AN 8158 deleted

August 6, 1991

Ray Gomez

SUBJECT: GREENPEACE/CHLORINE

I am enclosing some comments on the document entitled, "Chlorine: The Product is the Poison".

Bob Hinderer

cc: Carl Mattia (w/o attachments)

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GREENPEACE/CHLORINE COMMENTS

- The document is not an assessment, but an effort to use mixture of fact and conjecture to support their position.

- The author wants the reader to believe that because a number of chemicals in this class are well recognized as posing serious concerns, all chemicals in this class are the same.

- Many of the author's positions and conclusions are supported by data which is frequently of questionable relevance and by major leaps in faith. In many cases, important logic steps and technical support are missing.

- Some chlorinated organics resist breakdown and are persistent (paragraph 2, p. 2). However, VCM is degraded rapidly in air (1-2 days half-life) which route of loss into the environment.

- Most living things have not evolved methods to detoxify or excrete them (para. 5, p. 2). This is a false statement. Most organisms have systems which can metabolize and excrete these chemicals. However, the efficiency of this process is chemical and species specific.

- Many statements about chlorinated organics can be made for many classes of chemicals (i.e., cause many types of effects, can be detected everywhere, are a potential hazard to water resources).

- (Para. 5, p. 6) The Great Lakes is a sink for CL-organics as far away as Latin America. Many classes of chemicals make their way into the Great Lakes. However, the prime contribution of pollutants are from local source. The suggestion that Latin America contributes to the Great Lakes is ludicrous.

- The Great Lakes will take a long time to recover (Para. 6, p. 6). Lake Erie has recovered dramatically to pollution control efforts over the last 15 years.

- (P. 7) The authors seem to have skipped a step. They do not explain why a ban is needed vs. a reduction in release. They do not consider the future impact that the implementation of existing regulations will have. They have not even considered that there are no effect or no significant risk levels.

- (Para. 4, p. 19) The suggestion that the association of one with adverse effects means all are to blame is faulty logic. They also fail to point out that associations are difficult to establish in population studies (humans, animals, or plants).

- While they note many chlorinated organisms have been found in man (p. 21), they fail to note that the presence of a chemical per se does not mean that there is an unacceptable risk. The same can be said for the presence of these chemicals in the environment.

- (P. 26) The author would like us to believe that the reproduction failure was due to "a number of organochlorins". However, as one reads, it is clear that no one really knows. Many factors, physical and chemical can effect the embryonic and newborn stages.

- (P. 29) (Jacobson, 1988) Because of numerous confounding factors in these types of studies, there is no way of knowing what the cause (inorganic, organic, or others) might be.

- (P. 31) We agree that there has been an improvement in the concentrations of chlorinated organics in the Great Lakes. This is consistent with the improvement in the vitality of the Lakes. Although the authors concluded that diseases have flattened out, they fail to consider the impact of the continuing implementation of existing environmental regulations.

- A few tables are attached comparing the uptake, BOD, bioaccumulation, etc., for various chlorinated organics. As you see, they can differ by more than an order of magnitude. Some chemicals like DDT are readily absorbed and metabolized, but are retained in the fat. Other chemicals like VCM are readily absorbed and metabolized and are rapidly excreted. Still others, like PVC, are relatively inert. They cannot be absorbed (i.e., are not biologically available) and therefore do not pose a toxic hazard in the environment.

- The section on Environmental fate is provided from the EPA/ATSDR draft document on VCM. I have underlined some items of interest. Care should be taken in using any data not underlined, since it may be inaccurate/outdated.

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only when the temperature varies which causes the respiration and ventilation volumes to vary. The uptake rates in Table 4 are remarkably similar regardless of their partition coefficient. It is interesting that the rates at 25°C were faster than at 10°C. Depuration rates, however, appear to be dependent on the hydrophobic property of the chemical or its metabolites.

TABLE 4—*Uptake of chemicals by fish.*

Chemical	Temperature, °C	Log P^f	Uptake Rate Constant, ml/g/h
CCl_4	10	2.64	4
HCB[a]	10	5.23	19
PCB[b]	10	7.6[g]	12
DEHP[c]	25	4.2[h]	76[e]
Chlorpyrifos[d]	25	4.82	55

[a] Hexachlorobenzene, Neely et al [17].
[b] Tetrachlorobiphenyl, Branson et al [18].
[c] Di-2-ethyl hexylphthalate, Mayer [19].
[d] Chlorpyrifos, Neely [4].
[e] Rate constant from BIOFAC parameter estimating program, Dow Chemical Company, for C_w = 4.6 μg/litre.
[f] Octanol:water partition coefficient.
[g] Calculated log P, Neely et al [17].
[h] Estimated log P from water solubility, Chiou et al [20].

