JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

The Application of Fugacity and Activity to Simulating the Environmental Fate of Organic Contaminants

Don Mackay*,[†] and Jon A. Arnot[‡]

[†]The Canadian Centre for Environmental Modelling and Chemistry, Trent University, 1600 West Bank Drive Peterborough, ON, Canada K9J 7B8

[‡]Department of Physical & Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail Toronto, ON, Canada M1C 1A4

ABSTRACT: The concept of fugacity, which is widely used in chemical processing calculations, has also been successfully applied to a variety of environmental simulations of the fate and transport of organic contaminants. The challenges of estimating fugacities in environmental phases are discussed, especially for ill-defined phases such as soils, sediments, and biota for which activity coefficients and molar volumes cannot be measured. It is shown that by lumping these quantities and a reference fugacity in a single parameter, empirical partition coefficient data can be used to deduce fugacities and thus the relative equilibrium status between phases and directions of diffusive transport. For assessments of substances that display narcosis, chemical activities, which can be readily deduced from fugacities, can provide valuable estimates of the proximity of calculated or measured environmental concentrations to potentially toxic levels. Five illustrations are presented to demonstrate the value of applying the fugacity concept in environmental contexts, namely, the equilibrium distribution of diverse substances, the evaluation of air—water exchange processes, bioconcentration and bioaccumulation in fish, comprehensive risk assessment of regional chemical fate and exposure, and demonstrating the global distribution of chemicals by atmospheric and oceanic transport.

INTRODUCTION

The chemical engineering and chemical professions have made enormous strides in measuring, simulating, and predicting phase equilibrium relationships between liquids, gaseous, and solid phases. An accurate expression of these relationships is essential for the design and simulation of chemical processes such as distillation, solvent extraction, and gas absorption. A major advance has been the application of the concept of fugacity as an equilibrium criterion, largely resulting from the publication by Prausnitz of his seminal text *Molecular Thermodynamics of Fluid-Phase Equilibria* in 1969[1] and subsequent publications by Prausnitz and his students, colleagues and collaborators, as well as others. Their key contribution has been the development of methods of relating fugacity to concentration over a wide range of temperatures and pressures for mixtures of organic compounds that vary greatly in molecular structure and properties. Less widely appreciated is the contribution that the fugacity concept has made to environmental chemistry and engineering and particularly the understanding and prediction of phase equilibrium relationships of organic substances between the environmental phases or media of air and water and the more complex media of soils, sediments, aerosols, and biota. Interestingly, it was also in the 1960s that Rachel Carson published her seminal book *Silent Spring* that raised awareness of the contamination of the environment and biota, notably birds, by persistent organic contaminants such as dichlorodiphenyltrichloroethane (DDT).[2] What was not clear at that time was that the uptake of organic contaminants by organisms and, consequently, their adverse effects were largely driven by their fugacities in the environment. Understanding the relationships among discharge rates of organic chemicals, their concentrations, fugacities, partitioning characteristics, and levels of toxicity is thus crucial for effective management of chemicals of commerce.

The objective of this contribution to this Festschrift is to review the evolution of fugacity and chemical activity for deducing contaminant partitioning between phases of environmental and biological importance, thus contributing to the more sustainable use of chemicals. We discuss the advantages of using fugacity as an aid to providing invaluable insights into the environmental fate and behavior of organic contaminants. In doing so, a number of significant differences between chemical process simulation and environmental simulations are noteworthy.

ENVIRONMENTAL VERSUS CHEMICAL PROCESS CONDITIONS

First, and fortunately, environmental systems generally encompass a much narrower range of temperatures and pressures than apply to industrial systems. Second, and unfortunately, the compositions of many environmental phases are ill-defined and are variable temporally and spatially. As a result, the level of achievable accuracy when simulating environmental systems is typically a factor of 2 as distinct from the few percent achievable in chemical process calculations. Whereas chemical process simulations often involve the separation of substances such as petroleum distillates that are fairly similar in properties with liquid phase activity coefficients in the range of 1 to 20, organic

Special Issue: John M. Prausnitz Festschrift

Received: October 30, 2010
Accepted: February 7, 2011
Published: March 02, 2011

contaminants vary greatly in partitioning properties and activity coefficients in environmental phases can range to millions. This can result in surprising and counterintuitive behavior. We identify and discuss such differences.

