Environmental Impact of Solvents

17.1 THE ENVIRONMENTAL FATE AND MOVEMENT OF ORGANIC SOLVENTS IN WATER, SOIL, AND AIR[a]

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17.1.1 INTRODUCTION

Organic solvents are released into the environment by air emissions, industrial and waste-treatment effluents, accidental spillages, leaking tanks, and the land disposal of solvent-containing wastes. For example, the polar liquid acetone is used as a solvent and as an intermediate in chemical production. ATSDR[1] estimated that about 82 million kg of acetone was released into the atmosphere from manufacturing and processing facilities in the U.S. in 1990. About 582,000 kg of acetone was discharged to water bodies from the same type of facilities in the U.S. ATSDR[2] estimated that in 1988 about 48,100 kg of tetrachloroethylene was released to land by manufacturing facilities in the U.S.

Once released, there are numerous physical and chemical mechanisms that will control how a solvent will move in the environment. As solvents are released into the environment, they may partition into air, water, and soil phases. While in these phases, solvents may be chemically transformed into other compounds that are less problematic to the environment. Understanding how organic solvents partition and behave in the environment has led to better management approaches to solvents and solvent-containing wastes. There are many published reference books written about the environmental fate of organic chemicals in air, water, and soil.[3-7] The purpose of this section is to summarize the environmental fate of six groups of solvents (Table 17.1.1) in air, water, and soil. A knowledge of the likely pathways for the environmental fate of organic solvents can serve as the technical basis for the management of solvents and solvent-containing wastes.

Table 17.1.1. The six groups of solvents discussed in this section

Alcohols	*Chlorinated Fluorocarbons*
n-Butyl alcohol	Trichlorofluoromethane (F-11),
Isobutyl alcohol	1,1,2,2-Tetrachloro-1,2-difluoroethane (F-112)
Methanol	1,1,2-Trichloro-1,2,2-trifluoroethane (F-113)
	1,2,-Dichlorotetrafluoroethane (F-114)
Benzene Derivatives	
Benzene	*Ketones*
Chlorobenzene	Acetone
o-Cresol	Cyclohexanone
o-Dichlorobenzene	Methyl ethyl ketone
Ethylbenzene	Methy isobutyl ketone
Nitrobenzene	
Toluene	*Others*
o-Xylene	Carbon disulfide
	Diethyl ether
Chlorinated Aliphatic Hydrocarbons	Ethyl acetate
Carbon tetrachloride	Hexane
Dichloromethane	Decane (a major component of mineral spirits)
Tetrachloroethylene	Pyridine
1,1,1-Trichloroethane	Tetrahydrofuran
Trichloroethylene	

17.1.2 WATER

17.1.2.1 Solubility

One of the most important properties of an organic solvent is its solubility in water. The greater a compound's solubility, the more likely that a solvent or a solvent-containing waste will dissolve into water and become part of the hydrological cycle. Hence, water solubility can affect the extent of leaching of solvent wastes into groundwater, and the movement of dissolved solvent into rivers and lakes. Aqueous solubility also determines the efficacy of removal from the atmosphere through dissolution into precipitation. The solubility of solvents in water may be affected by temperature, salinity, dissolved organic matter, and the presence of other organic solvents.

17.1.2.2 Volatilization

Solvents dissolved in water may volatilize into the atmosphere or soil gases. A Henry's Law constant (K_H) can be used to classify the behavior of dissolved solvents. Henry's Law describes the ratio of the partial pressure of the vapor phase of an ideal gas (P_i) to its mole fraction (X_i) in a dilute solution, viz.,

$$K_{H(i)} = P_i / X_i \qquad\qquad\qquad [17.1.1]$$

In the absence of measured data, a Henry's Law constant for a given solvent may be estimated by dividing the vapor pressure of the solvent by its solubility in water (S_i) at the same temperature;

$$K_{H(i)} = P_i \, (atm) / S_i \, (mol/m^3 \; solvent) \qquad\qquad\qquad [17.1.2]$$

A K_H value of less than 10^{-4} atm-mol/m^3 suggests that volatilization would probably not be a significant fate mechanism for the dissolved solvent. The rate of volatilization is

more complex, and depends on the rate of flow, depth, and turbulence of both the body of water and the atmosphere above it. In the absence of measured values, there are a number of estimation techniques to predict the rate of removal from water.[8]

17.1.2.3 Degradation

The disappearance of a solvent from solution can also be the result of a number of abiotic and biotic processes that transform or degrade the compound into daughter compounds that may have different physicochemical properties from the parent solvent. Hydrolysis, a chemical reaction where an organic solvent reacts with water, is not one reaction, but a family of reactions that can be the most important processes that determine the fate of many organic compounds.[9] Photodegradation is another family of chemical reactions where the solvent in solution may react directly under solar radiation, or with dissolved constituents that have been made reactive by solar radiation. For example, the photolysis of water yields a hydroxyl radical:

$$H_2O + h\nu \rightarrow HO \bullet + H \qquad [17.1.3]$$

Other oxidants such as peroxy radicals ($RO_2\bullet$) and ozone can react with solvents in water. The subject of photodegradation is treated in more detail under atmospheric processes (17.1.4).

Biodegradation is a family of biologically mediated (typically by microorganisms) conversions or transformations of a parent compound. The ultimate end-products of biodegradation are the conversion of organic compounds to inorganic compounds associated with normal metabolic processes.[10] This topic will be addressed under Soil (17.1.3.3).

17.1.2.4 Adsorption

Adsorption is a physicochemical process whereby a dissolved solvent may be concentrated at solid-liquid interfaces such as water in contact with soil or sediment. In general, the extent of adsorption is inversely proportional to solubility; sparingly soluble solvents have a greater tendency to adsorb or partition to the organic matter in soil or sediment (see Soil, 17.1.3.2).

17.1.3 SOIL

17.1.3.1 Volatilization

Volatilization from soil may be an important mechanism for the movement of solvents from spills or from land disposed solvent-containing wastes. The efficacy and rate of volatilization from soil depends on the solvent's vapor pressure, water solubility, and the properties of the soil such as soil-water content, airflow rate, humidity, temperature and the adsorption and diffusion characteristics of the soil.

Organic-solvent vapors move through the unsaturated zone (the interval between the ground surface and the water-saturated zone) in response to two different mechanisms; convection and diffusion. The driving force for convective movement is the gradient of total gas pressure. In the case of diffusion, the driving force is the partial-pressure gradient of each gaseous component in the soil air. The rate of diffusion of a solvent in bulk air can be described by Fick's Law, viz.,

$$Q = -D_f \nabla_a \qquad [17.1.4]$$

where:

Q diffusive flux (mass/area-time)
D_f diffusion coefficient (area/time)
∇_a concentration gradient (mass/volume/distance)

Compared with the relatively unobstructed path for the diffusion of solvents in the atmosphere, diffusion coefficients for solvents in soil air will be less because of the tortuosity of the soil matrix pathways. Several functional relationships have been developed that relate the soil diffusion coefficient (D_s) to various soil properties (see Roy and Griffin[11]), such as the Millington Equation[12]

$$D_s = D_f \eta_a^{3.3} / \eta_t^2 \qquad\qquad [17.1.5]$$

where:

η_a the air-filled porosity, and
η_{tt} total soil porosity

17.1.3.2 Adsorption

As discussed in 17.1.2.4., adsorption by soil components can remove solvents dissolved in water. Furthermore, the rate of movement of dissolved solvents through soil may be retarded by adsorption-desorption reactions between the solvents and the solid phases. The partitioning of solvents between the liquid phase and soil is usually described by an adsorption isotherm. The adsorption of solvents may be described by the Freundlich Equation:

$$x/m = K_f C^{l/n} \qquad\qquad [17.1.6]$$

where:

x the mass adsorbed
m mass of sorbent
K_f the Freundlich constant, a soil-specific term
C the equilibrium concentration of the solvent in water, and
n the Freundlich exponent which describes the degree of non-linearity of the isotherm

When n is equal to one, the Freundlich Equation becomes a relatively simple partition function:

$$x/m = KC \qquad\qquad [17.1.7]$$

where K is an adsorption or distribution coefficient which is sometimes written as K_d. It has been known since the 1960s that the extent of adsorption of hydrophobic (sparingly soluble in water) solvents often correlates with the amount of organic matter in the soil.[13] When K_d is divided by the amount of organic carbon in the soil, the resulting coefficient is the organic carbon-water partition coefficient (K_{oc}):

$$K_d \times 100/organic\ carbon(\%) = K_{oc} \qquad\qquad [17.1.8]$$

The organic carbon-water partition coefficient is a compound-specific term that allows the user to estimate the mobility of a solvent in saturated-soil water systems if the amount or organic carbon is known. For hydrophilic solvents, K_{oc} values have been measured for many compounds. Other values were derived from empirical relationships drawn between water solubility or octanol-water partition coefficients.[13]

17.1.3.3 Degradation

Solvents may be degraded in soil by the same mechanisms as those in water. In biodegradation, microorganisms utilize the carbon of the solvents for cell growth and maintenance. In general, the more similar a solvent is to one that is naturally occurring, the more likely that it can be biodegraded into other compound(s) because the carbon is more available to the microbes. Moreover, the probability of biodegradation increases with the extent of water solubility of the compound. It is difficult to make generalities about the extent or rate of solvent biodegradation that can be expected in soil. Biodegradation can depend on the concentration of the solvent itself, competing processes that can make the solvent less available to microbes (such as adsorption), the population and diversity of microorganisms, and numerous soil properties such as water content, temperature, and reduction-oxidation potential. The rate and extent of biodegradation reported in studies appears to depend on the conditions under which the measurement was made. Some results, for example, were based on sludge-treatment plant simulations or other biological treatment facilities that had been optimized in terms of nutrient content, microbial acclimation, mechanical mixing of reactants, or temperature. Hence, these results may overestimate the extent of biodegradation in ambient soil in a spill or waste-disposal scenario.

First-order kinetic models are commonly used to describe biodegradation because of their mathematical simplicity. First-order biodegradation is to be expected when the organisms are not increasing in abundance. A first-order model also lends itself to calculating a half-life ($t_{1/2}$) which is a convenient parameter to classify the persistence of a solvent. If a solvent has a soil half-life of 6 months, then about half of the compound will have degraded in six months. After one year, about one fourth the initial amount would still be present, and after 3 half-lives (1.5 years), about 1/8 of the initial amount would be present.

Howard et al.[14] estimated ranges of half-lives for solvents in soil, water, and air. For solvents in soil, the dominant mechanism in the reviewed studies may have been biodegradation, but the overall values are indicative of the general persistence of a solvent without regard to the specific degradation mechanism(s) involved.

17.1.4 AIR

17.1.4.1 Degradation

As introduced in 17.1.2.3, solvents may be photodegraded in both water and air. Atmospheric chemical reactions have been studied in detail, particularly in the context of smog formation, ozone depletion, and acid rain. The absorption of light by chemical species generates free radicals which are atoms, or groups of atoms that have unpaired electrons. These free radicals are very reactive, and can degrade atmospheric solvents. Atmospheric ozone, which occurs in trace amounts in both the troposphere (sea level to about 11 km) and in the stratosphere (11 km to 50 km elevation), can degrade solvents. Ozone is produced by the photochemical reaction:

$$O_2 + h\nu \rightarrow O + O \qquad\qquad [17.1.9]$$

$$O + O_2 \rightarrow O_3 + M \qquad\qquad [17.1.10]$$

where M is another species such as molecular nitrogen that absorbs the excess energy given off by the reaction. Ozone-depleting substances include the chlorofluorocarbons (CFC) and carbon tetrachloride in the stratosphere.

17.1.4.2 Atmospheric residence time

Vapor-phase solvents can dissolve into water vapor, and be subject to hydrolysis reactions and ultimately, precipitation (wet deposition), depending on the solubility of the given solvent. The solvents may also be adsorbed by particulate matter, and be subject to dry deposition. Lyman[16] asserted that atmospheric residence time cannot be directly measured; that it must be estimated using simple models of the atmosphere. Howard et al.[14] calculated ranges in half-lives for various organic compounds in the troposphere, and considered reaction rates with hydroxyl radicals, ozone, and by direct photolysis.

17.1.5 THE 31 SOLVENTS IN WATER

17.1.5.1 Solubility

The solubility of the solvents in Table 17.1.1 ranges from those that are miscible with water to those with solubilities that are less than 0.1 mg/L (Table 17.1.2). Acetone, methanol, pyridine and tetrahydrofuran will readily mix with water in any proportion. The solvents that have an aqueous solubility of greater than 10,000 mg/L are considered relatively hydrophillic as well. Most of the benzene derivatives and chlorinated fluorocarbons are relatively hydrophobic. Hexane and decane are the least soluble of the 31 solvents in Table 17.1.1. Most material safety data sheets for decane indicate that the n-alkane is "insoluble" and that the solubility of hexane is "negligible." How the solubility of each solvent affects its fate in soil, water, and air is illustrated in the following sections.

Table 17.1.2. The solubility of the solvents in water at 25°C

Solubility, mg/L	Solvent (reference)	
∞	Acetone (1) Methanol (1) Pyridine (1) Tetrahydrofuran (1)	Miscible
239,000	Methyl ethyl ketone (4)	
77,000 76,000 64,000 60,050 25,950 23,000 20,400 13,000	n-Butyl alcohol (4) Isobutyl alcohol (4) Ethyl acetate (4) Diethyl ether (4) o-Cresol (17) Cyclohexanone (4) Methyl isobutyl ketone (4) Dichloromethane (4)	Relatively hydrophillic
2,100 1,900 1,780 1,495 1,100 1,080	Carbon disulfide (4) Nitrobenzene (18) Benzene (19) 1,1,1-Trichloroethane (4) Trichloroethylene (4) F-11 (4)	

Solubility, mg/L	Solvent (reference)	
805	Carbon tetrachloride (4)	
535	Toluene (20)	
472	Chlorobenzene (17)	
175	o-Xylene (4)	
170	F-113 (4)	Relatively hydrophobic
161	Ethylbenzene (17)	
156	o-Dichlorobenzene (17)	
150	Tetrachloroethylene (4)	
130	F-114 (4)	
120	F-112 (4)	
9.5	Hexane (21)	
0.05	Decane (22)	"Insoluble"

17.1.5.2 Volatilization from water

Henry's Law constants were compiled for each of the solvents in Table 17.1.1. The numerical values ranged over 7 orders of magnitude (Table 17.1.3). Based on these values, it can be expected that volatilization from water will be a significant fate mechanism for decane, hexane, the chlorinated fluorocarbons, carbon tetrachloride, tetrachloroethylene and trichloroethylene. Many of the solvents in Table 17.1.1 are characterized by K_H values of 10^{-3} to 10^{-2} atm-m^3/mole; volatilization from water can be an important pathway for these solvents, depending on the specific situation. Volatilization may be a relatively slow process for the remaining solvents. The actual rate of volatilization of some solvents from water has been experimentally measured.[4,17] However, experimental data are lacking for some compounds, and the diversity of experimental conditions makes generalizations difficult. Thomas[8] described a two-layer model of the liquid-gas interface that is based on a Henry's Law constant and mass-transfer coefficients. To illustrate the relative volatilities of the solvents in water, the half-lives of each solvent in a shallow stream were compiled (Table 17.1.4). The stream was assumed to be 1 meter deep and flowing at a rate of 1 meter per second. With the exception of hexane, it was also assumed that there was a breeze blowing across the stream at a rate of 3 meters per second. Under these conditions, the predicted half-lives of many of the solvents in Table 16.1.1 are less than 10 hours, indicating that volatilization into the atmosphere can be a relatively rapid pathway for solvents released to surface water. The volatilization of pyridine, isobutyl alcohol, and cyclohexanone may be a slow process, and other fate processes may be more important in water.

