CURRENT RESEARCH

Ex. 1

Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere

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■ Equations are derived to predict the rate of evaporation from aqueous solutions of compounds such as hydrocarbons and chlorinated hydrocarbons which are of low solubility. The rate of evaporation can be high even for compounds of low vapor pressure and "half lives" in solution can be as low as minutes or hours under laboratory or environmental conditions. The rate may be limited by diffusion or desorption. Transfer of contaminants from the water to air environments may thus occur much faster than has been generally appreciated.

Chlorinated hydrocarbons, such as pesticides and polychlorinated biphenyls (PCBs), have been transported widely throughout the global environment, even to remote Arctic and Antarctic regions. The mechanism of transport and accumulation in food chains of various species have received considerable recent attention (Woodwell et al., 1971, Stout, 1969, Risebrough and Brodine, 1970).

The major route by which these contaminants are transported is apparently through the atmosphere. Analysis of rainwater in England has shown concentrations of total pesticide residues of 104-229 ppt (parts per trillion) (Frost, 1969), DDT concentrations of 40 ppt have been reported in meltwater from Antarctic ice (Peterle, 1969). The residues are presumably either vapor or are adsorbed on dust particles and may be carried many thousands of miles from the original source. Some of these materials are applied by spraying techniques with the possibility of direct evaporation; however, most are used as solids, liquids, or wettable powders in which transport to the atmosphere can take place only by natural evaporative processes when exposed to the atmosphere.

There is an apparent contradiction in that these compounds are usually of high molecular weight and low vapor pressure, and thus evaporation should be slow. A factor which is often overlooked is the remarkably high activity coefficients of these compounds in water which cause unexpectedly high equilibrium vapor partial pressures and thus high rates of evaporation.

An attempt is made here to quantify the rates of evaporation of these materials from aqueous solution or suspension.

The approach taken is to calculate from equilibrium thermodynamic considerations the composition of vapor in equilibrium with the water solution. Generally the ratio of contaminant to water in the vapor is greater than the ratio in the liquid, thus evaporation causes the liquid concentration of contaminant to fall. The integrated mass balance differential equation gives a relationship between the contaminant concentration in the liquid and the mass of water evaporated. If an actual water evaporation rate is available the aqueous contaminant concentration can then be expressed as a function of time. Such evaporation rates for rivers and lakes are well documented in texts on meteorology and hydrology. The rate of loss of contaminant is thus calculated from a rate of water evaporation (which is available from these other sources) and the ratio of the contaminant to water in the vapor.

Since the evaporation rates predicted here cannot be easily confirmed by experiment under environmental conditions, the underlying assumptions should be clearly recognized. These assumptions will often be violated. First, the contaminant concentration is that truly in solution, not in suspended, colloidal, ionic, complexed, or adsorbed form. The analysis can be applied to contaminant in these other forms provided it can be converted to dissolved form as evaporation proceeds. Second, it is assumed that the vapor formed is in equilibrium with the liquid at the interface. This is generally accepted (Treybal, 1968) as applying to phase charge mass transfer processes such as distillation. Third is the assumption that the water diffusion or mixing is sufficiently fast that the concentration at the interface is close to that of the bulk of the water. The validity of this depends on the relative rates of evaporation and diffusion or mixing. The slower rate of these two will tend to control the overall rate. Here we estimate only the evaporation rate, which can be shown to control in some environmental conditions and in others to be unimportant, the overall rate being diffusion or mixing controlled. This is more fully discussed later. A fourth assumption is that the water evaporation rate is negligibly affected by the presence of the contaminant. This will be valid for low concentrations of nonsurface-active compounds as are considered here.

The validity of these assumptions can only be confirmed by comparison with experimental data, of which few are presently available.

We believe these equations represent with reasonable accuracy some of the physical processes involved in evaporation and are thus valuable in predicting rates of loss of such compounds from water bodies such as rivers, lakes, and oceans.