FUGACITY MODELS OF CHEMICAL FATE: A HISTORICAL PERSPECTIVE

Following the development by Gibbs of chemical potential as a criterion of equilibrium, Lewis introduced the concept of fugacity in 1901 as a more convenient and readily appreciated criterion of equilibrium.[3] As noted by Prausnitz in 1969, “It is difficult to visualize the chemical potential, but the concept of fugacity is less so. Fugacity is a 'corrected pressure' which for a component in a mixture of ideal gases is equal to the partial pressure of that component”.[1] In 1907 Lewis also introduced the companion concept of activity (a; dimensionless) which is essentially fugacity (f; Pa) divided by the reference fugacity (f_R; Pa).[4] In effect, activity is the ratio of the prevailing fugacity to the reference fugacity, or in simpler terms it is the fraction of saturation. If Raoult's law holds, activity is equal to mole fraction (x; dimensionless).

Fugacity calculations were first applied to environmental systems in 1979 in a feature article “Finding Fugacity Feasible” in *Environmental Science and Technology*.[5] The ideas suggested in that paper have been expanded upon by the authors and others in a number of environmental settings. The incentive for using fugacity in environmental systems originated in the pioneering work of Baughman and Lassiter who conceived in 1978 of the desirability of using evaluative or hypothetical environments to describe the differing behavior of organic chemicals.[6] The justification for this approach is that although the solvent properties of phases such as soils, sediments, and biota vary considerably, the magnitude of this variation is often of the order of a factor of 10 to 20. The differences in chemical properties such as vapor pressures or solubilities can be much larger, often by factors of 10^{12}. Differences in the environmental fate of chemicals are thus largely attributable to differences in chemical properties rather than those of solvent phases in the environment. A sequence of evaluative simulations or mass balance models has emerged of increasing complexity and fidelity to quantify how chemical properties control environmental fate. It starts with Level I which describes simple multimedia partitioning (equifugacity) at a steady state with no reaction or other losses. Level II describes equilibrium partitioning at a steady state with losses by reaction and advection or flow. Level III describes nonequilibrium partitioning between media of different fugacities at a steady state with reaction and intermedia transport. Finally, Level IV is similar to Level III but is dynamic or unsteady-state in nature. Details are given in the text by Mackay.[7]

Mass balance models of chemical fate in evaluative and real environments are now routinely used for regulatory purposes. In many respects fugacity-based mass balance models are analogous to heat balance models employing the criterion of temperature. They share the advantage that the equilibrium status of a contaminant in different compartments or regions in space is expressed directly, as is the direction of diffusion of mass or heat. Considerable simplifications are possible when adjacent phases are at, or close to, equilibrium as occurs when chemicals partition for prolonged periods of time within soils, or between water and suspended matter. In fugacity models, the analogue to the heat transfer coefficient for interphase heat transfer is a D value in which the driving force for diffusion is the fugacity difference. D values with units of $\mathrm{mol \cdot Pa^{-1} \cdot h^{-1}}$ are essentially fugacity-driven mass transfer coefficients, but they can also be used to express rates of reaction and other loss processes. The process rate is then Df $\mathrm{mol \cdot h^{-1}}$.

The major application of fugacity in an environmental context is thus as an aid to the derivation of mass balance models of chemical fate for both evaluative and real systems. These models serve the same purposes as chemical plant simulation models providing a complete and quantitative explanation of the prevailing conditions and phenomena. They can be used environmentally to predict chemical fate, bioaccumulation, exposures, and the risk of toxic effects. Dynamic versions can forecast times of recovery, for example, when planning or monitoring remediation efforts.

At first sight it seems unlikely that activity and fugacity can be used to quantify the toxicity of chemicals. The seminal work of Ferguson in 1939 showed that for a large number of chemicals, toxicity can be related to activity and hence to fugacity.[8] This insight was based on the earlier work of Overton and Meyer[9,10] who demonstrated that for chemicals that exert toxicity by a narcotic or baseline mode of action the concentration in the organism's lipid phases are relatively constant. Narcosis generally occurs at a concentration in the organism corresponding to an activity of approximately 0.03 plus or minus a factor of 3. For selective toxicants that exert toxicity by a biochemical mechanism an empirical “toxicity factor” can be invoked such as 100; thus, toxicity is expected at an activity of about 0.0003. These concepts have been discussed in detail by Mackay et al.[11,12] and others.[13,14] As a result, expressing the concentrations of chemicals in environmental and biological compartments in the environment in terms of activity, as well as fugacity and concentration is potentially valuable when assessing their proximity to levels at which toxic effects are likely. This is essentially the task of risk assessment.