17.1.5.3 Degradation in water

As mentioned in 17.1.3.3, Howard et al.[14] compiled ranges of half-life values for most of the organic solvents given in Table 17.1.1. If a "rapid" half-life is defined as in the range of 1 to 10 days, then about 12 of the solvents in Table 17.1.1 may degrade rapidly in surface water by primarily biodegradation (Figures 17.1.1 and 17.1.2). Abiotic mechanisms such as photo-oxidation, photolysis, and hydrolysis appear to be either slow or not significant. If "slow degradation" is defined as that taking longer than 100 days, then it appears that F-11 and most of the chlorinated hydrocarbons may be relatively persistent in surface water. The available data suggest that the half-life of nitrobenzene and isobutyl alcohol may be variable. Note that data were not available for all of the solvents listed in Table 17.1.1. In

Table 17.1.3. Henry's Law constants (K_H) for the solvents at 25°C

K_H, atm-m^3/mole	Solvent (reference)
6.98	Decane (22)
2.8	F-114 (4)
1.69	Hexane (21)
0.53	F-113 (4)
9.74 x 10^{-2}	F-112 (4)
9.70 x 10^{-2}	F-11 (4)
3.04 x 10^{-2}	Carbon tetrachloride (4)
1.49 x 10^{-2}	Tetrachloroethylene (4)
1.03 x 10^{-2}	Trichloroethylene (4)
9.63 x 10^{-3}	Tetrahydrofuran (4)
8.4 x 10^{-3}	Ethylbenzene (17)
8.0 x 10^{-3}	1,1,1-Trichloroethane (4)
7.0 x 10^{-3}	Pyridine (4)
5.94 x 10^{-3}	Toluene (4)
5.43 x 10^{-3}	Benzene (4)
5.1 x 10^{-3}	o-Xylene (4)
3.58 x 10^{-3}	Chlorobenzene (23)
2.68 x 10^{-3}	Dichloromethane (4)
1.4 x 10^{-3}	Carbon disulfide (4)
1.2 x 10^{-3}	o-Dichlorobenzene (4)
7.48 x 10^{-4}	Diethyl ether (11)
4 x 10^{-4}	Isobutyl alcohol (4)
1.35 x 10^{-4}	Methanol (4)
1.2 x 10^{-4}	Ethyl acetate (4)
9.4 x 10^{-5}	Methyl isobutyl ketone (4)
4.26 x 10^{-5}	Acetone (1)
2.44 x 10^{-5}	Nitrobenzene (2)
1.2 x 10^{-5}	Cyclohexanone (4)
1.05 x 10^{-5}	Methyl ethyl ketone (4)
5.57 x 10^{-6}	n-Butyl alcohol (4)
1.2 x 10^{-6}	o-Cresol (4)

Table 17.1.4. Estimated half-lives for the solvents in water at 20°C

Half life, h	Solvent
1.6	Tetrahydrofuran
2.6	Carbon disulfide
2.7	Hexane[a]
2.9	Toluene
3.0	Dichloromethane
3.1	Ethylbenzene
3.2	o-Xylene
3.4	Trichloroethylene, F-11
3.7	Carbon tetrachloride
4.0	F-112, F-113, F-114
4.2	Tetrachloroethylene
4.4	o-Dichlorobenzene
4.6	Chlorobenzene
5.3	Methanol
10	Ethyl acetate
18	Acetone
45	Nitrobenzene
74	Cyclohexanone
80	Isobutyl alcohol
90	Pyridine

[a]Based on a wind speed of 1 meter per second.[21]

groundwater, the half-life values proposed by Howard et al.[14] appear to be more variable than those for surface water. For example, the half-life of benzene ranges from 10 days in aerobic groundwater to 2 years in anaerobic groundwater.[19] Such ranges in half-lives make meaningful generalizations difficult. However, it appears that methanol, n-butyl alcohol, and other solvents (see Figures 17.1.1 and 17.1.2) may biodegrade in groundwater with a half-life that is less than 60 days. As with surface water, the chlorinated hydrocarbons may be relatively persistent in groundwater. Howard et al.[14] cautioned that some of their proposed half-life generalizations were based on limited data or from screening studies that were extrapolated to surface and groundwater. Scow[10] summarized that it is currently not possible to predict rates of biodegradation because of a lack of standardized experimental methods, and because the variables that control rates are not well understood. Hence, Figures 17.1.1 and 17.1.2 should be viewed as a summary of the potential for each solvent to degrade, pending more site-specific information.
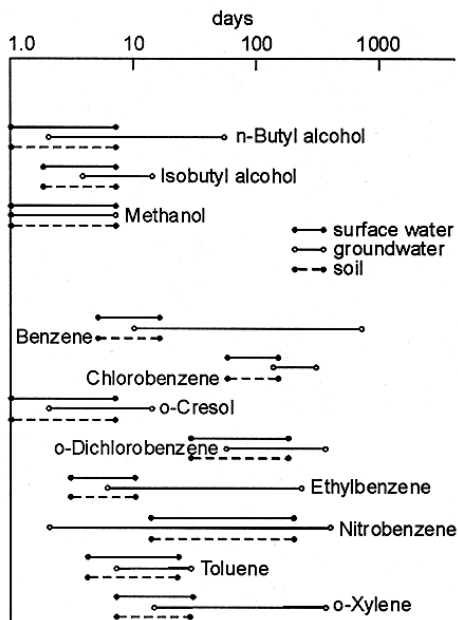
Figure 17.1.1. The ranges in degradation half-lives for the alcohols and benzene derivatives in surface water, groundwater, and soil (data from Howard et al.[14]).
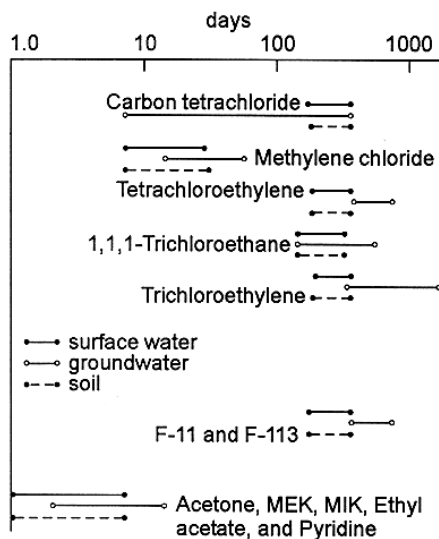
Figure 17.1.2. The ranges in degradation half-lives for the chlorinated aliphatic hydrocarbons, F-11 and F-113, and ketones in surface water, groundwater, and soil (data from Howard et al.[14]).

17.1.6 SOIL

17.1.6.1 Volatilization

Soil diffusion coefficients were estimated for most of the solvents in Table 17.1.1. Using the Millington Equation, the resulting coefficients (Table 17.1.5) ranged from 0.05 to 0.11 m^2/day. Hence, there was little variation in magnitude between the values for these particular solvents. As discussed in Thomas[24] the diffusion of gases and vapors in unsaturated soil is a relatively slow process. The coefficients in Table 17.1.5 do not indicate the rate at which olvents can move in soil; such rates must be either measured experimentally or predicted using models that require input data such as soil porosity, moisture content, and the concentrations of the solvents in the vapor phase to calculate fluxes based solely on advective movement. Variations in water content, for example, will control vapor-phase movement. The presence of water can reduce the air porosity of soil, thereby reducing the soil diffusion coefficient (Eq. 17.1.5). Moreover, relatively water-soluble chemicals may dissolve into water in the vadose zone. Hence, water can act as a barrier to the movement of solvent vapors from the subsurface to the surface.

Solvents spilled onto the surface of soil may volatilize into the atmosphere. The Dow Method[24] was used in this section to estimate half-life values of each solvent if spilled on the surface of a dry soil. The Dow Method is a simple relationship that was derived for the evaporation of pesticides from bare soil;

$$t_{1/2} \ (days) = 1.58 \times 10^{-8} \ (K_{oc}S/P_v) \qquad\qquad [17.1.11]$$

Table 17.1.5. Estimated soil diffusion coefficients D$_s$ (from Roy and Griffin[11])

Solvent	D$_s$, m^2/day
n-Butyl alcohol	0.062 (25ºC)
Isobutyl alcohol	0.050 (0ºC)
Methanol	0.111 (25ºC)
Benzene	0.060 (15ºC)
Chlorobenzene	0.052 (30ºC)
o-Cresol	0.053 (15ºC)
o-Dichlorobenzene	0.049 (20ºC)
Ethylbenzene	0.046 (0ºC)
Nitrobenzene	0.050 (20ºC)
Toluene	0.058 (25ºC)
o-Xylene	0.049 (15ºC)
Carbon tetrachloride	0.051 (25ºC)
Dichloromethane	0.070 (15ºC)
Tetrachloroethylene	0.051 (20ºC)
1,1,1-Trichloroethane	0.075 (20ºC)
Trichloroethylene	0.058 (15ºC)
F-11	0.060 (15ºC)
F-112	-
F-113	0.053 (15ºC)
F-114	0.056 (15ºC)
Acetone	0.076 (0ºC)
Cyclohexanone	-
Methyl ethyl ketone	-
Methyl isobutyl ketone	-
Carbon disulfide	0.074 (25ºC)
Diethyl ether	0.054 (0ºC)
Ethyl acetate	0.059 (25ºC)
Hexane	-
Mineral spirits	-
Pyridine	-
Tetrahydrofuran	-

Table 17.1.6. Estimated soil-evaporation half lives

Solvent	Half-life, min.
o-Cresol	38
Nitrobenzene	19
n-Butyl alcohol	18
Pyridine	8
Decane	4
Isobutanol Cyclohexanone	1
All other solvents	<1

where:

$t_{1/2}$	evaporation half-life (days)
K_{oc}	organic carbon-water partition coefficient (L/kg)
S	solubility in water (mg/L), and
P_v	vapor pressure (mm Hg at 20ºC)

The resulting estimated half-life is inversely proportional to vapor pressure; the greater the vapor pressure, the greater the extent of volatilization. Conversely, the rate of volatilization will be reduced if the solvent readily dissolves into water or is adsorbed by the soil. Organic carbon-water partition coefficients were compiled for each solvent (see 17.1.6.2.), and vapor pressure data (not shown) were collected from Howard.[4] The resulting half-life estimates (Table 17.1.6) indicated that volatilization would be a major pathway if the liquid solvents were spilled on soil; all of the half-life estimates were less than one hour. Thomas[24] cautioned, however, that soil moisture, soil type, temperature, and wind conditions were not incorporated in the simple Dow Model.

Table 17.1.7. The organic carbon-water partition coefficients (K$_{oc}$) of the solvents at 25°C

K$_{oc}$, L/kg	Solvent (reference)	
<1	Methanol (13), Tetrahydrofuran[a]	
1 4 7 8 9	Acetone (13) Methyl ethyl ketone (13) Pyridine (13) Ethyl acetate, isobutyl alcohol (13) Diethyl ether (13)	Mobile
10 20 24 25 63 67 72 97	Cyclohexanone (13) o-Cresol (17) Methyl isobutyl ketone (13) Dichloromethane (13) Carbon disulfide (13) Nitrobenzene (13) n-Butyl alcohol (4) Benzene (13)	
110 152 155 164 242 303 318 343 363 372 437 457 479	Carbon tetrachloride (4) Trichloroethylene (13) 1,1,1-Trichloroethane (13) Ethylbenzene (17) Toluene (26) Tetrachloroethylene (13) Chlorobenzene (13) o-Dichlorobenzene (25) o-Xylene (13) F-113 (13) F-114 (13) F-112 (13) F-11 (13)	Relatively mobile
1,950	Hexane (21)	Relatively Immobile
57,100[a]	Decane	

[a]Calculated using the relationship logK$_{oc}$ = 3.95 - 0.62logS where S = water solubility in mg/L (see Hassett et al.[25])

17.1.6.2 Adsorption

Organic carbon-water partition coefficients were compiled (Table 17.1.7) for each of the solvents in Table 17.1.1. A K$_{oc}$ value is a measure of the affinity of a solvent to partition to organic matter which in turn will control the mobility of the solute in soil and groundwater under convective flow. Although the actual amount of organic matter will determine the extent of adsorption, a solvent with a K$_{oc}$ value of less than 100 L/kg is generally regarded as relatively mobile in saturated materials. Hence, adsorption may not be a significant fate mechanism for 16 of the solvents in Table 17.1.1. In contrast, adsorption by organic matter may be a major fate mechanism controlling the fate of three of the benzene derivatives, and most of the chlorinated compounds. Hexane and particularly decane would likely be relatively immobile. However, when the organic C content of an adsorbent is less than about 1
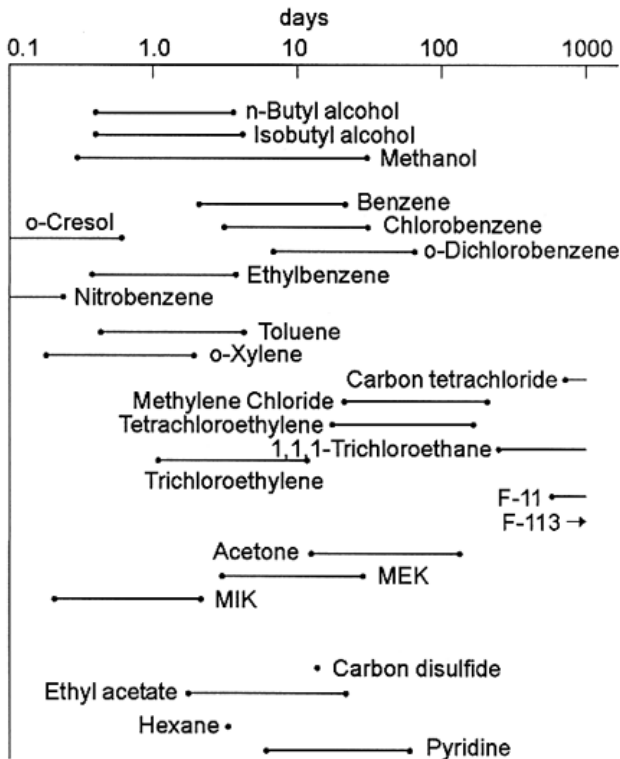
Figure 17.1.3. The ranges in atmospheric half-life of the solvents in Table 17.1.1 (data from Howard et al.[14] and ATSDR[21]).

g/kg, the organic C fraction is not a valid predictor of the partitioning of nonpolar organic compounds,[27] and other properties such as pH, surface area, or surface chemistry contribute to or dominate the extent of adsorption. Moreover, pyridine occurs at a cation (pKa = 5.25) over a wide pH range, and thus it is adsorbed by electrostatic interactions rather than by the hydrophobic mechanisms that are endemic to using K_{oc} values to predict mobility.

The desorption of solvents from soil has not been extensively measured. In the application of advection-dispersion models to predict solute movement, it is generally assumed that adsorption is reversible. However, the adsorption of the solutes in Table 17.1.1 may not be reversible. For example, hysteresis is often observed in pesticide adsorption-desorption studies with soils.[28] The measurement and interpretation of desorption data for solid-liquid systems is not well understood.[29,30] Once adsorbed, some adsorbates may react further to become covalently and irreversibly bound, while others may become physically trapped in the soil matrix.[28] The non-singularity of adsorption-desorption may sometimes result from experimental artifacts.[28,31]

17.1.6.3 Degradation

As discussed in 17.1.3.3., Howard et al.[14] also estimated soil half-life values (Figures 17.1.1 and 17.1.2) for the degradation of most of the solvents in Table 17.1.1. Biodegradation was cited as the most rapid process available to degrade solvents in a biologically active soil. The numerical values obtained were often the same as those estimated for surface water.

Consequently, it appears likely that the alcohols, ketones, o-cresol, ethyl acetate, and pyridine will degrade rapidly in soil if rapidly is defined as having a half-life of 10 days or less. Most of the benzene derivatives, F-11, and the chlorinated aliphatic hydrocarbons may be relatively persistent in soil. Analogous information was not located for diethyl ether, hexane, decane, or tetrahydrofuran. ATSDR[21] for example, found that there was little information available for the degradation of n-hexane in soil. It was suggested that n-hexane can degrade to alcohols, aldehydes, and fatty acids under aerobic conditions.

