suggest that whatever reaction scheme is available in their immediate locale will dictate the specific products. In addition, all the reaction schemes proceed through RO· and ROO· radicals which may add nitrogen oxides to form a wide variety of nitrogen-containing species. These species are not tabulated, but they should be considered as possible products for every reactive material.

TABLE 5. FATES AND RESIDENCE TIMES OF SOME CHEMICALS UNDER ASSESSMENT

Compound ^a	$k_{OH} \times 10^{12}$ $l^3 \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$	$k_{O_3} \times 10^{18}$ $l^3 \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$	Photolysis Probability	Physical Removal Probability	Atmospheric Residence Time Days	Anticipated Products
TYPE II ASSESSMENT						
Acrylonitrile ^h	2	≤ 0.05	--	Unlikely	5.6	H ₂ CO, HC(O)CN, HCOOH, CN.
Arsenic (26)	--	--	--	Possible	--	--
Cadmium ^c (26)	--	--	--	Probable	-7	--
Ethylene Dichloride (1, 27)	0.22	--	Possible	Unlikely	53	C1HCHO, H ₂ CClCOCl, H ₂ CO, H ₂ CClCHO
Perchloroethylene (1, 28)	0.17	0.002	Possible	Unlikely	67	Cl ₂ CO, Cl ₂ C(OH)COCl, Cl.
POH (Benzo(a)pyrene) (29, 30)	--	--	Possible	Probable	.8	B(a)P-1,6-quinone
Vinylidene chloride (1)	⁴ b	0.04	Possible	Unlikely	2.9	H ₂ CO, Cl ₂ CO, HCOOH
TYPE I ASSESSMENT						
Acetaldehyde ^d (3, 31)	16.	--	Probable	Unlikely	0.03-0.7 ^d	H ₂ CO, CO ₂
Acrolein (1)	⁴ b	⁴ b	Probable	Unlikely	0.2	OGH-CHO, H ₂ CO, HCOOH, CO ₂
Allyl chloride (1)	²⁸ b	18.3	Possible	Unlikely	0.3	HCOOH, H ₂ CO, ClCH ₂ CHO, chlorinated hydroxy carbonyls, ClCH ₂ COOH
Benzyl chloride (1)	³ b	0.004 ^b	Possible	Unlikely	3.9	CHO, Cl., chloromethylphenols, ring cleavage products
Bis(Chloromethyl) Ether (1, 26)	⁴ b	--	Possible	Probable ^e	0.02-2.9	Decomposition products (HCl + H ₂ CO), chloromethylformate, ClHCO

(continued)

TABLE 5. (Continued)

Compound	$k_{OH} \times 10^{12}$ $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	$k_3 \times 10^{18}$ $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	$k_0 \times 10^{18}$ $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	Photolysis Probability	Physical Removal Probability	Atmospheric Residence Time Days	Anticipated Products
Carbon Tetrachloride (31)	< 0.001	--	--	--	Unlikely	> 11000	Cl_2CO , Cl .
Chlorobenzene (1)	0.4^b	< 0.00005 ^b	< 0.00005 ^b	Possible	Unlikely	28	Chlorophenols, ring cleavage products
Chloroform (31)	0.1	--	--	--	Unlikely	120	Cl_2CO , Cl .
Chloromethyl methyl ether (1, 24)	3^b	--	--	Possible	Probable ^e	0.004-3.9	Decomposition products, chloromethyl and methyl formate, ClHCO
Chloroprene (1)	46^b	8^b	8^b	Probable	Unlikely	0.2	H_2CO , $\text{H}_2\text{C}=\text{CClCHO}$, OHCCHO , ClCOCHO , $\text{H}_2\text{CCHCClO}$, chlorohydroxy acids, aldehyde
o-, m-, p-Cresol ^f (32)	55.	0.6	0.6	--	Unlikely	0.2	Hydroxynitrotoluenes, ring cleavage products
Dichlorobenzene ^f (1)	0.3^b	< 0.00005 ^b	< 0.00005 ^b	Possible	Unlikely	39	Chlorinated phenols, ring cleavage products, nitro compounds
Dimethyl nitrosamine (1, 3, 24)	39^b	--	--	Probable	--	≤ 0.3	Photolysis products, aldehydes, NO
Dioxane (1)	3^b	--	--	--	Unlikely	3.9	$\text{OHCOCH}_2\text{CH}_2\text{OCHO}$, OHCOCHO , oxygenated formates
Dioxin (1)	--	--	--	Probable	--	--	--
Epichlorohydrin (1)	2^b	--	--	Possible	Unlikely	5.8	H_2CO , OHCOCHO , $\text{ClCH}_2\text{O}(\text{O})\text{OHCO}$
Ethylene Dibromide (1)	0.25	--	--	Possible	Unlikely	45	Br , BrCH_2CHO , H_2CO , BrHCO
Ethylene Oxide (1)	2^b	--	--	--	Unlikely	5.8	OHCOCHO
Formaldehyde ^d (3, 33)	10.	< 0.000002	< 0.000002	Probable	Unlikely	0.1-1.2 ^d	CO , CO_2
Hexachlorocyclopentadiene (1)	59^b	8^b	8^b	Probable	--	0.2	Cl_2CO , diacylchlorides, ketones, Cl .