4. To express biodegradability data in terms of meaningful rate constants, Bailey [10] illustrated the relationship between microbial biomass and the biodegradation of chlorodiphenyl oxide. Table 5 summarizes the relationship between biochemical oxygen demand (BOD), river die-away data, activated sludge die-away data, and $^{14}CO_2$ formation data. The biodegradability rate constant for chlorodiphenyl oxide, about 37 ml/g volatile solids (VS)/h predicts a half-life of ~4 h in an activated sludge wastewater treatment plant with 3700 mg/litre mixed liquor VS and up to 10 mg/litre chlorodiphenyloxide (see Appendix). The data in Table 5 show a range of rate constants for different experimental procedures. From this information, the following points are derived.

(*a*) Experiments involving long time periods may allow development of a microbial population acclimated to the compounds present. This leads to high apparent rate constants. The converse is also true and perhaps even more significant to apparent low rate constants developed from short-term experiments.

(*b*) Rate constants work well when the microorganisms have a similar history, for example, two river water samples from different locations, one with 7 and one with 13 mg VS/litre.

TABLE 5—*Typical biodegradability data for chlorodiphenyl oxide.*

Method	Time, h	Volatile Solids, mg/litre	Initial Concentration, mg/litre	Concentration at Time, mg/litre	Oxidation, %[a]	Rate of Conversion[b] ml/g VS/h	Rate of Total Oxidation[c] ml/g VS/h
Dilution Bottle BOD	120	~0.4	2	~1.8	28[d]	~300	5 800
	240	~0.4	2	~0	62[d]	~10 000	~6 400
	480	~0.4	2	~0	62[d]	~3 000	~3 200
River water Die away[e]	120	13	1	1			
	264	13	1	<0.1		320	37
	312	7	1	1			
	528	7	1	<0.1		300	
Activated Sludge Die Away	5.5	2 380[e]	0.039		19[d]		14.5
	6.5	3 185[e]	0.92		29[d]		14.0
	6.5	3 735[e]	9.2	<1	13[d]	37	5.4
	67	300[f]	0.94		32[d]		15.9
	120	2 000[f]	0.94		36[d]		1.5

[a] Biochemical oxygen demand as a percent of theoretical.

[b] Rate of conversion = $\frac{(C_i - C_t\ \mu g/ml)\ (1000\ ml/litre)}{(VS\ g/litre)\ (C_i\ \mu g/ml)\ (t, h)}$ = disappearance of parent compound

where

C_i = the initial concentration of chemical, and
C_t = the concentration of chemical at time, t.

[c] Rate of total oxidation = $\frac{(CO_2\ yield\ or\ BOD)\ (1000\ ml/litre)}{(VS\ g/litre)\ (t, h)}$ = CO_2 formation.

[d] Water from Tittabawassee River, summer 1975.
[e] Industrial activated sludge.
[f] Municipal activated sludge.
[g] Yield of $^{14}CO_2$ recovered, 75 percent yield of CO_2 observed at long times.

(*c*) Any biological system can be overloaded, for example, 9.2 mg/litre chlorodiphenyl oxide, over twice the water solubility, shows a slower rate constant.

(*d*) The rate constant for disappearance (Rate of Conversion, Table 5) of chlorodiphenyl oxide (ClDPO) is greater than the rate constant for ultimate biodegradation to carbon dioxide (CO_2) (Rate of Total Oxidation, Table 5).

(*e*) Some of the carbon of chlorodiphenyl oxide is incorporated in the growing biomass.

(*f*) There may be better measurements of active microbial biomass than VS, that is, starved microbes and nonmicrobial VS may affect the apparent active biomass.

(*g*) The rate of biodegradability from $^{14}CO_2$ formation and BOD may be quite different, for example, 50 percent BOD *could* produce 0 percent $^{14}CO_2$.

5. One of the better understood assumptions is the evaporation of chemicals from water in the "real" environment. Table 6 lists calculated rates of evaporation, water solubilities, vapor pressures, and molecular weights of a few compounds. The method of calculation, as suggested by Neely [*5*], is based on the exchange coefficients reported by Liss and Slater [*11*]. Evaporation of chemicals from water in the laboratory has been validated by Dilling [*12*] and others. One field study reported by Spacie et al [*13*] showed agreement between the calculated and observed evaporation of

TABLE 6—*Calculated rates of evaporation at 25 °C.*

Compound	Evaporation[b] Rate, k_3, cm/h	$t_{1/2}$,[c] h	Water Solubility, μg/litre	Vapor Pressure, mmHg
Benzene	14.5	4.8	820 000	9.5×10^{1}
Chlorobenzene	11.5	6.03	490 000	1.2×10^{1}
HCB	2.32	29.7	35	1×10^{-5}
PCB[a]	1.5	46	54	4.06×10^{-4}
DDT	0.93	73.9	1.0	1×10^{-7}
Chlorpyrifos	0.12	575	2 000	1.87×10^{-5}
Phenol	0.03	2 300	8×10^{7}	3.5×10^{-1}
DEHP	0.00052	132 600	600	2.38×10^{-7}

[a] Trichlorobiphenyl.