17.1.7 AIR

Once released into the atmosphere, the most rapid mechanism to attenuate most of the solvents in Table 17.1.1 appears to be by photo-oxidation by hydroxyl radicals in the troposphere. Based on the estimates by Howard et al.,[14] it appeared that nine of the solvents can be characterized by an atmospheric residence half-life of 10 days or less (Figure 17.1.3). The photo-oxidation of solvents yields products. For example, the reaction of OH radicals with n-hexane can yield aldehydes, ketones, and nitrates.[21]

The reaction of some of the solvents with ozone may be much slower. For example, the half-life for the reaction of benzene with ozone may be longer than 100 years.[19] Solvents such as carbon tetrachloride, 1,1,1-trichloroethane, and the chlorinated fluorocarbons may be relatively resistant to photo-oxidation. The major fate mechanism of atmospheric 1,1,1-trichloroethane, for example, may be wet deposition.[32]

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17.2 FATE-BASED MANAGEMENT OF ORGANIC SOLVENT-CONTAINING WASTES[a]

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17.2.1 INTRODUCTION

The wide spread detection of dissolved organic compounds in groundwater is a major environmental concern, and has led to greater emphasis on incineration and waste minimization when compared with the land disposal of solvent-containing wastes. The movement and environmental fate of dissolved organic solvents from point sources can be approximated by the use of computer-assisted, solute-transport models. These models require information about the composition of leachate plumes, and site-specific hydrogeological and chemical

[a]Publication authorized by the Chief, Illinois State Geological Survey

data for the leachate-site system. A given land-disposal site has a finite capacity to attenuate organic solvents in solution to environmentally acceptable levels. If the attenuation capacity of a site can be estimated, then the resulting information can be used as criteria to make decisions as to what wastes should be landfilled, and what quantities of solvent in a given waste can be safely accepted. The purpose of this section is to summarize studies[1-3] that were conducted that illustrate how knowledge of the environmental fate and movement of the solvents in Section 17.1 can be used in managing solvent-containing wastes. These studies were conducted by using computer simulations to assess the fate of organic compounds in leachate at a waste-disposal site.

17.2.1.1 The waste disposal site

There are three major factors that will ultimately determine the success of a land-disposal site in being protective of the environment with respect to groundwater contamination by organic solvents: (1) the environmental fate and toxicity of the solvent; (2) the mass loading rate, i.e., the amount of solvent entering the subsurface during a given time, and (3) the total amount of solvent available to leach into the groundwater. The environmental fate of the solvents was discussed in 17.1.

The hypothetical waste-disposal site used in this evaluation (Figure 17.2.1) had a single waste trench having an area of 0.4 hectare. Although site-specific dimensions may be assigned with actual sites, this hypothetical site was considered representative of many situations found in the field. The trench was 12.2 meters (40 ft) deep and was constructed with a synthetic/compacted-soil double-liner system. The bottom of the trench was in direct contact with a sandy aquifer that was 6.1 meters (20 ft) thick. The top of the water table was defined as being at the top of the sandy aquifer. Thus, this site was designed as a worst-case scenario. The sandy aquifer directly beneath the hazardous-waste trench would offer little resistance to the movement of contaminants. To further compound a worst-case situation, it was also assumed that the entire trench was saturated with leachate, generating a 12.2 meter (40 ft) hydraulic head through the liner. This could correspond to a situation where the trench had completely filled with leachate because the leachate collection system had either failed or the site had been abandoned.

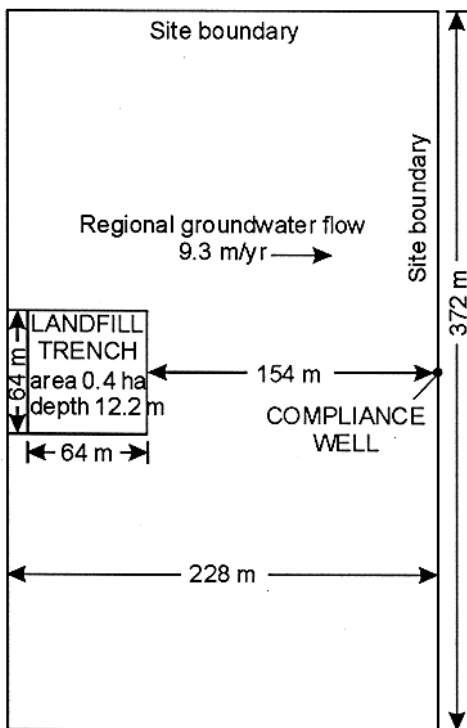The following aquifer properties, typical of sandy materials,[1] were used in the study:

Figure 17.2.1. Design of the waste-disposal site model used in the simulations (Roy et al.[1]).

saturated hydraulic conductivity = 10^{-3} cm/sec
saturated volumetric water content = 0.36 cm^3/cm^3
dry bulk density = 1.7 g/cm^3
hydraulic gradient = 0.01 cm/cm
mean organic carbon content = 0.18%

These aquifer properties yield a groundwater flow rate of 9.3 meters (30 ft) per year. The direction of groundwater flow is shown in Figure 17.2.1 to be from left to right. The edge of the disposal trench was 154 meters (500 ft) from a monitoring well that was open to the entire thickness of the aquifer. This monitoring well served as a worst-case receptor because it was placed in the center of the flow path at the site boundary and it served as the compliance point for the site. The downgradient concentrations of organic solvents at the compliance well, as predicted by a solute-transport model, were used to evaluate whether the attenuation capacity of the site was adequate to reduce the contaminants to acceptable concentrations before they migrated beyond the compliance point.

17.2.1.2 The advection-dispersion model and the required input

The 2-dimensional, solute-transport computer program PLUME was used to conduct contaminant migration studies. Detailed information about PLUME, including boundary conditions and quantitative estimates of dispersion and groundwater dilution, were summarized by Griffin and Roy.[3] In this relatively simple and conservative approach, PLUME did not take into account volatilization from water. Volatilization is a major process for many of the solvents (see Section 17.1). Adsorption was assumed to be reversible, and soil-water partition coefficients were calculated by assuming that the aquifer contained 0.18% organic carbon (see Roy and Griffin[4]). A degradation half-life was assigned to each solvent (Table 17.2.1). In many cases, conservative half-life values were used. For example, all of the ketones were assigned a half-life of 5 years, which is much longer than those proposed for ketones in groundwater (see Section 17.1). The movement of each solvent was modeled separately whereas it should be recognized that solvents in mixtures may have different chemical properties that can ultimately affect their fate and movement.

17.2.1.3 Maximum permissible concentrations

Central to the type of assessment is a definition of an environmentally acceptable concentration of each contaminant. These acceptable levels were defined as Maximum Permissible Concentrations (MPC), and were based on the toxicological assessments of solvents in drinking water by George and Siegel.[5] These MPC levels (Table 17.2.1) are not the same levels as the current Maximum Contaminant Levels (MCL) that were promulgated by the U.S. Environmental Protection Agency for drinking water.

17.2.1.4 Distribution of organic compounds in leachate

An initial solute concentration must be selected for the application of solute transport models. An initial concentration for each solvent was based on the chemical composition of leachates from hazardous-waste sites.[1] Where available, the largest reported concentration was used in the modeling efforts (Table 17.2.1). No published data were located for some of the solvents such as cyclohexanone. In such cases, the initial concentration was arbitrarily assigned as 1,000 mg/L or it was equated to the compound's solubility in water. Hexane, decane, and tetrahydrofuran were not included in these studies.

The amount of mass of each organic compound entering the aquifer via the double-liner system was calculated using these initial leachate concentrations. There was a continuous 12.2-meter head driving the leachate through the liner. Leachate was predicted to

break through the liner in 30 years. Under these conditions, approximately 131,720 L/year/acre of leachate would seep through the liner. The assumptions used in deriving this flow estimate were summarized in Roy et al.[1]

Table 17.2.1. The six groups of solvents discussed in this section, their corresponding Maximum Permissible Concentrations (MPC), the largest reported concentrations in leachate (LC), and the assigned half-lives from Roy et al.[1]

	MPC, μg/L	LC, mg/L	Half-life, years
Alcohols			
n-Butyl alcohol	2,070	1,000	5
Isobutyl alcohol	2,070	1,000	5
Methanol	3,600	42.4	5
Benzene Derivatives			
Benzene	1.6	7.37	20
Chlorobenzene	488	4.62	20
o-Cresol	304	0.21	20
o-Dichlorobenzene	400	0.67	50
Ethylbenzene	1,400	10.1	10
Nitrobenzene	19,800	0.74	20
Toluene	14,300	100	10
o-Xylene	14,300	19.7	10
Chlorinated Aliphatic Hydrocarbons			
Carbon tetrachloride	0.4	25.0	50
Dichloromethane	0.19	430	20
Tetrachloroethylene	0.80	8.20	20
1,1,1-Trichloroethane	6.00	590	50
Trichloroethylene	2.70	260	20
Chlorinated Fluorocarbons			
Trichlorofluoromethane (F-11)	0.19	0.14	50
1,1,2,2-Tetrachloro-1,2-difluoroethane (F-112)	0.19	120	50
1,1,2-Trichloro-1,2,2-trifluoroethane (F-113)	0.19	170	stable
1,2,-Dichlorotetrafluoroethane (F-114)	0.19	130	stable
Ketones			
Acetone	35,000	62	5
Cyclohexanone	3,500	1,000	5
Methyl ethyl ketone	30,000	53.0	5

	MPC, µg/L	LC, mg/L	Half-life, years
Methyl isobutyl ketone	143	10.0	5
Others			
Carbon disulfide	830	1,000	10
Diethyl ether	55,000	1,000	5
Ethyl acetate	55,000	1,000	5
Pyridine	207	1,000	20

A mass-loading rate was conservatively calculated for each solvent as,

$$M_{lr} = Q \times C_l \qquad [17.2.1]$$

where:

    M_{lr} the mass loading rate (mass/time/area),
    Q calculated leachate flux (131.7 kL/year/hectare), and
    C_l largest concentration of the solvent in leachate (mg/L)

17.2.2 MOVEMENT OF SOLVENTS IN GROUNDWATER

Ketones and alcohols have little tendency to be adsorbed by soil materials (see Section 17.1), and would appear at the compliance point only a few years after liner breakthrough (Figure 17.2.2). Because the mass loading rates were held constant, the ketones and alcohols assumed maximum steady-state concentrations after approximately 40 to 50 years (Figure 17.2.3). These two classes of organic solvents degrade readily, reducing their downgradient concentrations. The distribution of the benzene derivatives at the compliance well depended substantially on their soil-water partition coefficients, their tendencies to de-
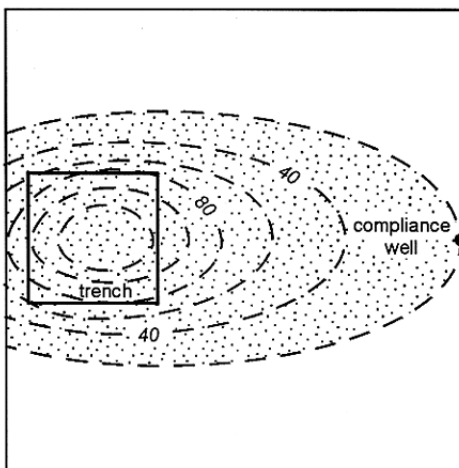

Figure 17.2.2. The predicted distribution of methyl ethyl ketone (mg/L) in the aquifer 100 years after the leachate has broken through the liner (Griffin and Roy[3]).
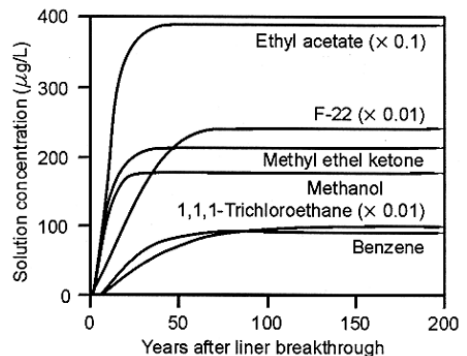
Figure 17.2.3. The predicted concentrations of methyl ethyl ketone, methanol, benzene, 1,1,1-trichloroethane, ethyl acetate, and F-22 at the compliance point as a function of time (Roy et al.[1]).

grade, and the initial concentrations. Under the conditions described, the relative steady-state concentrations of the benzene derivatives were: toluene > benzene > chlorobenzene > p-xylene > nitrobenzene > o-dichlorobenzene > o-cresol > ethyl benzene. Methylene chloride and 1,1,1-trichlorethane would dominate the chlorinated hydrocarbons. Among the group of unrelated organic solvents, the concentration of pyridine at the well was predicted to increase rapidly. Pyridine would eventually dominate this group in the relative order: pyridine > carbon disulfide > ethyl acetate > diethyl ether. The relative order of fluorocarbons at the compliance well in terms of concentration was: F-21, F-22 >> F-12 > F-113 > F-114 > F-112 > R-112a > FC-115 >> F-11.

In brief, the computer simulations predicted that all 28 organic compounds would eventually migrate from the waste trench, and be detected at the compliance well. The predicted concentrations varied by four orders of magnitude, and were largely influenced by the initial concentrations used in calculating the mass loading rate to the aquifer.

17.2.3 MASS LIMITATIONS

The next step in this analysis was to determine whether these predicted concentrations would pose an environmental hazard by evaluating whether the site was capable of attenuating the concentrations of the organic compounds to levels that are protective of human health. In Figure 17.2.4 the predicted steady-state concentrations of the organic compounds
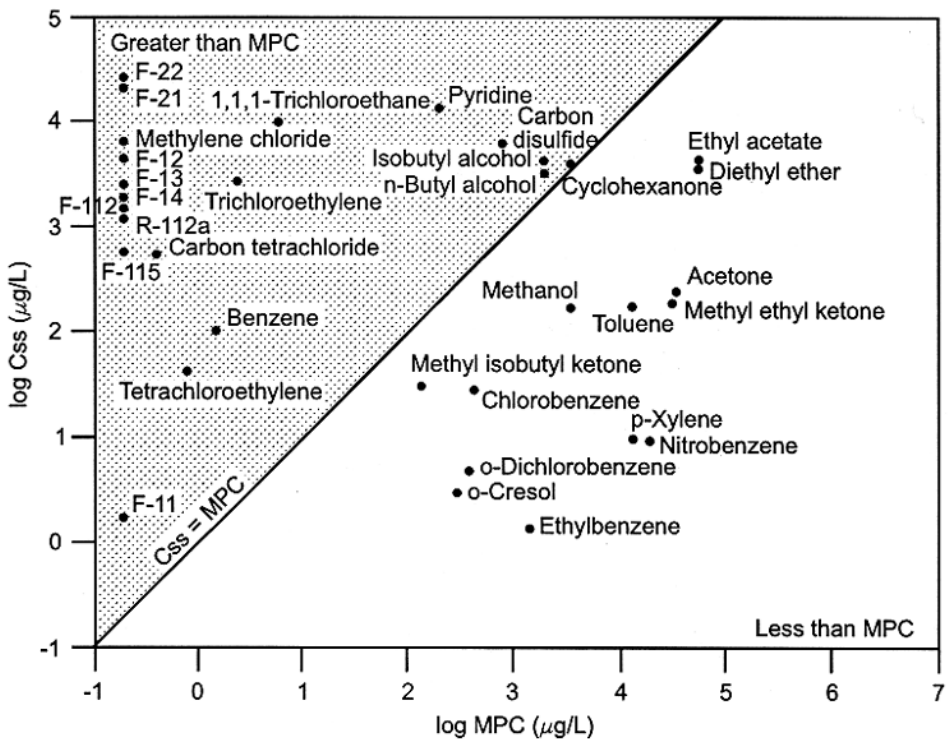

Figure 17.2.4. The predicted steady-state concentrations (Css) of each solvent in groundwater at the compliance point as a function of its Maximum Permissible (MPC) Concentration (Roy et al.[1]).

in groundwater at the compliance well were plotted against their MPCs. The boundary shown in Figure 17.2.4 represents the situation where the steady-state concentration (Css) equals the MPC. Consequently, the predicted Css is less than its corresponding MPC when the Css of a given compound plots in the lower-right side. In this situation, these organic compounds could enter the aquifer at a constant mass loading rate without exceeding the attenuation capacity of the site. The steady-state concentrations of twenty solvents exceeded their corresponding MPCs. The continuous addition of these organic compounds (i.e., a constant mass loading rate) would exceed the site's ability to attenuate them to environmentally acceptable levels in this worst-case scenario. There are two avenues for reducing the steady-state concentrations downgradient from the trench: (1) reduce the mass loading rate, and/or (2) reduce the mass of organic compound available to leach into the aquifer. Because, the RCRA-required double liner was regarded as the state-of-the-art with respect to liner systems, it was not technically feasible to reduce the volume of leachate seeping into the aquifer under the conditions imposed. The worst-case conditions could be relaxed by assuming a lower leachate head in the landfill or by providing a functional leachate-collection system. Either condition would be reasonable and would reduce the mass loading rate. Another alternative is to reduce the mass available for leaching. In the previous simulations, the mass available to enter the aquifer was assumed to be infinite. Solute transport models can be used to estimate threshold values for the amounts of wastes initially landfilled.[2] A threshold mass (M_t) can be derived so that the down-gradient, steady-state concentrations will be less than the MPC of the specific compound, viz.,

$$M_t = V(MPC \times 1000)\, t \qquad\qquad\qquad\qquad [17.2.2]$$

where:

M_t	the threshold mass in g/hectare
V	the volume of leachate entering the aquifer in L/yr/hectare
MPC	the maximum permissible concentration as g/L, and
t	time in years; the amount of time between liner breakthrough and when the predicted concentration of the compound in the compliance well equals its MPC.