Thermodynamic Basis

If we consider G grams of water containing m_i grams of the compound i which may be present either as a solution or as a separate phase (possibly colloidal), the equilibrium mole ratio of "i" in the vapor above the water is P_i/P_w where P_i and P_w are the partial vapor pressures of compound i and water, respectively. The mass ratio is thus, $P_iM_i/18\ P_w$ where M_i and 18 are the molecular weights of

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i and water, respectively. If E g/day of water evaporates from this solution, the rate of evaporation of i is $EP_iM_i/(18\,P_w)$. This may be equated to the change of mass of i in the solution with time:

$$\frac{dm_i}{dt} = -EP_iM_i/(18\,P_w) \quad (1)$$

If the concentration C_i (mg/l.) is small then,

$$m_i = GC_i10^{-6}$$

If we consider processes in which G changes only by a few percent, then any change in m_i will be attributable to changes in C_i. It will be shown later that C_i undergoes a very much greater relative change than does G, and

$$\frac{dm_i}{dt} = \left\{G\frac{dC_i}{dt} + C_i\frac{dG}{dt}\right\}10^{-6} \doteq G\frac{dC_i}{dt}10^{-6} \quad (2)$$

and thus

$$\frac{dC_i}{dt} = -EP_iM_i10^6/(18\,GP_w) \quad (3)$$

The partial pressure of i and its concentration in the aqueous solution may be linked by equating the fugacities in both phases. It can be assumed throughout that vapor phase fugacity coefficients are unity, thus equating the fugacity to the partial pressure P_i. The liquid phase fugacity is related to the concentration by Equation 4 below in which x_i the mole fraction is typically about 10^{-7}, γ_i the activity coefficient is about 10^7 and f_i^R the reference fugacity is the fugacity of pure liquid i at the same temperature and pressure.

$$P_i = x_i\gamma_if_i^R \quad (4)$$

In the case where pure i is a liquid at the system temperature and pressure, the reference fugacity can be equated to the saturation vapor pressure. If, as is the case with most pesticides, i is a solid, then the appropriate reference fugacity is the vapor pressure of the hypothetical supercooled liquid. Prausnitz (1969) and Tsonopoulos and Prausnitz (1971) have discussed this problem and methods of estimating the reference fugacity and activity coefficients in such cases.

Fortunately in this instance we do not require to know γ_i and f_i^R individually; only their product need be known. If we consider the case of pure i (solid or liquid) in equilibrium with water, then the fugacity of i in the aqueous phase will be the vapor pressure P_{is} of pure solid or liquid i. If the solubility x_{is} is known, then the product $\gamma_if_i^R$ must be equal to P_{is}/x_{is}. Since γ_i usually varies in such systems in proportion to the square of the mole fraction of water, it can be assumed constant. Thus Equation 4 may be rewritten for both solid and liquid i to express P_i as a function of concentration x_i or C_i and accessible properties P_{is} and x_{is} or C_{is} (mg/l.).

$$P_i = x_iP_{is}/x_{is} = C_i\overset{\circ}{P}_{is}/C_{is} \quad (5)$$

Evaporation Rates

Two cases can now be considered: first, evaporation from a saturated solution of i containing excess i as a separate phase. This would be colloidal, emulsion, or a wettable powder. The existence of such colloidal systems for hydrocarbon–water mixtures has been described by Peake and Hodgson (1966). Here P_i equals P_{is} and x_i equals x_{is} and C_i equals C_{is}. Substituting in Equation 3 and integrating from $t = 0$ to $t = t$ and $C_i = C_{io}$ to $C_i = C_i$ give

$$C_{io} - C_i = EP_{is}M_it10^6/(G\,18\,P_w) \quad (6)$$

A half-life, τ, may be defined as the time required for the concentration of i to drop to one half its initial value—that is,

$$\tau = C_{io}G\,18\,P_w/(2\,EP_{is}M_i10^6) \quad (7)$$

In the second case, evaporation takes place from a true solution in which i is present at a concentration less than saturation. Substituting Equation 5 in Equation 3 and integrating as before give Equation 8 from which a "half-life" may be estimated as in Equation 9.

$$\ln\,(C_{io}/C_i) = EP_{is}M_i10^6t/(18\,GP_wC_{is}) \quad (8)$$

$$\tau = 12.48\,GP_wC_{is}/(EP_{is}M_i10^6) \quad (9)$$

In summary, if i is present in water at a concentration above its saturation value and the solution remains satu-