[b] $$\frac{1}{k_3} = \frac{1}{20\,(44/Mw)^{1/2}} + \frac{TW}{VP \times Mw \times 16.04 \times 3000\,(18/Mw)^{1/2}}$$

[c] $t_{1/2} = (0.693)/(k_3) \times 100$ cm for a pond 1 m deep.

where
Mw = molecular weight,
VP = vapor pressure (mmHg),
W = water solubility (mg/litre), and
T = temperature (K).

DDT from a farm pond, but a much slower rate of evaporation than calculated for DDE from a pool and a quarry. They attribute the difference to a lack of *wind* and *turbulence* for the pool and quarry studies.

Although suspended solids have been shown not to affect the rate of evaporation [*14*], the *very small particles* that escaped filtration or centrifugation may have resulted in apparent concentrations of DDE in the pool and quarry which were really associated with the [illegible] calculation of evaporation rates of chemicals in water by the [illegible] assumes that the compounds are in true solution.

Model Ecosystem Approach

Model ecosystem fate studies such as described by Metcalf and Lu [*15*] are appealing because they resemble a small piece of a real environment. In theory the individual environmental rates previously discussed (evaporation, degradation, bioconcentration, and sediment binding) are all integrated in one test.

The most commonly generated data from the "Metcalf" model ecosystem are the biodegradability index (BI) values and ecological magnification (EM) values. The BI refers to the amount of polar metapolite extracted from an organism divided by the relative amount of nonpolar metabolites, while the EM refers to the total amount of parent compound in the organism divided by the amount in the surrounding water. The data and rankings for some benzene derivations, as reported by Lu and Metcalf [*16*] and Veith and Comstock [*8*], are the biodegradability data generated by the BOD method *without the aid of radiochemicals* (Table 7).

Both types of data to rank the biodegradability of the compounds in the series identified aniline and benzoic acid as the most biodegradable, but that is where the correlation ends. The *magnitude* of the BI data may be misleading for the following reasons.

1. The BI values for benzoic acid, 2.97, implies that this acid is 212 times more biodegradable than chlorobenzene, BI = 0.014. This factor is much larger than the three times suggested by the BOD_5 values, 66 and 24 percent, for benzoic acid and chlorobenzene, respectively. The ultimate degradation of chlorobenzene to CO_2, as indicated by BOD data, would evaporate from the model ecosystem. Apparently chemicals that degrade to CO_2 rather than polar metabolites will receive low BI values. The more water soluble benzoic acid may be more bioavailable for microbial degradation in the ecosystem than chlorobenzene. Perhaps the BI data described degradation in some aquatic environments and BOD data described degradation in another aquatic environment, for example, a wastewater treatment plant.

2. The BI values for pentachlorophenol (0.338) and 3,5,6-trichloro-2-pyridinol (0.311) falsely imply greater biodegradability than chlorobenzene

TABLE 7—*Biodegradability by model ecosystem and BOD measurements.*

Compounds	BOD_5[a] % of Theory	BOD_5[a] Rank in Series	Aquatic Ecosystem BI[b]	Aquatic Ecosystem Rank in Series
Phenol	76	...[c]	...	...
Aniline	68	1	1.78	2
Benzoic acid	66	1	2.97	1
Benzene	45	...[c]	...	...
Chlorobenzene	24	2	0.014	6
Nitrobenzene	0	3	0.023	5
Pentachlorophenol	0	3	0.338	3
3,5,6-Trichloro-2-pyridinol	0	3	0.311	4

[a]BOD in 5 days.

[b]From Lu and Metcalf [16]; BI = $\frac{\text{polar (thin layer chromatography origin)}}{\text{nonpolar (total C-14 minus polar)}}$.

[c]Not ranked because aquatic ecosystem data were unavailable for comparison.

(0.014). The fraction of the phenolic compounds that becomes conjugated (with glucuronide or sulphate) in the ecosystem is counted as "polar" (at the origin of the thin-layer chromatogram) which increases the apparent biodegradability. Deconjugation causes the parent compound to return undergraded. The conjugated fraction of the "polar" compounds should be subtracted to give a truer picture of the relative biodegradability.