Using this estimation technique, Roy et al.[1] estimated mass limitations for the compounds that exceeded their MPCs in the simulations. They found that benzene, carbon tetrachloride, dichloromethane, pyridine, tetrachloroethylene, 1,1,1-trichloroethylene, trichloroethylene and all chlorinated fluorocarbons would require strict mass limitations (<250 kg/ha). Other solvents could be safely landfilled at the site without mass restrictions: acetone, chlorobenzene, cresols, o-dichlorobenzene, diethyl ether, ethyl acetate, ethylbenzene, methanol, methyl ethyl ketone, methyl isobutyl ketone, nitrobenzene, toluene, and xylene. Some solvents (cyclohexanone, n-butyl alcohol, isobutyl alcohol, and carbon disulfide) would require some restrictions to keep the attenuation capacity of the site from being exceeded.

These studies,[1-3] demonstrated that the land disposal of wastes containing some organic solvents at sites using best-available liner technology may be environmentally acceptable. Wastes that contain chlorinated hydrocarbons, however, may require pretreatment such as incineration or stabilization before land disposal. If the mass-loading rate is controlled and the attenuation capacity of the site is carefully studied, the integrated and multidisciplinary approach outlined in this section can be applied to the management of solvent-containing wastes.

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17.3 ENVIRONMENTAL FATE AND ECOTOXICOLOGICAL EFFECTS OF GLYCOL ETHERS

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17.3.1 INTRODUCTION

Glycol ethers and their acetates are widely used as solvents in the chemical, painting, printing, mining and furniture industries. They are employed in the production of paints, coatings, resins, inks, dyes, varnishes, lacquers, cleaning products, pesticides, deicing additives for gasoline and jet fuel, and so on.[1] In 1997, the world production of glycol ethers was about 900,000 metric tons.[2]

There are two distinct series of glycol ethers namely the ethylene glycol ethers which are produced from ethylene oxide and the propylene glycol ethers derived from propylene oxide. The former series is more produced and used than the latter. Thus, inspection of the 42,000 chemical substances recorded by INRS (France) in the SEPIA data bank, between 1983 and 1998, reveals that 10% of them include ethylene glycol ethers and about 4% propylene glycol ethers.[2] However, due to the reproductive toxicity of some ethylene glycol monoalkyl ethers,[3-5] it is important to note that the worldwide tendency is to replace these chemicals by glycol ethers belonging to the propylenic series.[2]

Given the widespread use of glycol ethers, it is obvious that these chemicals enter the environment in substantial quantities. Thus, for example, the total releases to all environmental media in the United States for ethylene glycol monomethyl ether and ethylene glycol monoethyl ether in 1992 were 1688 and 496 metric tons, respectively.[6] However, despite the potential hazard of these chemicals, the problems of the environmental contaminations with glycol ethers have not received much attention. There are two main reasons for this. First, these chemicals are not classified as priority pollutants, and hence, their occurrence in the different compartments of the environment is not systematically investigated. Thus, for example, there are no glycol ethers on the target list for the Superfund hazardous waste site cleanup program.[6] Second, glycol ethers are moderately volatile colorless liquids with a high water solubility and a high solubility with numerous solvents. Consequently, the clas-

sical analytical methods routinely used for detecting the environmental pollutants do not provide reliable results with the glycol ethers, especially in the aquatic environments.

Under these conditions, the aim of this chapter is to review the available literature on the occurrence, environmental fate, and ecotoxicity of glycol ethers.

17.3.2 OCCURRENCE

Despite the poor applicability of the most widely used USEPA analytical methods, some ethylene, diethylene, and triethylene glycol ethers have been reported as present in Superfund hazardous waste sites in the US more often than some of the so-called priority pollutants.[6] More specifically, Eckel and co-workers[6] indicated that in Jacksonville (Florida), a landfill received a mixture of household waste and wastes from aircraft maintenance and paint stripping from 1968 to 1970. In 1984, sampling of residential wells in the vicinity revealed concentrations of 0.200, 0.050, and 0.010 mg/l of diethylene glycol diethyl ether, ethylene glycol monobutyl ether, and diethylene glycol monobutyl ether, respectively. One year later, concentrations of 0.050 to 0.100 mg/l of diethylene glycol diethyl ether were found in the most contaminated portion of the site. In 1989, some samples still indicated the presence of diethylene glycol diethyl ether and triethylene glycol dimethyl ether. This case study clearly illustrates that glycol ethers may persist in the environment for many years after a contamination. Concentrations of 0.012 to 0.500 mg/l of ethylene glycol monobutyl ether were also estimated in residential wells on properties near a factory (Union Chemical, Maine, USA) manufacturing furniture stripper containing N,N-dimethylformamide. In addition, in one soil sample located in that site, a concentration of 0.200 mg/kg of ethylene glycol monobutyl ether was also found. In another case study, Eckel and co-workers[6] showed that ethylene glycol diethyl ether was detected with estimated concentrations in the range from 0.002 to 0.031 mg/l in eight residential wells adjacent to a landfill (Ohio) receiving a mixture of municipal waste and various industrial wastes, many of them from the rubber industry. Last, ethylene glycol monomethyl ether was detected in ground-water samples at concentrations of 30 to 42 mg/l (Winthrop landfill, Maine).[6]

In 1991, the high resolution capillary GC-MS analysis of a municipal wastewater collected from the influent of the Asnières-sur-Oise treatment plant located in northern suburban Paris (France) revealed the presence of ethylene glycol monobutyl ether (0.035 mg/l), diethylene glycol monobutyl ether (0.015 mg/l), propylene glycol monomethyl ether (0.070 mg/l), dipropylene glycol monomethyl ether (0.050 mg/l), and tripropylene glycol monoethyl ether (<0.001 mg/l).[7] In the Hayashida River (Japan) mainly polluted by effluents from leather factories, among the pollutants separated by vacuum distillation and identified by GS-MS, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, and diethylene glycol monobutyl ether were found at concentrations of 5.68, 1.20, and 0.24 mg/l, respectively.[8]

In air samples collected in the pine forest area of Storkow (30 km south east of Berlin, Germany), the "Mediterranean Macchia" of Castel Porziano (Italy), and the Italian station located at the foot of Everest (Nepal), GC-MS analysis showed concentrations of ethylene glycol monobutyl ether of 1.25, 0.40, and 0.10 to 1.59 μg/m^3, respectively.[9]

17.3.3 ENVIRONMENTAL BEHAVIOR

Due to their high water solubilities and low 1-octanol/water partition coefficients (log P), the glycol ethers, after release in the environment, will be preferentially found in the aquatic media and their accumulation in soils, sediments, and biota will be negligible.

The available literature data on the biodegradation of glycol ethers reveal that most of these chemicals are biodegradable under aerobic conditions (Table 17.3.1), suggesting the compounds would not likely persist.

Table 17.3.1. Aerobic biodegradation of glycol ethers and their acetates in aquatic environments and soils

Name [CAS RN], Values	Comments	Ref.
Ethylene glycol monomethyl ether [109-86-4]		
5 d = 30% bio-oxidation, 10 d = 62%, 15 d = 74%, 20 d = 88%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), fresh water	10
5 d = 6% bio-oxidation, 10 d = 18%, 15 d = 23%, 20 d = 39%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), salt water	10
ThOD = 1.68 g/g, BOD_5 = 0.12 g/g, %ThOD = 7, COD = 1.69 g/g, %ThOD = 101	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
BOD_5 = 0.50 g/g, %ThOD = 30	same conditions, adapted seed	11
Ethylene glycol monomethyl ether acetate [110-49-6]		
ThOD = 1.63 g/g, BOD_5 = 0.49 g/g, %ThOD = 30, COD = 1.60 g/g, %ThOD = 98	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
Ethylene glycol monoethyl ether [110-80-5]		
5 d = 36% bio-oxidation, 10 d = 88%, 15 d = 92%, 20 d = 100%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), fresh water	10
5 d = 5% bio-oxidation, 10 d = 42%, 15 d = 50%, 20 d = 62%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), salt water	10
ThOD = 1.96 g/g, BOD_5 = 1.03 g/g, %ThOD = 53, COD = 1.92 g/g, %ThOD = 98	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
BOD_5 = 1.27 g/g, %ThOD = 65	same conditions, adapted seed	11
COD removed = 91.7%	mixed culture, acclimation in a semi-continuous system	12
BOD_5 = 0.353 g/g, BOD/ThOD = 18.1%	fresh water, standard dilution method, 10 mg/l	13
BOD_5 = 0.021 g/g, BOD/ThOD = 1.1%	sea water, 10 mg/l	13
Ethylene glycol monoethyl ether acetate [111-15-9]		
5 d = 36% bio-oxidation, 10 d = 79%, 15 d = 82%, 20 d = 80%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), fresh water	10
5 d = 10% bio-oxidation, 10 d = 44%, 15 d = 59%, 20 d = 69%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), salt water	10

Name [CAS RN], Values	Comments	Ref.
ThOD = 1.82 g/g, BOD$_5$ = 0.74 g/g, %ThOD = 41, COD = 1.76 g/g, %ThOD = 96	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
BOD$_5$ = 0.442 g/g, BOD/ThOD = 24.3%	fresh water, standard dilution method, 10 mg/l	13
BOD$_5$ = 0.448 g/g, BOD/ThOD = 24.7%	sea water, 10 mg/l	13
Ethylene glycol diethyl ether [629-14-1]		
ThOD = 2.31 g/g, BOD$_{10}$ = 0.10 g/g		14
Ethylene glycol monoisopropyl ether [109-59-1]		
ThOD = 2.15 g/g, BOD$_5$ = 0.18 g/g, %ThOD = 8, COD = 2.08 g/g, %ThOD = 97	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
Ethylene glycol monobutyl ether [111-76-2]		
5 d = 26% bio-oxidation, 10 d = 74%, 15 d = 82%, 20 d = 88%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), fresh water	10
5 d = 29% bio-oxidation, 10 d = 64%, 15 d = 70%, 20 d = 75%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), salt water	10
ThOD = 2.31 g/g, BOD$_5$ = 0.71 g/g, %ThOD = 31, COD = 2.20 g/g, %ThOD = 95	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
BOD$_5$ = 1.68 g/g, %ThOD = 73	same conditions, adapted seed	11
COD removed = 95.2%	mixed culture, acclimation in a semi-continuous system	12
BOD$_5$ = 0.240 g/g, BOD/ThOD = 10.4%	fresh water, standard dilution method, 10 mg/l	13
BOD$_5$ = 0.044 g/g, BOD/ThOD = 1.9%	sea water, 10 mg/l	13
5 d = 47% bio-oxidation, 15 d = 70%, 28 d = 75%	OECD Closed-Bottle test 301D, no prior acclimation/adaptation of seed, 20°C	15
28 d = 95% removal of DOC	OECD 301E, 10 mg/l, non-adapted domestic activated sludge	16
28 d = 100% removal	OECD 302B, 500 mg/l, non-adapted domestic activated sludge	16
1 d = 22% removal, 3 d = 63%, 5 d = 100%	OECD 302B, 450 mg/l, non-adapted domestic activated sludge	16
14 d = 96% BOD of ThOD	100 mg/l, activated sludge	16
Ethylene glycol monobutyl ether acetate [112-07-2]		
>90% DOC removal in 28 d	OECD 302B, Zahn-Wellens test	16
Diethylene glycol monomethyl ether [111-77-3]		
ThOD = 1.73 g/g, BOD$_5$ = 0.12 g/g, %ThOD = 7, COD = 1.71 g/g, %ThOD = 99	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11

Name [CAS RN], Values	Comments	Ref.
BOD_5 = 0.95 mmol/mmol	acclimated mixed culture, estimated by linear regression technique from a 20-day test	17
Diethylene glycol monomethyl ether acetate [629-38-9]		
ThOD = 1.68 g/g, BOD_{10} = 1.10 g/g		14
Diethylene glycol monoethyl ether [111-90-0]		
5 d = 17% bio-oxidation, 10 d = 71%, 15 d = 75%, 20 d = 87%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), fresh water	10
5 d = 11% bio-oxidation, 10 d = 44%, 15 d = 57%, 20 d = 70%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), salt water	10
ThOD = 1.91 g/g, BOD_5 = 0.20 g/g, %ThOD = 11, COD = 1.85 g/g, %ThOD = 97	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
BOD_5 = 0.58 g/g, %ThOD = 30	same conditions, adapted seed	11
COD removed = 95.4%	mixed culture, acclimation in a semi-continuous system	12
BOD_5 = 5.50 mmol/mmol	acclimated mixed culture	17
Diethylene glycol diethyl ether [112-36-7]		
ThOD = 2.17 g/g, BOD_{10} = 0.10 g/g		14
Diethylene glycol monobutyl ether [112-34-5]		
ThOD = 2.17 g/g, BOD_5 = 0.25 g/g, %ThOD = 11, COD = 2.08 g/g, %ThOD = 96	effluent from a biological sanitary waste treatment plant, 20 ± 1°C, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
COD removed = 95.3%	mixed culture, acclimation in a semi-continuous system	12
BOD_5 = 5.95 mmol/mmol	acclimated mixed culture	17
5 d = 27% bio-oxidation, 10 d = 60%, 15 d = 78%, 20 d = 81%	BOD APHA SM, no prior acclimation/adaptation of seed, 20°C	15
5 d = 3% bio-oxidation, 15 d = 70%, 28 d = 88%,	OECD Closed-Bottle test 301D, no prior acclimation/adaptation of seed, 20°C	15
28 d >60% removal	OECD 301C, modified MITI test, adapted activated sludge	16
28 d = 58% removal	OECD 301C, modified MITI test, adapted activated sludge	16
1 d = 14% removal, 3 d = 19%, 5 d = 60%, 6 d = 100%	OECD 302B, modified Zahn-Wellens test, industrial non-adapted activated sludge	16
9 d = 100% removal	OECD 302B, modified Zahn-Wellens test, non-adapted activated sludge	16
14 d = 94% removal	OECD 301A, domestic secondary effluent sewage, DOC measured	16