Table I. Evaporation Parameters and Rates for Various Compounds at 25°C

Compounds	Solubility, mg/l.	Vapor pressure, mm Hg	$\tau E/G$	F, %	τ for L = 1 meter
Alkanes					
n-Octane	0.66	14.1	1.2×10^{-7}	>99	3.8 sec
2,2,4-Trimethylpentane	2.44	49.3	1.3×10^{-7}	>99	4.1 sec
Aromatics					
Benzene	1780	95.2	7.0×10^{-5}	62	37.3 min
Toluene	515	28.4	5.8×10^{-5}	70	30.6 min
o-Xylene	175	6.6	7.4×10^{-5}	61	38.8 min
Cumene	50	4.6	2.7×10^{-5}	92	14.2 min
Naphthalene	33	0.23	3.3×10^{-4}	19	2.9 hr
Biphenyl	7.48	0.057	2.5×10^{-4}	24	2.2 hr
Pesticides					
DDT	1.2×10^{-3}	1×10^{-7}	1.0×10^{-2}	0.7	3.7 days
Lindane	7.3	9.4×10^{-6}	7.9×10^{-1}	0.009	289 days
Dieldrin	0.25	1×10^{-7}	2.0	0.004	723 days
Aldrin	0.2	6×10^{-6}	2.8×10^{-2}	0.3	10.1 days
PCB's					
Aroclor 1242 ($C_{12}H_7Cl_3$)	0.24(6)	4.06×10^{-4}	6.8×10^{-4}	9.7	5.96 hr
Aroclor 1248 ($C_{12}H_6Cl_4$)	5.4×10^{-2}	4.94×10^{-4}	1.1×10^{-4}	46	58.3 min
Aroclor 1254 ($C_{12}H_5Cl_5$)	1.2×10^{-2}	7.71×10^{-5}	1.4×10^{-4}	39	1.2 min
Aroclor 1260 ($C_{12}H_4Cl_6$)	2.7×10^{-3}	4.05×10^{-5}	5.5×10^{-5}	72	28.8 min
Other					
Mercury	3×10^{-2}	1.3×10^{-3}	3.4×10^{-5}	87	17.9 min

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rated, its rate of evaporation will be described by Equation 6 until its concentration equals the saturation value. The rate will then be described by Equation 8.

Discussion

These equations represent situations in which perfect mixing and equilibration of the liquid phase occurs—that is, as the compound evaporates from the upper layers no concentration gradients appear. This situation may or may not be approached in practice, and in many cases the rate of evaporation will be substantially reduced by the delay in transferring material from the bulk of the liquid to the depleted interfacial area. It should be possible to estimate a mixing time or diffusion time characteristic of the time required to transport material to the interface. This could be obtained from eddy or molecular diffusivities or flow velocities. Comparison of the evaporation time and the mixing time will permit an order of magnitude estimation of which resistance controls the overall rate. Evaporation from a deep quiescent lake and a fast flowing shallow river represent two extremes of mixing time from months to seconds.

It is apparent from Equation 5 that the partial pressure of i although tending to be reduced by the low values of P_{iw} is greatly enhanced by the low values of C_{iw}. Essentially the decrease in vapor pressure expected by dilution (Raoult's law) is compensated by exceptionally high activity coefficients. This has been recognized previously by Rasnow and Schultzky (1931) who derived an equation which has been used to estimate "co-distillation" rates of DDT with water for example by Acree et al. (1963). Although the ratio of i to water in the vapor formed on evaporation is small, it is very much greater than the ratio in the liquid. The "relative volatility" is not the small ratio P_{iw}/P_w but rather $\gamma_i P_{iw}/P_w$ which is of the order of unity. As a result the loss of even a small amount of liquid by evaporation results in a marked drop in the liquid phase concentration of i.