There are other interpretations of BOD data. BOD data can also be used to predict biotreatability in a secondary treatment facility and the need for additional biodegradability studies. BOD_5 values greater than 50 percent of the theoretical oxygen demand usually indicate efficient removal during activated sludge treatment under optimum operating conditions. These compounds are not persistent in the aquatic environment and should not require further biodegradability testing. Perhaps similar interpretation can be made from BI data, for example, compounds with BI values >1 may be removed efficiently in treatment plants.

The EM values for the benzene derivatives and their predicted bioconcentration potentials are shown in Table 8. The bioconcentration potentials, too, were predicted without the aid of radiochemicals. These predictions are based on measured partition coefficients (octanol:water) and a regression correlation reported by Neely et al [17].

Again, both types of data, "bioconcentration predictions" and EMs identify the most accumulative compounds in the series, chlorobenzene and pentachlorophenol, but the order is reversed. Generally, the other com-

TABLE 8—*Biomagnification by model ecosystem and partition coefficient correlations.*

Compounds	Bioconcentration Factor Predicted[d] $\log_{10} P$	BCF	Rank in Series	Aquatic Ecosystem Ecological Magnification	Rank in Series
Pentachlorophenol	5.07 (5.01)[b]	750	1	296	2
Chlorobenzene	2.84 (2.84)[b]	90	2	450	1
Nitrobenzene	2.13 (2.03)[b]	19	3	21	4
3,5,6-Trichloro-2-pyridinol	1.85 (1.79)[b]	13	3	29	3
Phenol	1.66 (2.27)[b]	8	...	...	...
Aniline	1.48 (1.51)[b]	4	4	16	4
Benzoic acid	0.94 (0.85)[b]	2	4	6	6

[a]From Leo et al [27]; $\log_{10} P$ = octanol:water partition coefficient.

[b]Value reported by Lu and Metcalf [16].

[c]Not ranked because aquatic ecosystem data were unavailable for comparison.

[d]From Neely et al [17], $\log_{10}$ BCF = 0.56 log P + 0.124; BCF at steady state in rainbow trout muscle.

pounds in the series can be grouped together as having a low accumulative potential compared to DDT. Either type of data would be useful in identifying the compounds with low accumulative potential.

For some chemicals, the biomagnification data from ecosystems may be more predictive of the overall fate of a chemical in the real environment than bioconcentration data alone. Biomagnification is the increase in concentration of a chemical relative to a lower food-chain trophic level, whereas bioconcentration is the increase in the aquatic organism relative to the ambient concentration in water. Clouding the issue further is the possible role of bioaccumulation, increased chemical concentration relative to the concentration in the organisms' diet.

Some of the other advantages of model ecosystem fate studies are the large data base—perhaps a few hundred compounds—and the characterization of major breakdown products.

One limitation of model ecosystems is the preferred use of radio-labeled compounds. Can the hundreds of unlabeled compounds be ignored? How should we select the most promising new chemical (product) from a series of new chemicals? Or, how should be prioritize a large list of industrial chemicals for additional studies? Even if all the chemicals of interest were radio-labeled, there are serious questions about what to do with model

chain organisms be omitted from the model ecosystem without significantly changing the BI or EM values? The most obvious interpretation of the data is to rank chemicals in terms of their potential to biomagnify and biodegrade.

Identification of the most accumulative compounds is a necessary requirement for laboratory fate studies. Some compounds with very high bioconcentration factors, 10^3 to 10^4, show lower than expected EM values, Table 9. Since the accumulation values for DDT, PCB, hexachlorobenzene (HCB), and di-2-ethylhexyl phthalate (DEHP) in the real aquatic environment are high, the laboratory data should also rank these compounds among the highest in accumulative potential. Table 9 shows that both types of model ecosystem data, terrestrial-aquatic and aquatic, failed to predict HCB and DEHP as accumulative compounds. All of the values in

TABLE 9—*Predicting the more accumulative compounds.*

Compounds	Bioconcentration Factors[a]	Ecological Magnification[g]	
	Trout Muscle	Terrestrial and Aquatic	Aquatic
PCB[f]	12 400 ± 2290	11 900	17 840
HCB	7 880 ± 350	287	343
DDT	1 390[b] (191)[c]	84 545	16 950
DEHP	800[e] (143)[d, b]	130	3

[a] Determined according to the accelerated bioconcentration test method, Branson et al [18].
[b] Calculated from regression correlation, Neely et al [17], and octanol:water partition coefficient; log P (DDT) = 5.57 (Dow Chemical Company data).
[c] Log P (DDT) = 3.98 [16].
[d] Log P (DEHP) = 3.58 [16].
[e] Fathead minnow data, Mayer [19].
[f] Tetrachlorobiphenyl.
[g] Lu and Metcalf [16].