Name [CAS RN], Values	Comments	Ref.
BOD_5 = 0.05 g/g (5.2% ThOD), BOD_{10} = 0.39 g/g (57% ThOD), BOD_{20} = 1.08 g/g (72% ThOD)		16
BOD = 0.25 g/g, COD = 2.08 g/g	Dutch standard method, adapted sewage	16
Diethylene glycol monobutyl ether acetate [124-17-4]		
BOD_5 = 13.3% ThOD, BOD_{10} = 18.4%, BOD_{15} = 24.6%, BOD_{20} = 67%		16
Triethylene glycol monoethyl ether [112-50-5]		
5 d = 8% bio-oxidation, 10 d = 47%, 15 d = 63%, 20 d = 71%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), fresh water	10
5 d = 1% bio-oxidation, 10 d = 10%, 15 d = 12%, 20 d = 22%	filtered domestic wastewater, non-acclimated seed, 3, 7, 10 mg/l (at least two), salt water	10
ThOD = 1.89 g/g, BOD_5 = 0.05 g/g, %ThOD = 3, COD = 1.84 g/g, %ThOD = 97	effluent from a biological sanitary waste treatment plant, $20 \pm 1°C$, unadapted seed, BOD = APHA SM 219, COD = ASTM D 1252-67	11
COD removed = 96.6%	mixed culture, acclimation in a semi-continuous system	12
BOD_5 = 1.15 mmol/mmol	acclimated mixed culture, estimated by linear regression technique from a 20-day test	17
Triethylene glycol monobutyl ether [143-22-6]		
COD removed = 96.3%	mixed culture, acclimation in a semi-continuous system	12
Propylene glycol monomethyl ether [107-98-2]		
50% removal: <1 d (0.2 ppm), <2 d (9.9 ppm), <5 d (100 ppm)	sand = 72%, silt = 16%, clay = 12%, OC = 2.5%, 9.9×10^6 bacteria/g of soil	18
50% removal: <1 d (0.4 ppm), <7 d (100 ppm)	sand = 74%, silt = 12%, clay = 14%, OC = 2.0%, 5.1×10^6 bacteria/g of soil	18
50% removal: <4 d (0.4 ppm), >56 d (100 ppm), <23 d (100 ppm with nutrients)	sand = 94%, silt = 4%, clay = 2%, OC = 0.4%, 9.3×10^5 bacteria/g of soil	18
BOD_{20} = 58% of ThOD		18
Propylene glycol monomethyl ether acetate [108-65-6]		
50% removal: <1 d (2.5 ppm), <1 d (20 ppm),	sand = 72%, silt = 16%, clay = 12%, OC = 2.5%, 9.9×10^6 bacteria/g of soil	18
50% removal: <1 d (20 ppm)	sand = 74%, silt = 12%, clay = 14%, OC = 2.0%, 5.1×10^6 bacteria/g of soil	18
50% removal: <1 d (20 ppm)	sand = 94%, silt = 4%, clay = 2%, OC = 0.4%, 9.3×10^5 bacteria/g of soil	18
BOD_{20} = 62% of ThOD		18

Name [CAS RN], Values	Comments	Ref.
Propylene glycol monophenyl ether [770-35-4]		
50% removal: <1 d (1.4 ppm), <2 d (10 ppm), <5 d (107 ppm)	sand = 72%, silt = 16%, clay = 12%, OC = 2.5%, 9.9 x 10^6 bacteria/g of soil	18
50% removal: <1 d (1.5 ppm), <7 d (104 ppm)	sand = 74%, silt = 12%, clay = 14%, OC = 2.0%, 5.1 x 10^6 bacteria/g of soil	18
50% removal: <5 d (1.5 ppm), <23 d (108 ppm)	sand = 94%, silt = 4%, clay = 2%, OC = 0.4%, 9.3 x 10^5 bacteria/g of soil	18
BOD_{20} = 52% of ThOD		18

Note: ThOD = theoretical oxygen demand or the weight ratio of oxygen required per mg of compound for complete conversion of the compound to dioxide and water; BOD = biochemical oxygen demand; COD = chemical oxygen demand; DOC = dissolved organic carbon.

Metabolism pathways involving oxidation of the alcohol functionality and cleavage of the ether bond have been proposed for a reduced number of glycol ethers.[18-20]

While glycol ethers can be considered as biodegradable under aerobic conditions, Eckel et al.[6] have stressed that under anaerobic conditions, such as in the groundwater plume emanating from a landfill, these chemicals may persist for many years. In the same way, due to their physico-chemical properties, glycol ethers can act as cosolvents in mixtures with highly hydrophobic contaminants enhancing the solubility, mobility, and hence, the ecotoxicity of these chemicals.

Abiotic degradation processes for organic chemicals include aqueous photolysis, hydrolysis, and atmospheric photooxidation. The primary abiotic degradation process affecting glycol ethers is atmospheric photooxidation mediated by hydroxyl (OH) radicals formed in the atmosphere.[16] Photooxidation of glycol ethers is generally estimated from quantitative structure-property (QSPR) models due to the scarcity of experimental data.[21-23] Thus, for example, Grosjean[23] estimated atmospheric half-lives of 2 to 20 hours for ethylene glycol ethers (taking OH = 10^6 molecules cm^{-3}).

17.3.4 ECOTOXICITY

17.3.4.1 Survival and growth

The ecotoxicological effects of glycol ethers and their acetates have been measured on various organisms occupying different trophic levels in the environment. Most of the available data deal with lethality, immobilization of the organisms, inhibition of cell multiplication, or growth (Table 17.3.2).

Table 17.3.2. Effects of glycol ethers and their acetates on survival and growth of organisms

Species		Results	Comments	Ref.
Ethylene glycol monomethyl ether [109-86-4]				
Bacteria	*Pseudomonas putida*	16-h TGK >10000 mg/l	toxicity threshold, inhibition of cell multiplication	24
	Pseudomonas aeruginosa	4-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
Blue-green algae	*Microcystis aeruginosa*	8-d TGK = 100 mg/l	toxicity threshold, inhibition of cell multiplication	26
Algae	*Scenedesmus quadricauda*	8-d TGK >10000 mg/l	toxicity threshold, inhibition of cell multiplication	26
Yeasts	*Candida sp.*	4-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
Fungi	*Cladosporium resinae*	4-m biocidal = 10-17% 42-d NG = 20%	tested in jet fuel and water mixtures NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	25 27
	Gliomastix sp.	4-m biocidal = 17-25%	tested in jet fuel and water mixtures	25
Protozoa	*Chilomonas paramaecium*	48-h TGK = 2.2 mg/l	toxicity threshold, inhibition of cell multiplication	28
	Uronema parduczi	20-h TGK > 10000 mg/l	toxicity threshold, inhibition of cell multiplication	29
	Entosiphon sulcatum	72-h TGK = 1715 mg/l	toxicity threshold, inhibition of cell multiplication	30
Coelenterates	*Hydra vulgaris* (syn. *H. attenuata*)	72-h LC50 = 29000 mg/l	semi-static, adult polyps	31
Crustacea	*Daphnia magna*	24-h LC50 >10000 mg/l 24-h EC50 >10000 mg/l	static, nominal concentrations static, nominal concentrations, immobilization	32 33
	Artemia salina	24-h TLm >10000 mg/l	static, 24.5°C	10
Fish	*Carassius auratus*	24-h TLm >5000 mg/l	static, 20 ± 1°C, measured concentrations	34
	Leuciscus idus melanotus	48-h LC50 >10000 mg/l 48-h LC0 >10000 mg/l 48-h LC100 >10000 mg/l	static (Juhnke)	35
	Oryzias latipes	24-h LC50 >1000 mg/l 48-h LC50 >1000 mg/l	static, same results at 10, 20, and 30°C	36

	Species	Results	Comments	Ref.
Fish	*Pimephales promelas*	20% mortality = 50 mg/l, 0% mortality = 100 mg/l, 30% mortality = 200 mg/l, 70% mortality = 500 mg/l, 70% mortality = 700 mg/l, 100% mortality = 1000 mg/l	static with daily renewal, adults, 7-d of exposure	37
	Poecilia reticulata	7-d LC50 = 17434 mg/l	semi-static, 22 ± 1°C, rounded value	38
	Lepomis macrochirus	96-h LC50 >10000 mg/l	static, nominal concentrations, L = 33-75 mm	39
	Menidia beryllina	96-h LC50 >10000 mg/l	static, sea water, nominal concentrations, L = 40-100 mm	39
Amphibia	*Xenopus laevis*	0% mortality=2500 mg/l, 0% mortality = 7500 mg/l, 0% mortality = 15000 mg/l	static with daily renewal, adults, 4-d of exposure	37

Ethylene glycol monomethyl ether acetate [110-49-6]

	Species	Results	Comments	Ref.
Fish	*Carassius auratus*	24-h TLm = 190 mg/l	static, 20 ± 1°C, measured concentrations	34
	Lepomis macrochirus	96-h LC50 = 45 mg/l	static, nominal concentrations, L = 33-75 mm	39
	Menidia beryllina	96-h LC50 = 40 mg/l	static, sea water, nominal concentrations, L = 40-100 mm	39

Ethylene glycol monoethyl ether [110-80-5]

	Species	Results	Comments	Ref.
Bacteria	*Pseudomonas aeruginosa*	4-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
	Vibrio fischeri	5-min EC50 = 376 mg/l, 15-min EC50 = 403 mg/l, 30-min EC50 = 431 mg/l	reduction in light output, 15°C	40
Yeasts	*Candida sp.*	4-m biocidal = 2-5%	tested in jet fuel and water mixtures	25
Fungi	*Cladosporium resinae*	4-m biocidal = 5-10% 42-d NG = 10%	tested in jet fuel and water mixtures NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	25 27
	Gliomastix sp.	4-m biocidal = 10-17%	tested in jet fuel and water mixtures	25

Species		Results	Comments	Ref.
Coelente-rates	*Hydra vulgaris* (syn. *H. attenuata*)	72-h LC50 = 2300 mg/l	semi-static, adult polyps	31
Crustacea	*Daphnia magna*	24-h EC50 = 54000 mg/l	static, nominal concentrations, immobilization	41
		48-h EC50 = 7671 mg/l	static, 22 ± 1°C, nominal concentrations, immobilization	42
	Artemia salina	24-h TLm >10000 mg/l	static, 24.5°C	10
Fish	*Carassius auratus*	24-h TLm >5000 mg/l	static, 20 ± 1°C, measured concentrations	34
	Poecilia reticulata	7-d LC50 = 16399 mg/l	semi-static, 22 ± 1°C, rounded value	38
	Lepomis macrochirus	96-h LC50 >10000 mg/l	static, nominal concentrations, L = 33-75 mm	39
	Menidia beryllina	96-h LC50 >10000 mg/l	static, sea water, nominal concentrations, L = 40-100 mm	39

Ethylene glycol monoethyl ether acetate [111-15-9]

Crustacea	*Artemia salina*	24-h TLm = 4000 mg/l	static, 24.5°C	10
Fish	*Carassius auratus*	24-h TLm = 160 mg/l	static, 20 ± 1°C, measured concentrations	34

Ethylene glycol monopropyl ether [2807-30-9]

Bacteria	*Pseudomonas aeruginosa*	4-m biocidal = 0-2%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 0-2%	tested in jet fuel and water mixtures	25
Yeasts	*Candida sp.*	4-m biocidal = 2-5%	tested in jet fuel and water mixtures	25
Fungi	*Cladosporium resinae*	4-m biocidal = 2-5%	tested in jet fuel and water mixtures	25
	Gliomastix sp.	4-m biocidal = 2-5%	tested in jet fuel and water mixtures	25

Ethylene glycol monoisopropyl ether [109-59-1]

Fungi	*Cladosporium resinae*	42-d NG = 10%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27
Fish	*Carassius auratus*	24-h TLm >5000 mg/l	static, 20 ± 1°C, measured concentrations	34
	Poecilia reticulata	7-d LC50 = 5466 mg/l	semi-static, 22 ± 1°C, rounded value	38

Ethylene glycol monobutyl ether [111-76-2]

Bacteria	*Pseudomonas putida*	16-h TGK = 700 mg/l	toxicity threshold, inhibition of cell multiplication	24
	Pseudomonas aeruginosa	4-m biocidal = 1-2%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 1-2%	tested in jet fuel and water mixtures	25

Species		Results	Comments	Ref.
Blue-green algae	*Microcystis aeruginosa*	8-d TGK = 35 mg/l	toxicity threshold, inhibition of cell multiplication	26
Algae	*Scenedesmus quadricauda*	8-d TGK = 900 mg/l	toxicity threshold, inhibition of cell multiplication	26
	Selenastrum capricornutum	7-d EC50 >1000 mg/l, NOEC = 125 mg/l, LOEC = 250 mg/l	growth rate inhibition	16
Yeasts	*Candida sp.*	4-m biocidal = 2-3%	tested in jet fuel and water mixtures	25
Fungi	*Cladosporium resinae*	4-m biocidal = 2-3% 42-d NG = 5%	tested in jet fuel and water mixtures NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	25 27
	Gliomastix sp.	4-m biocidal = 2-3%	tested in jet fuel and water mixtures	25
Protozoa	*Chilomonas paramaecium*	48-h TGK = 911 mg/l	toxicity threshold, inhibition of cell multiplication	28
	Uronema parduczi	20-h TGK = 463 mg/l	toxicity threshold, inhibition of cell multiplication	29
	Entosiphon sulcatum	72-h TGK = 91 mg/l	toxicity threshold, inhibition of cell multiplication	30
Coelenterates	*Hydra vulgaris (syn. H. attenuata)*	72-h LC50 = 690 mg/l	semi-static, adult polyps	31
Mollusca	*Crassostrea virginica*	24-h LC50 = 181 mg/l (143 - 228), 48-h LC50 = 160 mg/l (125 - 204), 72-h LC50 = 114 mg/l (93.9 - 138), 96-h LC50 = 89.4 mg/l (72 - 110)	static, 22 ± 1°C, 10 organisms/tank	43
Crustacea	*Daphnia magna*	24-h LC50 = 1720 mg/l, 24-h LC0 = 1140 mg/l, 24-h LC100 = 2500 mg/l 24-h EC50 = 1815 mg/l (1698-1940), 24-h EC0 = 1283 mg/l, 24-h EC100 = 2500 mg/l 48-h EC50 = 835 mg/l	static, nominal concentrations / static, nominal concentrations, immobilization / static, immobilization	32 / 33 / 16
	Artemia salina	24-h TLm = 1000 mg/l	static, 24.5°C	10

	Species	Results	Comments	Ref.
Crustacea	*Panaeus setiferus*	24-h LC50 > 430 mg/l, 48-h LC50 = 173 mg/l (123 - 242), 72-h LC50 = 147 mg/l (116 - 186), 96-h LC50 = 130 mg/l (104 - 162)	static, average size = 1.5 cm	43
Fish	*Carassius auratus*	24-h TLm = 1700 mg/l	static, 20 ± 1°C, measured concentrations	34
	Leuciscus idus melanotus	48-h LC50 = 1575 mg/l, 48-h LC0 = 1350 mg/l 48-h LC100 = 1620 mg/l 48-h LC50 = 1395 mg/l, 48-h LC0 = 1170 mg/l, 48-h LC100 = 1490 mg/l	static (Juhnke) static (Lüdemann)	35
	Pimephales promelas	96-h LC50 = 2137 mg/l	static	16
	Poecilia reticulata	7-d LC50 = 983 mg/l	semi-static, 22 ± 1°C, rounded value	38
	Notropis atherinoides	72-h LC50 >500 mg/l	static	16
	Lepomis macrochirus	96-h LC50 = 1490 mg/l	static, nominal concentrations, L = 33-75 mm	39
		24-h LC50 = 2950 mg/l, 96-h LC50 = 2950 mg/l		44
	Cyprinodon variegatus	24-h LC50 = 149 mg/l (125 - 176), 48-h LC50 = 126 mg/l (107 - 147), 72-h LC50 = 121 mg/l (105 - 138), 96-h LC50 = 116 mg/l (100 - 133)	static, 22 ± 1°C	43
	Menidia beryllina	96-h LC50 = 1250 mg/l	static, sea water, nominal concentrations, L = 40-100 mm	39
Ethylene glycol dibutyl ether [112-48-1]				
Fungi	*Cladosporium resinae*	42-d NG = 5%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27
Diethylene glycol monomethyl ether [111-77-3]				
Bacteria	*Pseudomonas aeruginosa*	4-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
Yeasts	*Candida sp.*	4-m biocidal = 5-10%	tested in jet fuel and water mixtures	25

Species		Results	Comments	Ref.
Algae	*Scenedesmus subspicatus*	72-h EC50 > 500 mg/l, 72-h EC20 > 500 mg/l, 72-h EC90 > 500 mg/l	biomass	45
	Selenastrum capricornutum	96-h EC50 > 1000 mg/l	biomass	45
Fungi	*Cladosporium resinae*	4-m biocidal = 10-17% 42-d NG = 20%	tested in jet fuel and water mixtures NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	25 27
	Gliomastix sp.	4-m biocidal > 25%	tested in jet fuel and water mixtures	25
Crustacea	*Daphnia magna*	24-h LC50 = 1495 mg/l (1300 - 1600), 48-h LC50 = 1192 mg/l (1100 - 6500)	static, nominal concentrations	45
Fish	*Oncorhynchus mykiss*	96-h LC50 > 1000 mg/l	semi-static, nominal concentrations	45
	Carassius auratus	24-h TLm >5000 mg/l	static, 20 ± 1°C, measured concentrations	34
	Pimephales promelas	24-h LC50 = 6400 mg/l (6200 - 6600), 48-h LC50 = 6000 mg/l (6000 -6100), 72-h LC50 = 6000 mg/l (6000 -6100), 96-h LC50 = 5700 mg/l (5600 - 5900)	static	45
	Lepomis macrochirus	96-h LC50 = 7500 mg/l	static, nominal concentrations, L = 33-75 mm	39