The half-lives, τ, may now be calculated from Equation 9 by use of known solubility and vapor pressure data. This equation is probably more frequently applicable to real situations since hopefully unsaturated solutions of these materials are in the environment. It is instructive to tabulate values of the dimensionless quantity, $\tau E/G$, which is a measure of the time required for evaporation for each compound and then relate these values to particular situations. Also tabulated is F, fraction of the mass of i present which is evaporated when 0.01% of the water is evaporated—i.e., tE/G is 10^{-4} in Equation 8.

The solubility data in Table I were obtained for hydrocarbons from McAuliffe (1966), for pesticides from Gunther et al. (1968), for PCBs from the correlation of Tsonopoulos and Prausnitz (1971) and for mercury from Stock et al. (1934). Vapor pressure data were obtained for hydrocarbons from API Project 44 data compiled by Wilhoit and Zwolinski (1971) and from the "Handbook of Chemistry and Physics" (51st Edition), for pesticides from Edwards (1966), and for PCBs by extrapolation of Monsanto (1967) data using an Antoine equation with a C parameter of 200°K, the A and B parameters being fitted from data in the temperature range 150–300°C.

Hydrocarbons and PCBs evaporate quickly but the pesticides rather more slowly mainly because of their low vapor pressures.

Few experimental data are available to confirm these equations. Acree et al. (1963) evaporated aqueous solution of DDT and showed in three experiments at 25°C that an initial mass of 250 grams of water containing 0.36, 0.60, and 0.84 ppb DDT lost 5.4, 5.0, and 5.2% of the water in 24 hr and 77.7, 80.0, and 71.5% of the DDT initially present. The water was unmixed and the surface placid. The constancy of the percent evaporated is expected from Equation 8 as is DDT's greater relative volatility than water despite its very low vapor pressure. Since the water was unmixed, the interface would be depleted in DDT and the slow diffusion of DDT from the bulk would tend to reduce the rate of DDT evaporation to a value lower than that predicted by Equation 8. This lower rate is observed, since Equation 8 predicts that when 5.2% of the water is evaporated, 97% of the DDT initially present will evaporate. This difference between the predicted 97% and the average experimental figure of 76.4% corresponds to a factor of 2.5 decrease in rate which is reasonable and can be explained mainly by the mixing rate and possibly by some uncertainty in the solubility and hence activity coefficient of DDT.

In an extreme case, if a solution of octane in water is allowed to evaporate under similar conditions, τ would be 0.4 sec.

These surprisingly small half-lives must be considered when analyzing solutions of hydrocarbons and pesticides in water since significant amounts may evaporate during analysis.

Environmental Applications

The equations may be applied to environmental conditions. One difficulty is that mixing or diffusion in a large lake or in surface water on a field may be slow so the above equations will represent maximum rates of evaporation achievable. Reasonable estimates of these rates (and certainly relative rates) can be obtained and may indicate that diffusion is the rate-controlling mechanism.

It is convenient to consider 1 m² of water of depth L meters and derive an equation similar to Equation 9. Since $G = 10^6 L$, then,

$$\tau = 12.48\, LP_w C_{iw}/(EP_w M_i) \qquad (10)$$

Rates of evaporation from lakes have been discussed by Sellers (1965). Typically in the middle latitudes of the Northern Hemisphere evaporation rates from lakes vary from about 1.5 mm/day to 4.5 mm/day depending on the season, with a yearly evaporation ranging from 800–2200 mm. The Atlantic Ocean loses 1040 mm/year by evaporation. The rate of evaporation from land masses depends on the precipitation and for North America is about 400 mm/year. If a value of 1000 mm/year evaporation is assumed, this corresponds to a value of E of about 2740 g/m² day. This value is used in calculating values of τ in Table I for a depth of water L of 1 meter.

The rates calculated may be conservative since the presence of atmospheric water vapor reduces the evaporation rate of water but not that of the contaminant, thus increasing the ratio of contaminant to water in the material evaporated.

In a fast-flowing shallow river of depth 1 meter (where good mixing is probable), values of τ are quite low. For DDT, τ is 3.7 days. Even shorter half-lives occur for Aroclor 1242 (5.9 hr) and Aroclor 1260 (0.5 hr). An interesting consequence of these short half-lives is the difficulty introduced in monitoring effluents from industrial and municipal sources. If a monitoring station is located 1 hr downstream from a source of, say Aroclor 1242, into the river, then by the time the water reaches the station, potentially about one tenth may already have evaporated.