Table 9 are lower than some reported for chemicals in the real aquatic environment, for example, bioconcentration factor (BCF) = 200 000 for PCB in Great Lakes fish. A lower percent fat in the laboratory fish may explain some of the difference between laboratory and field data but not the difference between compounds. Perhaps some of the residues in fish from "clean" lakes are higher than fish from lakes with higher suspended solid which absorb chemicals. The calculated trout muscle bioconcentration factor for DDT may appear to be comparatively low due to the analytical problems associated with measuring high partition coefficient values for DDT used in the calculations. Otherwise, the bioconcentration factor data appear to predict the more accumulative compounds.

Conclusions

1. The fate of chemicals in the aquatic environment can be predicted from laboratory data.
2. The decision-making process about chemicals is improved by the environmental rates approach compared to the model ecosystems approach for the following reasons.
   (*a*) Environmental properties data can be used for the same objectives as ecosystem data (biodegradation and bioconcentration); also, when expressed as rates, the environmental properties data can be used to predict environmental concentrations.
   (*b*) Rate data allow a greater understanding of what happens to chemicals in the aquatic environment over a period of time rather than at a single time.
   (*c*) Environmental rates can be estimated rapidly for a large number of chemicals and in many cases without the aid of radio-labeled compounds.
   (*d*) Some of the ecosystem data is misleading, for example, the implied biodegradability of chlorobenzene is low and the biomagnification of HCB is low relative to DDT.
3. Among the exciting subjects for future research efforts in environmental chemistry are:
   (*a*) Estimating rates of adsorption and release of chemicals from aquatic sediments
   (*b*) Correlating bioconcentration rates with fish species, fat content, temperature, metabolism, partition coefficients, and the structure of the chemical
   (*c*) Assigning meaningful rates to the degradation of chemicals: biological, chemical, and photochemical degradation
   (*d*) Correcting evaporation rates in the field for wind, turbulence, and suspended solid

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6. ENVIRONMENTAL FATE

6.1 OVERVIEW

Effluents and emissions from vinyl chloride and PVC manufacturers are responsible for the majority of vinyl chloride released to the environment. When released to the atmosphere, vinyl chloride is expected to be removed by reaction with photochemically generated hydroxyl radicals (half-life = 1.2 to 1.8 days). Reaction products include HCl, formaldehyde, formyl chloride, acetylene, chloroacetaldehyde, chloroacetylchloranil, and chloroethylene. In photochemical smog situations, vinyl chloride has a half-life of 3 to 7 h. When released to water, volatilization is expected to be the primary fate process (half-life = 8.7 to 43.3 h). In waters containing photosensitizers, such as humic materials, sensitized photodegradation may also be important. When released to soil, vinyl chloride will either volatilize rapidly from soil surfaces, or leach readily through soil, ultimately entering groundwater.

6.2 RELEASES TO THE ENVIRONMENT

The major source of release of vinyl chloride to the environment is believed to be emissions and effluents from plastic industries (primarily vinyl chloride and PVC manufacturers). Vinyl chloride released in wastewater is expected to volatilize fairly rapidly (on the order of hours to days) into the atmosphere. Other sources of release include disposal of vinyl chloride wastes in landfills, incomplete combustion of PVC, tobacco smoke, spills, and biodegradation of trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane in groundwater (IARC 1979, HSDB 1987, Wakeman and Johnson 1978, Wilson and Wilson 1985, Smith and Dragun 1984). EPA estimated that prior to 1975, 110 million kg/year of vinyl chloride escaped into the atmosphere from PVC production facilities in the United States (IARC 1979). Worldwide emissions of vinyl chloride into the atmosphere during 1982 was ~400 million lb (Hartmans et al. 1985).

6.3 ENVIRONMENTAL FATE

6.3.1 Air

Based on a vapor pressure of 2660 mm Hg at 25°C, essentially all vinyl chloride in the atmosphere is expected to exist in vapor form (Verschueren 1983, Eisenreich et al. 1981). Consequently, removal from the atmosphere by dry deposition is not expected to be an important fate process. Vinyl chloride has a relatively high partition coefficient between air and water (H = 50), which suggests that significant amounts of vinyl chloride would not be removed from the atmosphere by wet deposition (EPA 1985b).