Diethylene glycol dimethyl ether [111-96-6]

Fungi	*Cladosporium resinae*	42-d NG = 20%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27

Diethylene glycol monoethyl ether [111-90-0]

Bacteria	*Vibrio fischeri*	5-min EC50 = 1000 mg/l, 5-min EC50 = 1290 mg/l 15-min EC50 = 10954 mg/l (10592.8 - 11327.5)	reduction in light output, nominal concentrations	46 47
Fungi	*Cladosporium resinae*	42-d NG = 20%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27
Coelenterates	*Hydra vulgaris* (syn. *H. attenuata*)	72-h LC50 = 17000 mg/l	semi-static, adult polyps	31

	Species	Results	Comments	Ref.
Crustacea	*Daphnia magna*	48-h LC50 = 4670 mg/l (3620 - 6010), 48-h LC50 = 3340 mg/l (2120 - 5280)	static, 21.1°C, measured concentrations static, 23.3°C, measured concentrations	48
	Orconectes immunis	96-h LC50 = 34700 mg/l (29100 - 41400)	flow-through, 15.5°C, 0.47 g, measured concentrations	48
	Artemia salina	24-h TLm >10000 mg/l	static, 24.5°C	10
Insecta	*Tanytarsus dissimilis*	48-h LC50 = 18800 mg/l	static, 22.3°C, measured concentrations	48
Echinodermata	*Arbacia punctulata*	4-h EC50 = 10661 mg/l (5576.5 - 20895.9)	static, marine, early embryo growth, nominal concentrations	47
		1-h EC50 = 3370 mg/l (3145.4 - 3610.8)	static, marine, sperm cell, nominal concentrations	47
		5-h EC50 = 4116 mg/l (3408 - 4907)	static, marine, increase in DNA, nominal concentrations	49
Fish	*Oncorhynchus mykiss*	96-h LC50 = 13400 mg/l (11400 - 15700)	flow-through, 14.9°C, 0.68 g, measured concentrations	48
	Carassius auratus	24-h TLm >5000 mg/l	static, 20 ± 1°C, measured concentrations	34
		96-h LC50 = 20800 mg/l (15700 - 27500)	flow-through, 20.1°C, 0.92 g, measured concentrations	48
	Gambusia affinis	96-h LC50 = 15200 mg/l (12400 - 18700) 96-h LC50 = 12900 mg/l (11100 - 15000)	flow-through, 18.3°C, 0.23 g, measured concentrations flow-through, 19.9°C, 0.25 g, measured concentrations	48
	Ictalurus punctatus	96-h LC50 = 6010 mg/l	flow-through, 17.3°C, 0.72 g, measured concentrations	48
	Lepomis macrochirus	96-h LC50 >10000 mg/l	static, nominal concentrations, L = 33-75 mm	39
		96-h LC50 = 21400 mg/l (19100 - 23900)	flow-through, 18.3°C, 0.44 g, measured concentrations	48
	Pimephales promelas	96-h LC50 = 13900 mg/l (11600 - 16700) 96-h LC50 = 9650 mg/l (7910 - 11800)	flow-through, 24.8°C, 1.44 g, measured concentrations flow-through, 18.1°C, 0.35 g, measured concentrations	48
	Menidia beryllina	96-h LC50 >10000 mg/l	static, sea water, nominal concentrations, L = 40-100 mm	39
Amphibia	*Rana catesbeiana*	96-h LC50 = 20900 mg/l (19400 -22600)	flow-through, 17.2°C, 3.54 g, measured concentrations	48

Diethylene glycol diethyl ether [112-36-7]

	Species	Results	Comments	Ref.
Fungi	*Cladosporium resinae*	42-d NG = 20%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27

Species		Results	Comments	Ref.
Diethylene glycol monobutyl ether [112-34-5]				
Bacteria	*Pseudomonas putida*	16-h TGK = 255 mg/l	toxicity threshold, inhibition of cell multiplication	24
		16-h EC10 = 1170 mg/l	growth inhibition, 25 ± 2°C	50
Blue-green algae	*Microcystis aeruginosa*	8-d TGK = 53 mg/l	toxicity threshold, inhibition of cell multiplication	26
Algae	*Scenedesmus quadricauda*	8-d TGK = 1000 mg/l	toxicity threshold, inhibition of cell multiplication	26
	Scenedesmus subspicatus	96-h EC50 > 100 mg/l	limit test	50
Fungi	*Cladosporium resinae*	42-d NG = 5%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27
Protozoa	*Chilomonas paramaecium*	48-h TGK = 2774 mg/l	toxicity threshold, inhibition of cell multiplication	28
	Uronema parduczi	20-h TGK = 420 mg/l	toxicity threshold, inhibition of cell multiplication	29
	Entosiphon sulcatum	72-h TGK = 73 mg/l	toxicity threshold, inhibition of cell multiplication	30
Crustacea	*Daphnia magna*	24-h LC50 = 2850 mg/l, 24-h LC0 = 1750 mg/l, 24-h LC100 = 3850 mg/l	static, nominal concentrations	32
		24-h EC50 = 3200 mg/l (2990-3424), 24-h EC0 = 2333 mg/l, 24-h EC100 = 5000 mg/l	static, nominal concentrations, immobilization	33
		48-h EC50 >100 mg/l 48-h NOEC >100 mg/l	directive 84/449/ EEC, C2	16
Fish	*Carassius auratus*	24-h TLm = 2700 mg/l	static, 20 ± 1°C, measured concentrations	34
	Leuciscus idus melanotus	48-h LC50 = 1805 mg/l, 48-h LC0 = 1140 mg/l, 48-h LC100 = 2185 mg/l	static (Juhnke)	35
		48-h LC50 = 2304 mg/l, 48-h LC0 = 1820 mg/l, 48-h LC100 = 2400 mg/l	static (Lüdemann)	35
		48-h LC50 = 2750 mg/l	static	16
	Poecilia reticulata	7-d LC50 = 1149 mg/l	semi-static, 22±1°C, rounded value	38
	Lepomis macrochirus	96-h LC50 = 1300 mg/l	static, nominal concentrations, L = 33-75 mm	39
	Menidia beryllina	96-h LC50 = 2000 mg/l	static, sea water, nominal concentrations, L = 40-100 mm	39

	Species	Results	Comments	Ref.
Triethylene glycol monomethyl ether [112-35-6]				
Bacteria	*Pseudomonas aeruginosa*	4-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
Yeasts	*Candida sp.*	4-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
Fungi	*Cladosporium resinae*	4-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
	Gliomastix sp.	4-m biocidal = 17-25%	tested in jet fuel and water mixtures	25
Triethylene glycol monoethyl ether [112-50-5]				
Bacteria	*Pseudomonas aeruginosa*	4-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
	Sulfate-reducing bacteria	3-m biocidal = 2-5%	tested in jet fuel and water mixtures	25
Yeasts	*Candida sp.*	4-m biocidal = 5-10%	tested in jet fuel and water mixtures	25
Fungi	*Cladosporium resinae*	4-m biocidal = 10-17%	tested in jet fuel and water mixtures	25
	Gliomastix sp.	4-m biocidal = 17-25%	tested in jet fuel and water mixtures	25
Crustacea	*Artemia salina*	24-h TLm >10000 mg/l	static, 24.5°C	10
Fish	*Carassius auratus*	24-h TLm >5000 mg/l	static, 20 ± 1°C, measured concentrations	34
Propylene glycol monomethyl ether [107-98-2]				
Fungi	*Cladosporium resinae*	42-d NG = 20%	NG = no visible mycelial growth and spore germination, 1% glucose-mineral salts medium, 30°C	27
Propylene glycol monomethyl ether acetate [108-65-6]				
Fish	*Lepomis macrochirus*	24-h LC50 = 206 mg/l 96-h LC50 = 164 mg/l		44

It is difficult to draw definitive conclusions from the data listed in Table 17.3.2. Indeed, most of the data have been retrieved from rather old studies performed without GLP protocols. In addition, the toxicity values are generally based on nominal concentrations and the endpoints are different. However, from the data listed in Table 17.3.2, it appears that despite a difference of sensibility among species, glycol ethers do not present acute and subacute ecotoxicological effects to the majority of the tested organisms. However, it is interesting to note that the acetates seem to be more toxic that the corresponding parent compounds.[10,34,39,51] In mammals, the acute toxicity of glycol ethers is also relatively low. The main target organs are the central nervous and haematopoitic systems. However, on the basis of the available data no significant difference exists between the acute toxicity of glycol ethers and their corresponding acetates.[52]

17.3.4.2 Reproduction and development

The reproductive and developmental toxicity of the ethylene glycol monomethyl and monoethyl ethers is well documented. Several longer-chain glycol ethers also have been investigated for their reproductive and developmental effects against rodents and rabbits.[53-56] Conversely, there is a lack of information on the reproductive and developmental ecotoxicity of glycol ethers and their acetates. Bowden et al.[31] have tested the teratogenic effects of four glycol ethers through their ability to inhibit the regeneration of isolated digestion regions of *Hydra vulgaris* (syn. *H. attenuata*). They have shown that the concentrations of ethylene glycol monomethyl, monoethyl, monobutyl, and diethylene glycol monoethyl ethers that were 50% inhibitory to regenerating digestive regions (IC50) after 72-h of exposure were 19,000, 1400, 540, and 19,000 mg/l, respectively. More specifically, at 10,000 mg/l of ethylene glycol monomethyl ether, the digestive regions regenerated the mouth and some tentacles. At 19,000 mg/l only tentacle buds were seen, while 38,000 mg/l produced disintegration of the coelenterates. Ethylene glycol monoethyl ether at 900 mg/l allowed the regeneration of the mouth, some tentacles and the basal disc. At 1900 mg/l four digestive regions showed wound healing while the remainder were dead. A concentration of 3700 mg/l was lethal to both polyps and digestive regions. At concentrations up to 370 mg/l of ethylene glycol monobutyl ether, digestive regions regenerated some tentacles and in some cases the basal disc. Normal wound healing only was observed at 740 mg/l while at 920 mg/l the wounds were healed but the region expanded. Last, the digestive regions at 10,000 mg/l of diethylene glycol monoethyl ether regenerated the mouth and some tentacles. At 20,000 mg/l only tentacle buds were seen while a concentration of 40,000 mg/l was lethal to both polyps and digestive regions. Using the LC50 (Table 17.3.2)/IC50 ratio as developmental hazard index, Bowden et al.[31] ranked the four studied glycol ethers as follows: Ethylene glycol ethyl ether (1.7) > ethylene glycol monomethyl ether (1.5) > ethylene glycol monobutyl ether (1.3) > diethylene glycol monoethyl ether (0.9). Johnson et al.[57,58] have also ranked glycol ethers according to the difference between their lowest concentrations overtly toxic to adults (A) and their lowest concentrations interfering with development (D) of the artificial embryos of reaggregated adult *Hydra attenuata* cells. The A/D ratios found by these authors were the following: Ethylene glycol monoethyl ether (5.0) > ethylene glycol monobutyl ether (4.4) > ethylene glycol monophenyl ether (3.3) > diethylene glycol dibutyl ether (2.3) > diethylene glycol monoethyl ether (2.2) > ethylene glycol monomethyl ether (1.3) > ethylene glycol monomethyl ether acetate (1.0) = ethylene glycol monoethyl ether acetate (1.0). Daston et al.[37] have shown that A/D ratios were not constant across species and hence, there was no basis for using this parameter for developmental hazard assessment. Thus, for example, the A/D ratios calculated from the lowest observed effect levels (LOELs) of the ethylene glycol monomethyl ether were 8, >3, 0.5, and <0.3 for the mouse, *Xenopus laevis, Pimephales promelas,* and *Drosophila melanogaster*, respectively. If the A/D ratios were calculated from the NOELs (no observed effect levels), the values became >4, ≥6, 0.4, and ≤0.3 for the mammal, amphibian, fish, and insect, respectively.

Teratogenicity of glycol ethers has been deeply investigated on the fruit fly, *Drosophila melanogaster*. Statistically significant increases in the incidence of wing notches and bent humeral bristles have been observed in *Drosophila melanogaster* exposed during development to ethylene glycol monomethyl ether (12.5, 15, 18, 22, and 25 mg/vial) and ethylene glycol monoethyl ether (54, 59, 65, 71, and 78 mg/vial).[59] Wing notches, rare in control flies, were found in 13.8% of flies treated with ethylene glycol monomethyl ether

(7.5 µl/g).[60] In general, male pupae are much more affected by ethylene glycol monomethyl ether than female pupae. However, teratogenicity appears strain dependent. Higher detoxification occurs with increased alcohol dehydrogenase (ADH) activity. Ethylene glycol monomethyl ether is much more toxic than its oxidation product, methoxyacetic acid, at the level of adult eclosion. Teratogenic effects were observed in an ADH-negative strain in spite of lacking ADH activity suggesting that apparently, ethylene glycol monomethyl ether is a teratogenic compound by itself against *Drosophila melanogaster*.[61] Last, it is interesting to note that recently, Eisses has shown[62] that administration of ethylene glycol monomethyl ether to larvae of fruit fly, containing the highly active alcohol dehydrogenase variant ADH-71k, exposed the mitotic germ cells and the mitotic somatic cells of the imaginal discs simultaneously to the mutagen methoxyacetaldehyde and the teratogen methoxyacetic acid, respectively. Consequently, the chances for specific gene mutations, though non-adaptive, were likely increased by a feedback mechanism.

17.3.5 CONCLUSION

Despite their widespread use, glycol ethers and their acetates have received little attention as potential environmental contaminants. Based on their physico-chemical properties, they would tend to remain in the aquatic ecosystems where their bioconcentration, biomagnification and sorption onto sediments will appear negligible. Volatilization from water and hydrolysis or photolysis in the aquatic ecosystems are generally of minimal importance. Glycol ethers are also poorly sorbed to soil and their rapid removal in the atmosphere is expected. While glycol ethers are biodegradable under aerobic conditions, these chemicals may persist for many years under anaerobic conditions.

Based on the available acute ecotoxicity data, glycol ethers and their acetates can be considered as practically non-toxic. However, there is a lack of information on their long-term effects on the biota. This is particularly annoying because the developmental toxicity of some of them has been clearly identified against mammals. Consequently, there is a need for studies dealing with the potential long-term effects of these chemicals against organisms occupying different trophic levels in the environment in order to see whether or not the classical methodological frameworks used for assessing the environmental risk of xenobiotics remain acceptable for this class of chemicals.

17.3.6 ACKNOWLEDGMENT

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17.4 ORGANIC SOLVENT IMPACTS ON TROPOSPHERIC AIR POLLUTION

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17.4.1 SOURCES AND IMPACTS OF VOLATILE SOLVENTS

Solvents, either by design or default, are often emitted in to the air, and the total mass of emissions of solvents is not small. In a typical city in the United States, solvents can rival automobile exhaust as the largest source category of volatilized organic compound (VOC) emissions into the atmosphere.[1] In the United Kingdom, solvent usage accounted for 36% of the estimated total VOC mass emissions in 1995.[2] Such widespread emissions leads to increased concentrations of many different compounds in the ambient environment, and their release has diverse impacts on air quality.

A large variety of solvent-associated compounds are emitted, many of which are hydrocarbons, oxygenates. Those solvents may have multiple atmospheric impacts. For example, toluene is potentially toxic and can reach relatively high concentrations at small spatial scales, such as in a workplace. Toluene also contributes to the formation of tropospheric ozone at urban scales, while at regional scales toluene can lower the rate of tropospheric ozone formation. Other solvents likewise can have a range of impacts, ranging from local contamination to modification of the global climate system.