Mercury, a widespread contaminant, has also a surprisingly short half-life. The half-life in a lake of depth 10 meters is about 3.0 hr. This suggests that mixing or diffusion is the controlling mechanism and the upper layers of

dissolved metallic mercury. Ionic or adsorbed mercury will not evaporate at these rates.

In applying these equations to pesticides on soil, certain difficulties are encountered and certain additional factors must be considered (Edwards, 1966). Among these are the adsorption of pesticides on different soil types by leaching, microbial population of the soil, and the formulation of the pesticide.

Conclusion

Because of their high activity coefficients in water, hydrocarbons and chlorinated hydrocarbons potentially will evaporate at high rates and have short half-lives in water bodies. Evaporation from rivers and lakes may thus represent a major mechanism of the transport of pollutants through the environment. The equations presented here provide a method of calculating this potential rate of evaporation for compounds whose vapor pressure and water solubility are known. The actual rate of evaporation under environmental conditions may of course be substantially slower owing to diffusion or desorption rates.

The approach developed here may be of value in calculations of the environmental behavior of hydrocarbons and chlorinated hydrocarbons in rivers, lakes, and lagoons arising from industrial emissions, spills, and discharges of gasoline and lubricating oil from outboard motors. The data for pesticides may be useful in calculations of the retention time in water or in moist soils.

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Mercury Removal from Waste Water with Starch Xanthate–Cationic Polymer Complex

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■ Sequential addition of starch xanthate and a cationic polymer [e.g., poly(vinylbenzyltrimethylammonium chloride) or polyethylenimine] to a mercury(II) solution precipitates both polymers and the mercury as a cohesive floc that is easily removed by filtration. Some xanthate groups on the starch backbone may form mercury(II) salts while others react with the polycation to form a polyelectrolyte complex. The amount of xanthate required to precipitate the cationic polymer and mercury is determined by streaming current measurement. Effectiveness of mercury removal depends on the ratios of mercury, cationic polymer, and xanthate. Residual mercury concentrations were as low as 3.8 μg/l. after single treatment of solutions that had initial mercury(II) concentrations of 1.0×10^6 μg/l.

Removal of mercury(II) ion from waste water by treatment with xanthates of simple alcohols has been proposed by Nanjo et al. (1971). They found that $(ROCS_2)_2^-$ Hg^{2+} precipitates when the mercury(II) concentration is less than that of the xanthate, but if the mercury(II) concentration is greater, the soluble $[(ROCS_2)^- Hg^{2+}]^+$ species is formed. Starch xanthate is known to precipitate zinc(II) and other heavy metals (Russell et al., 1962).

Jellinek and Luh (1969) coprecipitated ions of many heavy metals, other than mercury, in polyelectrolyte complexes (PEC) (Michaels and Bixler, 1968) of polycarboxylic acids and polyethylenimine (PEI). However, the formation constants of the acid-metal complexes were so small that appreciable amounts of the metals remained in solution. Replacement of the polycarboxylic acids in their process by starch xanthate could increase its efficiency since mercury(II) xanthates are very insoluble [K_{sp} Hg(II) ethyl xanthate is 1.7×10^{-38} (Kakovsky, 1957)] and since starch xanthate can also form insoluble PEC by reaction with a polymeric amine (Carr et al., 1973).

Materials

Reagents. All solutions and dispersions were prepared with distilled water that had no detectable mercury.

Starch xanthates having degrees of substitution (DS, average number of substituent groups per glucose unit) in the range 0.11-0.40 were prepared in a high shear mixer as described by Swanson et al. (1964), diluted to about 10% concentration (w/v, starch basis), and stored at 34°F. Portions of these stock dispersions were diluted to 1% (w/v, starch basis) daily for performing all titrations and precipitations.

The cationic polymers poly(vinylbenzyltrimethylammonium chloride) (PVBTMAC, experimental resin QX-2611.7, The Dow Chemical Co.) and PEI (Montrek 1000, The Dow Chemical Co.) were received and stored as aque-

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