(continued)

TABLE 5. (Continued)

Compound	$k_{OH} \times 10^{12}$ cm ³ molecule ⁻¹ sec ⁻¹	$k_{O_3} \times 10^{18}$ cm ³ molecule ⁻¹ sec ⁻¹	Photolysis Probability	Physical Removal Probability	Atmospheric Residence Time Days	Anticipated Products
Maleic Anhydride (1)	60 ^b	160 ^b	Possible	Possible	0.1	CO ₂ , CO; acids, aldehydes and esters which should photolyze
Manganese ^c (26)	--	--	--	Probable	-7	--
Methyl chloroform (33)	0.012	--	Possible	Unlikely	970	H ₂ CO, Cl ₂ CO, Cl ₂
Methylene chloride (28)	0.14	--	Possible	Unlikely	83	Cl ₂ CO, CO, ClHCO, Cl ₂
Methyl Iodide (1)	0.004 ^b	--	Possible	Unlikely	2900	H ₂ CO, I ^c , IHCO, CO
Nickel ^c (26)	--	--	--	Probable	-7	--
Nitrobenzene (1)	0.06 ^b	< 0.00005 ^b	Possible	Unlikely	190	Nitrophenols, ring cleavage products
2-Nitropropane (1)	55 ^b	--	Possible	Unlikely	0.2	H ₂ CO, CH ₃ CHO
N-Nitrosodiethylamine (1)	26 ^b	--	Probable	--	< 0.4	Photolysis products, aldehydes, nitramines
Nitrosoethylurea (1)	13 ^b	--	Possible	--	< 0.9	Photolysis products, aldehydes nitramines
Nitrosomethylurea (1)	20 ^b	--	Possible	--	< 0.6	Photolysis products, aldehydes nitramines
Nitrosomorpholine (1)	28 ^b	--	Possible	--	< 0.4	Photolysis products, aldehydic ethers
Phenol (1)	17 ^b	1 ^b	--	Possible	0.6	Dihydroxybenzenes, nitrophenols, ring cleavage products
Phosgene ^e (1)	0	--	--	Possible	--	CO ₂ , Cl ^c , HCl

(Continued)

TABLE 5. (Continued)

Compound	$k_{OH} \times 10^{12}$ $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	$k_{O_3} \times 10^{16}$ $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	Photolysis Probability	Physical Removal Probability	Atmospheric Residence Time Days	Anticipated Products
Polychlorinated Biphenyls (1)	< 1 ^b	0.00005 ^b	Possible	Unlikely	> 11	Hydroxy PCB's, ring cleavage products
Propylene oxide (1, 31)	1.3	--	--	Unlikely	6.9	$\text{CH}_3\text{C}(\text{O})\text{OCHO}$, $\text{CH}_3\text{C}(\text{O})\text{CHO}$
Toluene (1, 31)	6.	0.0003	--	Unlikely	1.9	Benzaldehyde, cresols, ring cleavage products, nitro compounds
Trichloroethylene (1, 28)	2.2	0.006	Possible	Unlikely	5.2	Cl_2CO , ClHCO , CO , Cl^{\cdot}
o-, m-, p- Xylene ^f (1, 31)	- 16.	- 0.001	--	Unlikely	0.7	Substituted benzaldehydes, hydroxy xylenes, ring cleavage products, nitro compounds

a. Numbers in parentheses refer to the reference from which data was obtained.

b. Rate constant calculated by method of Hendry and Kenley (EPA-560/12-79-001), Reference 1.

c. Material is not expected to exist in vapor phase at normal temperatures. Residence time calculation assumes the chemical is substantially adsorbed on aerosol particles and that the aerosols have a residence time of approximately 7 days.

d. The shorter residence time includes a photolysis rate as given in Reference 3.

e. Decomposition in moist air is expected. Check Reference 26 and references therein. The shorter residence time includes the cited decomposition rate.

f. Values given are averages for the various isomers.

g. Reaction with $\text{O}(\text{D})$ is possible: $k = 3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, and $[\text{O}(\text{D})] = 0.2 \text{ molecules cm}^{-3}$ implies a tropospheric lifetime of 440 years. In addition, slow hydrolysis is expected. Check References 2, 24, and 29.

h. Data obtained in private communication from Ed. Edney, 1980.

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