This diversity of potential impacts is due, in part, to differences in the chemical properties and reactions that a compound may undergo in the atmosphere, differences in emissions patterns, and differences in the spatial and temporal scales of atmospheric phenomena. Transport and fate of chemical species is closely tied to the speed at which the compound degrades (from seconds to centuries, depending on the compound) as well as to the environmental conditions in which the compound is emitted. If a compound degrades very quickly, it may still have toxic effects near a source where concentrations can be high. In contrast, extremely stable compounds (such as chlorofluorocarbons; CFCs) are able to circumvent the globe, gradually accumulating to non-negligible concentrations.[3]

Of the myriad of solvents emitted into the air, the ones of primary concern are those with the greatest emissions rates, and/or those to which the environment has a high sensitivity. Compounds with very large emissions rates include tri- and tetrachloroethylene (e.g., from dry-cleaning), aromatics (benzene, toluene and xylenes, e.g., from coatings), alcohols, acetone and, historically, CFCs. While those compounds are often emitted from solvent use, other applications lead to their emission as well. For example, gasoline is rich in aromatics and alkanes, and in many cases fuel use dominates emissions of those compounds. CFCs have been used as refrigerants and as blowing agents. This diversity of originating sources makes identifying the relative contribution of solvents to air quality somewhat difficult since there are large uncertainties in our ability to quantify emissions rates from various source categories.

Solvents with a high environmental sensitivity include benzene (a potent carcinogen), xylenes (which are very effective at producing ozone), formaldehyde (both toxic and a strong ozone precursor), and CFCs (ozone depleters and potential greenhouse gases). Most of the solvents of concern in terms of impacting ambient air are organic, either hydrocarbons, oxygenated organics (e.g., ethers, alcohols and ketones) or halogenated organics (e.g., dichlorobenzene). Some roles of these compounds in the atmosphere are discussed below.

While the toxicity of some solvents is uncertain, the role of emissions on direct exposure is not in question. Indoors, vaporized solvents can accumulate to levels of concern for acute and/or chronic exposure. However, the toxicity of solvents outdoors is not typically of as great of concern as indoors except very near sources. Outdoors, solvents have adverse effects other than toxicity. The importance of CFC emissions on stratospheric ozone, for example, is significant, but the problem is well understood and measures are in place to alleviate the problem. Reactive compounds can also aid in the formation of other pollutants, referred to as secondary pollutants because they are not emitted, but formed from directly emitted primary precursors. Of particular concern is tropospheric ozone, a primary constituent of photochemical smog. In the remainder of this chapter, the impacts of solvents on air quality are discussed, with particular attention given to the formation of tropospheric ozone. This emphasis is motivated by current regulatory importance as well as by lingering scientific issues regarding the role of volatile organics in secondary pollution formation.

17.4.2 MODES AND SCALES OF IMPACT

Many organic solvents are toxic, and direct exposure to the compound through the atmosphere (e.g., via inhalation) can be harmful. While toxic effects of solvents rely on direct exposure, many solvents also contribute to the formation of secondary pollutants such as tropospheric ozone or particulate matter (PM), which cause health problems and damage the environment on larger spatial scales such as over urban areas and multi-state/country regions. Very slowly reacting solvent compounds also impact the atmosphere on the global scale, which may cause imbalances in living systems and in the environment. While some mechanisms of environmental imbalance are understood, the risks associated with global atmospheric impacts are highly uncertain.

Transport of solvents in the atmosphere is similar to most other gaseous pollutants, and is dominated by the wind and turbulent diffusion. There is little difference between the transport of different solvent compounds, and the fact that most solvents have much higher molecular weights than air does not lead to enhanced levels at the ground. Heavy solvents are, for the most part, as readily diffused as lighter solvents, although they may not vaporize as fast. The higher levels of many solvents measured near the ground are due to proximity to emissions sources, which are near the surface, and the fact that most solvents degrade chemically as they mix upwards. A major difference in the evolution of various solvents is how fast they react chemically. Some, such as formaldehyde, have very short lifetimes while others, such as CFCs, last decades.

17.4.2.1 Direct exposure

Volatilization of solvents allows air to serve as a mode of direct exposure to many compounds known to be toxic. Generally, direct exposure is a risk near strong or contained sources, and can cause both acute and chronic responses. Most of the non-workplace exposure to solvents occurs indoors. This is not surprising since, on average, people spend a vast majority of their time indoors, and solvents are often used indoors. Outdoors, solvents rapidly disperse and can oxidize, leading to markedly lower levels than what is found indoors near a source. For example, indoor formaldehyde levels are often orders of magnitude greater than outdoors. There still are cases when outdoor exposure may be non-negligible, such as if one spends a significant amount of time near a major source. Toxic effects of solvents are fairly well understood, and many countries have developed regulatory structures to protect people from direct exposure. The toxic effects of solvent emissions on ecosystems are less well understood, but are of growing concern.

17.4.2.2 Formation of secondary compounds

In addition to transport, organic compounds emitted into the air may also participate in complex sets of chemical reactions. While many of these reactions "cleanse" the atmosphere (most organic compounds ultimately react to form carbon dioxide), a number of undesirable side effects may also occur. Such adverse impacts include the formation of respiratory irritants and the destruction of protective components of the atmosphere. Ozone is a classic example of the complexity of secondary atmospheric impacts. Ozone is a highly reactive molecule consisting of three oxygen atoms (O_3). In one part of the atmosphere ozone is beneficial, in another, it is a pollutant of major concern. Solvents and other organic emissions may either increase or decrease ozone concentrations, depending on the compound, location of reaction, and background chemistry. The mechanisms of some adverse secondary responses are discussed below.

17.4.2.3 Spatial scales of secondary effects

Two layers of the Earth's atmosphere are known to be adversely impacted by solvents - the troposphere and the stratosphere. These two layers are closest to Earth, and have distinct chemical and physical properties. The troposphere (our breathable atmosphere) is the closest layer, extending from the Earth to a height of between 10 to 15 km. The rate of chemical reaction generally determines the spatial scale over which emissions have an impact in the troposphere. Most non-halogenated solvents have lifetimes of a week or less, and elevated concentrations will only be found near the sources.[4] Compounds that do not react rapidly in the troposphere (e.g., CFCs) are relatively uniformly distributed, and may eventually reach the stratosphere. The stratosphere is the next vertical layer of the atmosphere, extending from the tropopause (the top of the troposphere) to about 50 km in altitude. Little vertical mixing occurs in the stratosphere, and mixing between the troposphere and the stratosphere is slow.

Impacts on the stratosphere can be considered global in scale, while impacts on the troposphere are generally urban or regional in scale. Distinct chemical systems of interest concerning solvents in the atmosphere are stratospheric ozone depletion, global climate change, and tropospheric photochemistry leading to enhanced production of ozone, particulate matter, and other secondary pollutants such as organonitrates.

17.4.2.3.1 Global impacts

Because some solvent compounds are nearly inert, they can eventually reach the stratosphere where they participate in global scale atmospheric dynamics such as the destruction of stratospheric ozone and unnatural forcing of the climate system. Stratospheric ozone depletion by chlorofluorocarbons (CFCs) is a well-known example of global scale impacts. CFCs were initially viewed as environmentally superior to organic solvents. They are generally less toxic than other similarly acting compounds, less flammable and are virtually inert in the troposphere. Replacing solvents using volatile organic compounds (VOCs) with CFCs was hoped to reduce the formation of tropospheric ozone and other secondary pollutants. Because of their inert properties, there are no effective routes for the troposphere to remove CFCs, and, over the decades, emissions of CFCs have caused their accumulation, enabling them to slowly leak into the stratosphere. In the stratosphere, the strong ultraviolet (UV) light photodissociates CFCs, releasing chlorine, which then catalytically attacks ozone. CFC use has been largely eliminated for that reason. Partially halogenated organic solvents do not contribute as seriously to this problem since they react faster in the tropo-

sphere than CFCs, so the associated chlorine does not reach the stratosphere as efficiently. CFCs and other solvent compounds also have a potential impact on global climate change.

17.4.2.3.2 Stratospheric ozone depletion

Natural concentrations of stratospheric O_3 are balanced by the production of ozone via photolysis of oxygen by strong UV light, and destruction by a number of pathways, including reactions with nitrogen oxides and oxidized hydrogen products that are present. Photolysis of an oxygen molecule leads to the production of two free oxygen atoms:
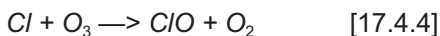
$$O_2 + h\nu \longrightarrow O + O \qquad\qquad [17.4.1]$$

Each oxygen atom can then combine with an oxygen molecule to form ozone:

$$O + O_2 \longrightarrow O_3 \qquad\qquad [17.4.2]$$

Ozone is then destroyed when it reacts with some other compound, e.g., with NO:

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad\qquad [17.4.3]$$

Addition of either chlorine or bromine atoms leads to extra, and very efficient, pathways for ozone destruction. The free chlorine (or bromine) atom reacts with ozone, and the product of that reaction removes a free oxygen atom:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad [17.4.4]$$

$$\underline{ClO + O \longrightarrow Cl + O_2} \qquad [17.4.5]$$

Net (reactions 4+5 together): $\qquad O_3 + O \longrightarrow 2\,O_2 \qquad [17.4.6]$
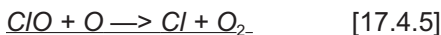
Removing a free oxygen atoms also reduce ozone since one less ozone molecule will be formed via reaction 17.4.2. Thus, the chlorine atom reactions effectively remove two ozone molecules by destroying one and preventing the formation of another. Additionally, the original chlorine atom is regenerated to catalytically destroy more ozone. This reaction cycle can proceed thousands of times, destroying up to 100,000 molecules of O_3 before the chlorine is removed from the system (e.g., by the formation of HCl).

Reduction of ozone is greatly enhanced over the poles by a combination of extremely low temperatures, decreased transport and mixing, and the presence of polar stratospheric clouds that provide heterogeneous chemical pathways for the regeneration of atomic chlorine. The resulting rate of O_3 destruction is much greater than the rate at which it can be naturally replenished.

Current elevated levels of CFCs in the troposphere will provide a source of chlorine to the stratosphere for decades, such that the recent actions taken to reduce CFC emissions (through the Montreal Protocol) will have a delayed impact.

17.4.2.3 Global climate forcing

Over the past decade, the potential for non-negligible changes in climate caused by human activity has been an issue of great concern. Very large uncertainties are associated with both estimations of possible effects on climate as well as estimations of the potential impacts of changes in climate. However, current consensus in the international scientific community is that observations suggest "a discernible human influence on global climate".[3]

Solvent compounds, especially CFCs and their replacements, participate in climate change as "greenhouse gases". Greenhouse gases allow short-wave solar radiation to pass through, much of which the earth absorbs and re-radiates as long-wave radiation. Greenhouse gases absorb the long-wave radiation, causing the atmosphere to heat up, thereby acting as a blanket to trap radiation that would normally vent back to space. Climate change is a controversial and complex issue, but it is likely that restrictions such as those from the Kyoto Protocol will be adopted for emissions of compounds strongly suspected of exacerbating climate change. Many countries have already adopted stringent policies to reduce greenhouse gas emissions.

17.4.2.4 Urban and regional scales

Another area of concern regarding outdoor air is exposure to secondary pollutants that are due, in part, to chemical reactions involving solvent compounds. Examples include the formation of elevated levels of ozone, formaldehyde, organonitrates, and particulate matter. Formaldehyde, a suspected carcinogen, is an oxidation product of organic compounds. Tropospheric ozone and organonitrates, as discussed below, are formed from a series of reactions of organic gases and nitrogen oxides in the presence of sunlight. Particulate matter formation is linked to ozone, and some solvents may react to form particulate matter. The particulate matter of concern is small (generally less than 2.5 µm in diameter) usually formed by gas-to-aerosol condensation of compounds via atmospheric chemical reactions. Ozone and particulate matter are both regulated as "criteria" pollutants in the United States because they have been identified as risks to human health. Ozone is believed to cause respiratory problems and trigger asthma attacks, and PM has a variety of suspected adverse health outcomes (e.g., respiratory and coronary stress and failure). Many organonitrates, such as peroxyacetyl nitrate, are eye irritants and phytotoxins. Currently, the formation and effects of ozone are better understood than those of fine particulate matter and organonitrates. The following section of this chapter discusses the effects, formation, and control of tropospheric ozone. The role of solvents in forming particulate matter is currently viewed as less urgent.

17.4.3 TROPOSPHERIC OZONE

Tropospheric ozone, a primary constituent of photochemical smog, is naturally present at concentrations on the order of 20-40 parts per billion (ppb).[4] However, elevated levels of ground-level ozone are now found virtually worldwide, reaching in some cities concentrations of up to 10 times the natural background.

17.4.3.1 Effects

Ozone is believed to be responsible for both acute (short-term) and chronic (long-term) impacts on human health, especially on lung functions. Major acute effects of ozone are decreased lung function and increased susceptibility to respiratory problems such as asthma attacks and pulmonary infection. Short-term exposure can also cause eye irritation, coughing, and breathing discomfort.[5-7] Evidence of acute effects of ozone is believed to be "clear and compelling".[8] Chronic health effects may present a potentially far more serious problem; however, definitive evidence is difficult to obtain. Recent studies do suggest that ambient levels of ozone induce inflammation in human lungs, which is generally accepted as a precursor to irreversible lung damage,[6] and chronic animal exposure studies at concentrations within current ambient peak levels indicate progressive and persistent lung function and structural abnormalities.[5,8]

Crop damage caused by air pollution has also received much attention. It is estimated that 10% to 35% of the world's grain production occurs in regions where ozone pollution likely reduces crop yields.[9] Air pollution accounts for an estimated several billion dollar crop loss every year in the United States alone, and research and analysis suggests that about 90% of this crop loss can be directly or indirectly attributed to ozone.[10] Evidence also indicates that ozone may cause short- and long-term damage to the growth of forest trees,[11] as well as altering the biogenic hydrocarbon emissions of vegetation.[12]

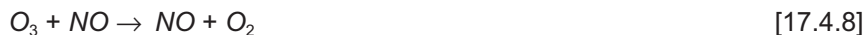## 17.4.3.2 Tropospheric photochemistry and ozone formation

In the lowest part of the atmosphere, chemical interactions are very complex. A large number of chemical compounds are present, the levels of many of these compounds are greatly elevated, and emissions vary rapidly due to both natural and anthropogenic sources. Ozone formation in the troposphere results from non-linear interactions between NO_x, VOCs, and sunlight.[4,13] In remote regions, ozone formation is driven essentially by methane,[14] however elsewhere most VOCs participate in ozone generation. For example, measurements of non-methane organic compounds in the South Coast Air Basin of California during the 1987 Southern California Air Quality Study, identified more than 280 ambient hydrocarbon and oxygenated organic species,[15] many of which originated from solvents and contribute in differing degrees to ozone generation.

The only significant process forming O_3 in the lower atmosphere is the photolysis of NO_2 (reaction with sunlight), followed by the rapid reactions of the oxygen atoms formed with O_2.

The only significant process forming O_3 in the lower atmosphere is the photolysis of NO_2 (reaction with sunlight), followed by the rapid reactions of the oxygen atoms formed with O_2.

$$NO_2 + h\nu \rightarrow O(^3P) + NO \qquad\qquad [17.4.7]$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$
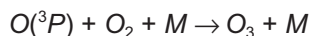
This is reversed by the rapid reaction of O_3 with NO,

$$O_3 + NO \rightarrow NO + O_2 \qquad\qquad [17.4.8]$$

This reaction cycle results in a photostationary state for O_3, where concentrations only depend on the amount of sunlight available, dictated by the NO_2 photolysis rate (k_1) and the $[NO_2]/[NO]$ concentration ratio.

$$\left[O_3\right]_{steady-state} = \frac{k_1\left[NO_2\right]}{k_2\left[NO\right]} \qquad\qquad [17.4.9]$$

Because of this photostationary state, ozone levels generally rise and fall with the sun, behavior that is referred to as "diurnal."

If the above NO_x cycle were the only chemical process at work, the steady-state concentrations of ozone would be relatively low. However, when VOCs such as organic solvent compounds are present, they react to form radicals that may either (1) consume NO or (2) convert NO to NO_2. This additional reaction cycle combined with the above photostationary state relationship causes O_3 to increase.