Reaction of vinyl chloride vapor with photochemically generated hydroxyl radicals is predicted to be the primary degradation mechanism for this compound in the atmosphere. The half-life for this reaction in the typical atmosphere has been ~1.5 to 1.8 days (EPA 1985b). Products of this reaction are HCl, formaldehyde, formyl chloride, carbon monoxide, carbon dioxide, chloroacetaldehyde, acetylene, chloroethylene, chloroacetylchloranil, and H_2O (EPA 1985b). In photochemical smog situations, the reaction half-life of vinyl chloride is predicted to range between 3 and 7 h (HSDB 1987). Reaction with ozone (half-life = 4.2 to 33 days), reaction with oxygen atoms [$O(^3P)$] (half-life = 373 to 532 days), and direct photolysis are relatively insignificant degradation mechanisms in the atmosphere (EPA 1985b).

6.3.2 Water

The primary loss process for vinyl chloride in natural water systems is volatilization into the atmosphere. The half-life for vinyl chloride volatilization from a typical pond, river, and lake has been estimated to be 43.3, 8.7, and 34.7 h, respectively. These values are based on an experimentally determined reaeration rate ratio of ~2 and assumed oxygen reaeration rates of 0.008, 0.04, and 0.01 $hour^{-1}$ for a typical pond, river, and lake, respectively (EPA 1985b). Predicted half-lives should be considered rough estimates since the presence of various salts in natural water systems may affect the volatility of vinyl chloride significantly (EPA 1985b). In waters containing photosensitizers, such as humic materials, photodegradation may be fairly rapid. This suggests that in some waters sensitized photodegradation would also be a significant removal mechanism (HSDB 1987, EPA 1985b).

Chemical hydrolysis of vinyl chloride does not appear to be environmentally important. The hydrolytic half-life for vinyl chloride has been estimated to be <10 years (EPA 1985b). Vinyl chloride is not expected to oxidize chemically by reaction with photochemically generated hydroxyl radicals, molecular oxygen, or alkyl peroxy radicals in natural water systems. Limited available data on the biodegradation of vinyl chloride indicate that this compound is resistant to microbial degradation under aerobic conditions (EPA 1985b). Vinyl chloride is not expected to adsorb significantly to suspended solids and sediments in water or bioaccumulate significantly in aquatic organisms (HSDB 1987).

6.3.3 Soil

The relatively high vapor pressure of vinyl chloride (2660 mm Hg at 25°C) indicates that this compound should volatilize quite rapidly from dry soil surface. The effective half-life (due to volatilization) of vinyl chloride placed 10 cm deep in dry soil is predicted to be 12 h (EPA 1985b). Evaporation from moist soil surfaces is also expected to be significant since this compound does not adsorb strongly to soil and appears to volatilize fairly rapidly from water.

Experimental data regarding adsorption of vinyl chloride to soil were not located. Based on the regression equations given by Lyman et al. (1982) and Sabljic (1984), the soil adsorption coefficient (K_{OC}) for vinyl chloride has been estimated to range between 17 and 131. These K_{OC}

values suggest that this compound would be highly mobile in soil. Thus, vinyl chloride has the potential to leach into groundwater.

Based on data in aquatic media, chemical reaction of vinyl chloride in soil does not appear to be a significant fate process, and it appears that vinyl chloride would be resistant to biodegradation under aerobic conditions.

7. POTENTIAL FOR HUMAN EXPOSURE

7.1 OVERVIEW

Anthropogenic sources are responsible for all of the vinyl chloride found in the environment. Most of the vinyl chloride released to the environment will eventually locate in the atmosphere while much smaller amounts will eventually locate in groundwater. Vinyl chloride has been detected in the ambient air in the vicinity of vinyl chloride and PVC manufacturing plants and hazardous waste sites. Vinyl chloride is expected to leach into groundwater from spills, landfills, and industrial sources.

Segments of the general population living in the vicinity of emission sources are exposed to vinyl chloride by inhalation of contaminated air. Average daily intake of vinyl chloride by inhalation for these people ranges from trace amounts to 2100 μg/day. The average daily intake of vinyl chloride by inhalation is expected to be essentially zero for the remainder of the population. However, short-term inhalation exposure to relatively high levels may occur during use of new cars. This is due to volatilization of vinyl chloride from vinyl polymers within the car interior.

The majority of the general population is not expected to be exposed to vinyl chloride through ingestion of drinking water. However, people who have PVC water pipes that have not been treated adequately to remove vinyl chloride monomer may ingest ~0.06 to 2.8 μg/day of vinyl chloride from drinking water. The average daily intake of vinyl chloride through diet is predicted to be essentially zero.