Although many types of reactions are involved,[4,13,16,17] the major processes for most VOCs can be summarized as follows:

$$VOC + OH \rightarrow RO_2 + products$$ [17.4.10a]

$$RO_2 + NO \rightarrow NO_2 + radicals$$ [17.4.10b]

$$radicals \rightarrow ... \rightarrow OH + products$$ [17.4.10c]

$$products \rightarrow ... \rightarrow ... + CO_2$$ [17.4.10d]

The last two pseudo-reactions given comprise many steps, and the products often include formaldehyde, carbon monoxide and organonitrates. The rate of ozone increase caused by these processes depends on the amount of VOCs present, the type of VOCs present, and the level of OH radicals and other species with which the VOCs can react. One of the major determinants of a compound's impact on ozone is the rate of the reaction of the particular VOC with the hydroxyl radical via reaction [17.4.10a], above. The total amount of ozone formed is largely determined by the amount of VOC and NO_x available.

The dependence of O_3 production on the initial amounts of VOC and NO_x is frequently represented by means of an *ozone isopleth diagram.* An example of such a diagram is shown in Figure 17.4.1. The diagram is a contour plot of ozone maxima obtained from a large number of air quality model simulations using an atmospheric chemical mechanism. Initial concentrations of VOC and NO_x are varied; all other variables are held constant. Notice that there is a "ridge" along a certain VOC-to-NO_x ratio where the highest ozone concentrations occur at given VOC levels. This is referred to as the "optimum" VOC-to-NO_x ratio. While the atmosphere is more complicated than this idealized system, important features are very similar.

VOC-to-NO_x ratios sufficiently low to retard ozone formation from an optimum ratio (represented in the upper left quadrant of Figure 17.4.1) can occur in central cities and in plumes immediately downwind of strong NO_x sources. Rural environments tend to be characterized by fairly high VOC-to-NO_x ratios because of the relatively rapid removal of NO_x
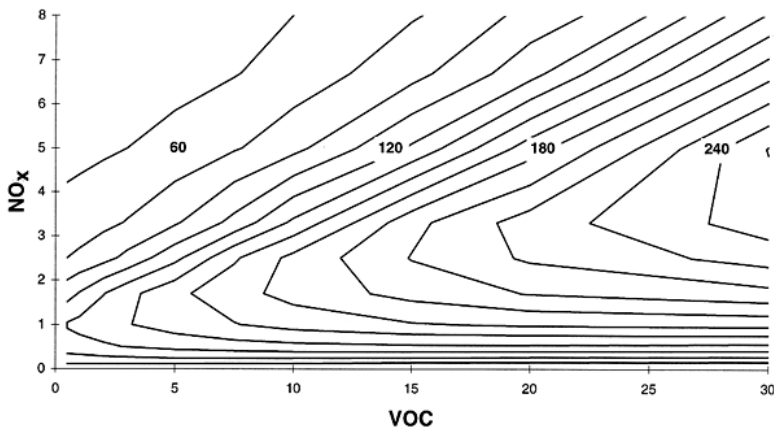

Figure 17.4.1. Ozone isopleth diagram showing the dependencies of ozone on varying levels of initial VOCs and NO_x. Concentrations are given in ppb. [Adapted from M.S. Bergin et al., *Enc. of Env. Analysis and Remediation*, **29**, 3029, (1998)]

from non-local sources as compared to that of VOCs, coupled with the usual absence of strong local NO_x sources and the presence of natural VOC sources. In such rural environments, the formation of ozone is limited more by the absence emissions of NO_x, and most ozone present was directly transported from upwind. Indeed, in most of the troposphere, except in areas of strong NO_x sources, the availability of NO_x governs ozone production.

17.4.3.3 Assessing solvent impacts on ozone and VOC reactivity

As mentioned previously, the contribution of solvents to the VOC levels, and hence ozone formation, is significant. For example, in Los Angeles, about 25% of the VOC mass is from solvent use.[1] This fraction is down from earlier years due to various controls such as using water-based paints and enclosing/controlling paint spraying operations. On the other hand, reduction in the use of CFCs as propellants has led to an increase in organic emissions from substituted compounds.[2] However, the impact on ozone formation by a specific source is not directly proportional to the amount of VOC emitted by that source. A major determinant of the ozone forming potential is the reactivity of the compound or compound mixture emitted. Reactivity can be viewed as the propensity for a compound to form ozone, and this propensity varies dramatically between compounds and between environments.[18,19]

As seen in Table 17.4.1, 'box' model (single cell) simulations designed to represent summertime conditions in Los Angeles, California indicate that the amount of carbon associated with each class of compound only roughly corresponds to the amount of ozone formed from those compounds. Methane, which reacts very slowly but comprises most of the carbon, contributes little to ozone formation. Alkenes and aromatics are only a small part of the total carbon, but lead to much of the ozone formation.

Table 17.4.1. Percentage of ozone production attributable to each organic. The percentages shown should be viewed as only approximate, and will depend upon local emissions characteristics. (*While not considered organic carbon, carbon monoxide acts to facilitate ozone formation similar to organic compounds.) [Adapted from F.M. Bowman and J.H. Seinfeld, *J. Geophys. Res.*, 99, 5309, (1994) and M.S. Bergin et al., *Env. Sci. Technol.*, 29, 3029 (1998)]

Compound Class	Percent of carbon in each specified class	Percent of ozone due to specified organic class
carbon monoxide*	35	6
methane	40	1
aldehydes and ketones	1	3
non-methane alkanes, ~4C	8	17
non-methane alkanes, ~8C	5	16
aromatics, including toluene	3	5
aromatics, including xylenes and others	3	13
ethene	2	12
biogenic alkenes ans isoprene	1	10
other alkenes	2	17

17.4.3.3.1 Quantification of solvent emissions on ozone formation

Two methods are generally employed to quantify the role pollutants play in forming ozone: experimental and computational. Both types of estimation approaches have their limitations. In the case of physical experiments, it is difficult to fully simulate ambient conditions, so the results do not have general applicability. In the case of computational approaches, uncertainties and approximations in the model for airshed conditions, in its formulation, and in the chemical mechanism cause uncertainties in the predicted ozone impacts. For these reasons, modeling predictions and experimental measurements are used together.

17.4.3.3.1.1 <u>Experimental analysis</u>

Experimental analysis is performed using environmental 'smog' chambers, either with a series of single hydrocarbons irradiated in the presence of NO_x or using complex mixtures to simulate, for example, automobile exhaust emitted into characteristic urban ambient conditions. Such chambers are large reaction vessels (some with internal volumes of cubic meters), in which air and small amounts of hydrocarbons and NO_x are injected, and then irradiated with real or artificial light. Both indoor and outdoor chambers are used so behaviors can be evaluated under natural radiative conditions and under controlled conditions. While these experiments[18-23] clearly indicate differences in ozone formation from individual hydrocarbons, they do not represent some important physical systems of urban pollution such as the mixing processes and continuing emissions cycles. Such experiments have focused both on groups of compounds as well as specific VOCs, including solvents. A particular limitation has been studying very low vapor pressure solvents because it is difficult to get enough of the compound into the vapor phase in the chamber to appreciably change the ozone levels. Another limitation is the expense of using smog chambers to simulate a large range of conditions that might occur in the atmosphere. On the other hand, smog chambers are very powerful, if not fundamental, for developing chemical mechanisms that describe the reaction pathways that can be used in computational approaches.

17.4.3.3.1.2 <u>Computational analysis (air quality models)</u>

Given the limitations of physical experiments to simulate atmospheric conditions, computer models have been developed to assess the impact of emissions on ozone. These models, called airshed models, are computerized representations of the atmospheric processes responsible for air pollution, and are core to air quality management.[23] They have been applied in two fashions to assess how solvents affect ozone. One approach is to conduct a number of simulations with varying levels of solvent emissions.[2] The second approach is to evaluate individual compounds and then calculate the incremental reactivity of solvent mixtures.[19,21,24-28]

Derwent and Pearson[2] examined the impact of solvent emissions on ozone by simulating air parcel trajectories ending in the United Kingdom and perturbing the emissions to account for an anticipated 30% mass reduction in VOCs from solvents between 1995 and 2007. They found a small decrease in ozone-from 78 to 77 ppb in the mean peak ozone in the UK, and a 9 ppb reduction from 129 ppb outside of London. A more substantial decrease of 33 ppb from the 129 ppb peak outside of London was found from reducing non-solvent mass VOC emissions by 30% outside of the UK and 40% within the UK. This suggests that the VOC emissions from sources other than solvents have a higher average reactivity, as is discussed by McBride et al.[29]

While the types of simulations conducted by Derwent and Pearson[2] are important to understanding the net effect of solvent emissions on ozone, there is an unanswered associated and important question, that being which specific solvents have the greatest impacts.

This question is critical to assessing if one solvent leads to significantly more ozone formation than a viable substitute (or *vice versa*).

To evaluate the contribution of individual organic compounds to ozone formation, the use of *incremental reactivities* (IR) was proposed,[18-21] defined as the change in ozone caused by a change in the emissions of a VOC in an air pollution episode. To remove the dependence on the amount of VOC added, incremental reactivity is defined by equation [17.4.11] as the limit as the amount of VOC added approaches zero, i.e., as the derivative of ozone with respect to VOC:

$$IR_i = \frac{\partial[O_3]}{\partial[VOC_i]}$$
[17.4.11]

Here, IR_i is the incremental reactivity and the subscript i denotes the VOC being examined. This definition takes into account the effects of all aspects of the organic's reaction mechanism and the effects of the environment where the VOC is emitted. A similar quantity is the relative reactivity,[23] RR_i:

$$RR_i = \frac{R_i}{\sum\limits_{i=1}^{N} F_{B_i} R_i}$$
[17.4.12]

where:

F_{B_i}	mass fraction of compound i in the reference mixture
IR_i	incremental reactivity of species i (grams ozone formed per gram compound i emitted)

In this case, the incremental reactivity is normalized by the reactivities of a suite of organics, thus removing much of the environmental dependencies found when using IRs defined by [17.4.11]. This metric provides a means for directly comparing individual compounds to each other in terms of their likely impact on ozone.

A number of investigators have performed calculations to quantify incremental and/or relative reactivities for various solvents and other organics[23-28,30] and references therein. Those studies found very similar results for the relative reactivities of most compounds found in solvents. Figure 17.4.2 (based on references 23, 24 and 26) shows the relative reactivities for some of the more common compounds, as well as possible solvent substitutes and isoprene, a naturally emitted organic. (For a more extensive list of relative reactivities, see 19, 27 and 30.) As can be seen, even normalized compound reactivities can vary by orders of magnitude. Some compounds even exhibit "negative" reactivities, that is that their emission can lead to ozone decreases under specific conditions. In particular, negative reactivities are found most commonly when the levels of NO_x are low, e.g., in non-urban locations. For example, Kahn et al.,[26] found that a solvent can promote ozone formation in one area (e.g., near downtown Los Angeles), but retard ozone formation further downwind. Kahn also found that the relative reactivities of the eight different solvents studied were similar in very different locations, e.g., Los Angeles, Switzerland and Mexico City.

Looking at Figure 17.4.2, it is apparent that alkenes and aromatic hydrocarbons with multiple alkyl substitutions (e.g., xylenes and tri-methyl benzene) have relatively high reactivities. Alcohols, ethers and alkanes have lower reactivities. Halogenated organics have some of the lowest reactivities, so low that they are often considered unreactive. This suggests that there are two ways to mitigate how solvents contribute to air quality problems. The more traditional method is to reduce the mass of organic solvent emissions (e.g., by using water-based paints). A second approach is to reduce the overall reactivity of the solvent
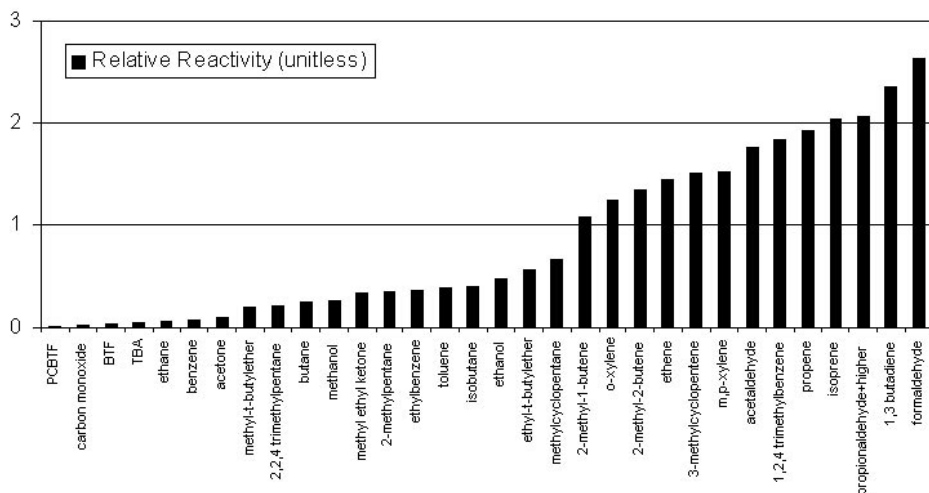
Figure 17.4.2. Solvent relative reactivities based on mass of ozone formed per gram of solvent emitted into the gas phase. PCBTF is para-chlorobenzo-trifluoride, BTF is benzo-trifluoride and TBA is tertiary butyl acetate. [Adapted from M.S. Bergin et al., *Env. Sci. Technol.*, **29**, 3029 (1998) and M. Khan et al., *Atmos. Env.*, **33**, 1085 (1999)].

used, e.g., by switching to ethers, alcohols, alkanes or halogenated compounds. Solvent substitution, however, is complicated by the need to maintain product quality.

17.4.4 REGULATORY APPROACHES TO OZONE CONTROL AND SOLVENTS

Historically, regulatory approaches to reducing ozone concentrations have relied reducing the mass emissions of VOCs,[2,4] and this has led to stringent controls on solvents. Two factors are important in determining if an organic solvent is considered a VOC: its reactivity (discussed above) and its vapor pressure. In the U.S., traditionally, if a compound was less reactive than ethane, it was considered unreactive. Such compounds include many halogenated species and some acetates and ethers. Recently, acetone was also added as an unreactive compound. A vapor pressure threshold is also used in many areas (e.g., Europe) since it is viewed that compounds with very low vapor pressures will not be emitted rapidly into the atmosphere. It has been argued that a vapor pressure limit may not be appropriate since, given time, even lower vapor pressure compounds will have ample time to evaporate. Just recently, California is considering regulations that more fully account for the full range of reactivities that solvents possess. This is due, in part, to make it easier for manufacturers to meet stringent regulations being adopted in that state to help them meet their air quality goals. It is likely that other areas will also have to employ increasingly more stringent regulations, to both lower ozone and alleviate other environmental damage.

In many countries, greater focus is now being placed on reducing NO_x emissions to mitigate ozone formation. This has important ramifications for solvent use, indicating the

regulatory focus is now turning from VOCs towards NO_x, the other main precursor to ozone. Another imminent regulatory issue is the control of ambient fine particulate matter. While the role of solvent emissions in forming particulate matter is not well understood, studies to date do not suggest they are a major contributor.

17.4.5 SUMMARY

Solvents are, and will continue to be, one of the major classes of organic compounds emitted into the atmosphere. These compounds have a wide range of air quality impacts. Accumulation of toxic compounds indoors is of concern, although outdoors the concern of toxicity is significantly less substantial due to rapid dilution. In the stratosphere, some of the halogenated solvents lead to depletion of the protective layer of ozone, while in the troposphere solvents generally lead to increased ozone levels, where it adversely affects health and the environment. The former has led to regulations of CFCs, and the latter to regulations of organic solvents. Some solvents are also considered to be precursors to the formation of secondary tropospheric pollutants other than ozone, such as particulate matter, however these relationships are currently less certain.

In the aggregate, total VOC emissions from solvents in the U.S. are the second largest single source category in polluted urban areas, falling just behind motor vehicle VOC emissions both in terms of mass and urban ozone production. For now, regulations are designed to reduce the loss of ozone in the stratosphere and the formation of excess ozone in the troposphere. However, while some solvents are very reactive, others are substantially less reactive, suggesting that there is considerable opportunity to reduce urban ozone formation from solvents by utilizing substitutes with low ozone forming potentials. Currently, most regulations are targeted at reducing the mass of VOC emissions, not their relative impacts on ozone.

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