NIOSH estimated that 27,000 workers are definitely exposed to vinyl chloride and that workers probably exposed may be as many as 2.2 million. Intake is expected to occur primarily through inhalation and less importantly by absorption through skin. Workplace air in some PVC manufacturing plants was found to contain 100 to 800 mg/m^3 (39 to 312 ppm) vinyl chloride with peak concentrations of up to 87,300 mg/m^3 (34,000 ppm). A NIOSH survey of three vinyl chloride manufacturers reported a time-weighed-average exposure of 0.18 to 69 mg/m^3 (0.07 to 27 ppm) vinyl chloride in workplace air.

7.2 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

7.2.1 Air

Air in rural/remote and urban/suburban areas of the United States typically contain no detectable amount of vinyl chloride (Stephens et al. 1986; Grimsrud and Rasmussen 1975a,b; Harkov et al. 1984; Wallace et al. 1984; EPA 1985b). Limited monitoring data indicate that in areas near vinyl chloride and polyvinyl chloride manufacturers, the

concentration of vinyl chloride in air typically ranges from trace levels to ~105 $\mu g/m^3$ (Gordon and Meeks 1977, Pellizzari et al. 1979, IARC 1979, EPA 1985b), but may exceed 2600 $\mu g/m^3$ (1 ppm) (Fishbein 1979). Elevated levels of vinyl chloride may also be found in the vicinity of hazardous waste landfills. Concentrations ranging from below detection limits to 5 to 8 $\mu g/m^3$ (0.002 to 0.003 ppm) have been monitored in the air above some landfills (Stephens et al. 1986, Baker and Mackay 1985). Homes near a hazardous waste site in Southern California were found to contain levels as high as 1040 $\mu g/m^3$ (0.4 ppm) (Stephens et al. 1986).

Typical values for the average daily intake of vinyl chloride by inhalation in urban/suburban and rural/remote areas have been estimated to be essentially zero. Assuming that the average intake of air is 20 m^3/day, the average daily intake of vinyl chloride by people living in source-dominated areas has been estimated to range from trace amounts to 2100 μg/day.

7.2.2 Water

Vinyl chloride has been detected at varying concentrations in surface, ground, and drinking waters throughout the United States (EPA 1985b). Concentrations as high as 9.8 $\mu g/L$ in surface water, 380 $\mu g/L$ in groundwater, and 10 $\mu g/L$ in drinking water have been reported (Dyksen and Hess 1982, HSDB 1987). There was no report in the literature of vinyl chloride being detected in sediment.

The level of vinyl chloride in groundwater in the United States was determined during the 1982 EPA Groundwater Supply Survey. Water supplies from 945 sites geographically located throughout the United States were studied. Results indicate that vinyl chloride was positively identified in only 0.74% of groundwater supplies (detection limit 1 $\mu g/L$). The maximum concentration detected was 8.4 $\mu g/L$ (Westrick et al. 1984). Other studies have also reported the occurrence of vinyl chloride in groundwater throughout the United States at levels at or below 380 $\mu g/L$ (Cotruvo 1985, Goodenkauf and Atkinson 1986, Page 1981, Coniglio et al. 1980, Stuart 1983).

The concentration of vinyl chloride in finished drinking waters in the United States was studied during the 1976-1977 EPA National Organics Monitoring Survey (NOMS). Only 2 samples out of 113 contained detectable levels (>0.1 $\mu g/L$), and these averaged 0.14 $\mu g/L$ (HSDB 1987). Results of other studies also indicate that the majority of drinking water supplies in the United States contain no detectable levels of vinyl chloride (HSDB 1987, Coniglio et al. 1980). Based on these studies, it is assumed that the average daily intake of vinyl chloride by ingestion of drinking water for most persons in the United States would be essentially zero. Estimates provided in EPA (1985a) indicate that 0.9% of the United States population is exposed to levels of vinyl chloride in drinking water ≥1.0 $\mu g/L$, and 0.3% of the population is exposed to levels >5 $\mu g/L$.

Probably outdated data

7.2.3 Soil

Monitoring data for vinyl chloride in soil were not located in the available literature.

7.2.4 Other

In the past, vinyl chloride had been detected in various foods as a result of migration from polyvinyl chloride food wrappings and containers (EPA 1985b). Vinyl chloride has been found in vinegar at levels up to 9.4 ppm, in edible oils at 0.15 to 14.8 ppm, and in butter at 0.05 ppm when these foods were packaged and stored in PVC containers (IARC 1979). At present, the Food and Drug Administration (FDA) regulates use of vinyl chloride polymers available for use in production of articles intended to contact food. These articles include food-packaging materials, coatings, plastisols, gaskets, and parts for food-processing (see Sect 9, Regulatory and Advisory Status). A recent study on the migration of vinyl chloride from PVC under conditions closely simulating actual food packaging and storage revealed that at very low concentrations of vinyl chloride in PVC packaging material, there was essentially zero migration of vinyl chloride (Kontominas et al. 1985).

It is reported that migration of vinyl chloride from rigid PVC water pipes into drinking water occurs, and that it is directly proportional to the residual level of vinyl chloride in the pipe itself. Under certain conditions, reaction with chlorine in the water may result in the complete removal of vinyl chloride from drinking water (Fishbein 1979, Ando and Sayato 1984). During one study, it was found that drinking water which ran through recently installed PVC pipes contained vinyl chloride at 1.4 μg/L, while water which ran through a 9-year-old system contained 0.03 to 0.06 μg/L (HSDB 1987). This suggests that use of PVC pipe in water distribution systems contributes to intake of vinyl chloride through ingestion of contaminated drinking water. Assuming that the average daily intake of water is 2 L, the average intake of vinyl chloride from water contaminated with vinyl chloride from PVC pipes is expected to range from 0.06 to 2.8 μg/day.

The interior air of two new cars was analyzed and the level of vinyl chloride was found to range from 824 to 3120 $\mu g/m^3$ (0.3 to 1.2 ppm) (EPA 1985b). The source of vinyl chloride was believed to be volatilization from vinyl plastics found in the car interiors. Levels of vinyl chloride in the air in new cars may exceed estimates of minimal risk levels for acute and intermediate exposure.

Vinyl chloride has been detected in tobacco smoke (EPA 1985b). Cigarettes and little cigars have been found to contain 5.6 to 28 ng vinyl chloride per cigarette (IARC 1979).

7.3 OCCUPATIONAL EXPOSURES

NIOSH estimates definite worker exposure to vinyl chloride to be 27,000 persons and probable worker exposure to be 2.2 million (Sittig 1985). This includes ~5000 workers employed in vinyl chloride synthesis, 5000 workers involved with polymerization processes, and as many as 350,000 workers associated with fabrication plants. Exposure is believed to occur primarily through inhalation and less frequently by absorption

through skin (Sittig 1985). In the past, concentrations of vinyl chloride in workplace air in some plants producing PVC have been reported to range from 100 to 800 mg/m^3 (39 to 315 ppm) with peak concentrations up to 87,300 mg/m^3 (34,000 ppm) (IARC 1979). Currently, the Occupational Safety and Health Administration (OSHA) sets standards for occupational exposure to vinyl chloride (see Sect. 9, Regulatory and Advisory Status). A recent NIOSH survey of three vinyl chloride plants indicated that the time-weighted-average exposure to vinyl chloride varied between 0.2 to 70 mg/m^3 (0.08 to 27 ppm) (IARC 1979).

7.4 POPULATIONS AT HIGH RISK

Data were not located specifically regarding subpopulations unusually sensitive to the effects of vinyl chloride. Individuals located near or downwind of production facilities, hazardous waste disposal sites, and landfills may potentially be exposed to higher ambient atmospheric levels.

Workers involved in the production or polymerization of vinyl chloride may constitute a group at risk because of the potential for occupational exposure. Since the mid 1970s, however, atmospheric levels in the workplace have often been reduced to ≤1 ppm (Fishbein 1979, Kilian et al. 1975, Hansteen et al. 1978). Occupationally exposed men may represent a sensitive subgroup because occupational exposure in men has been associated with an increased incidence of fetal loss in their wives (Infante et al. 1976, Waxweiler et al. 1977). No threshold concentration has been determined for this effect. Women (or couples) of child-bearing age may constitute a group at risk, because data suggest that ambient exposure to low (but not quantified) environmental levels is associated with an increase in the incidence of malformations at birth (Infante 1976; Edmonds et al. 1975, 1978; Theriault et al. 1983). No threshold has been determined for this effect.

Inhalation studies in animals demonstrated that exposure early in life resulted in greater risk of developing cancer than did exposure later in life (Drew et al. 1983). Although human studies that address the effect of age on cancer risk were not located, the animal data suggest that exposure during the younger years may result in increased cancer risk. Other animal studies suggest that prenatal exposure may increase cancer risk (Maltoni et al. 1980, 1981). Although human data were not located, the animal data may suggest that the prenatal exposure of humans to vinyl chloride may increase risk of cancer.

Animal studies have demonstrated that pretreatment with xenobiotics or drugs that induce mixed-function oxidase (MFO) potentiates the hepatotoxicity of vinyl chloride (Jaeger et al. 1974, Reynolds et al. 1975, Conolly et al. 1978). Although human data were not located, the animal data suggest that human exposure to environmental pollutants or drugs that induce MFO may result in increased sensitivity to vinyl chloride.