FUGACITIES OF CONTAMINANTS IN ENVIRONMENTAL MEDIA

The conventional relationship among fugacity f_i (Pa), concentration in solution in a liquid phase, and partial pressure (Pa) in the vapor phase is

$$f_i = x_i \gamma_i f_{Ri} = y_i \varphi P_T \quad (1)$$

where x_i is the mole fraction in solution, γ_i is the activity coefficient in solution, f_{Ri} is the reference fugacity (Pa), y_i is the mole fraction in the vapor phase, φ_i is the fugacity coefficient in the vapor phase, and P_T is total pressure (Pa). Under environmental conditions of atmospheric pressure and relatively low temperatures (say −30 to +40 °C) for a substance that does not associate or dissociate in the vapor phase, φ_i can be assumed to be approximately 1.0, and eq 1 can be simplified to:

$$f_i = x_i \gamma_i {P^S}_L = y_i P_T \quad (2)$$

where ${P^S}_L$ is the vapor pressure of the pure liquid state chemical at the specified temperature and is also the reference fugacity.

For illustrative purposes it is instructive to apply eq 2 to benzene partitioning between a water solution and air at a water concentration of 10 $\mathrm{mg \cdot L^{-1}}$ or $\mathrm{g \cdot m^{-3}}$ as may occur under oil spill conditions. At 25 °C benzene has a molar mass of 78.1 $\mathrm{g \cdot mol^{-1}}$, an aqueous solubility of 1780 $\mathrm{g \cdot m^{-3}}$, a vapor pressure of 12 700 Pa, and an octanol−water partition coefficient (K_{OW}; dimensionless) of 135.[15] The solubility of 1780 $\mathrm{g \cdot m^{-3}}$ corresponds to 22.79 $\mathrm{mol \cdot m^{-3}}$

and to a mole fraction of $410 \cdot 10^{-6}$ since the molar volume of water (v_W) is $18 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$. The activity coefficient of benzene in water γ_i at saturation is the reciprocal of the mole fraction solubility, since at saturation $x_i\gamma_i$ is 1.0; thus γ_i is $1/x_i$, namely, 2437. It is usually assumed that at lower subsaturation and dilute conditions γ_i remains relatively constant. At saturation, the fugacity can be assumed to equal the vapor pressure and reference fugacity of 12700 Pa. Clearly, at a concentration of 10 $g \cdot m^{-3}$ the chemical activity, or fraction of saturation, is 10/1780 or 0.0056, and the fugacity f_i and partial pressure are 71.3 Pa. The Henry's law constant of benzene between water and air (H; $Pa \cdot m^3 \cdot mol^{-1}$) can be assumed to be the ratio of vapor pressure and solubility and is 12700/22.79 or 557.3 $Pa \cdot m^3 \cdot mol^{-1}$. This simple example illustrates that very large activity coefficients can be experienced by environmental contaminants in water. Benzene exerts a partial pressure 2437 times its "Raoult's law" value; thus rapid transport from water is expected to air and other phases. For sparingly soluble C_8 alkanes the activity coefficient in water exceeds 5 million. An important implication is that sparingly soluble substances, such as DDT and high molar mass hydrocarbons, necessarily can only establish very low concentrations in water, but their fugacities, activities, and adverse effects can still be substantial.

As is discussed later, for environmental calculations involving ill-defined phases such as soils, it is convenient to relate fugacity and concentration directly by equating concentration C ($mol \cdot m^{-3}$) to the product of fugacity and a single parameter Z with units of $mol \cdot m^{-3} \cdot Pa^{-1}$. These "$Z$ values" are specific to the chemical and the solvent phase in which it is dissolved or sorbed and are also pressure- and temperature-dependent. Z can be conceived as being the ratio of concentration to fugacity or the (possibly hypothetical) concentration necessary to achieve unit fugacity. It expresses the capacity of the phase for the chemical and is analogous to a heat capacity but is on a volumetric rather than a mass basis.

It can be readily shown that for an ideal vapor phase Z is $1/(RT)$ and for an aqueous solution Z is $1/H$ or more fundamentally $1/(v_S\gamma_i f_R)$, where v_S is the molar volume of solution ($m^3 \cdot mol^{-1}$). In the case of benzene at 25 °C, Z_A (air) is 0.000404 and Z_W (water) is 0.00179. It is noteworthy that the air—water partition coefficient (K_{AW}; dimensionless) is Z_A/Z_W, and in the case of benzene is 0.225. For other phases Z values can be deduced using empirical or estimated partition coefficients since Z_1/Z_2 is K_{12}. Z values thus separate a partition coefficient into two phase-specific terms. The fundamental relationship among concentration C ($mol \cdot m^{-3}$), fugacity, and Z values in liquid and solid phases is thus:

$$C = x/v_S \tag{3}$$

but since

$$x = f/\gamma_i f_R \tag{4}$$

$$C = f/(v_S\gamma_i f_R) = Zf \tag{5}$$

where

$$Z = 1/(v_S\gamma_i f_R) \tag{6}$$

Calculations based on these principles are relatively common for organic contaminants in the environment at concentrations that are usually and fortunately low. It is not uncommon to experience activity coefficients γ in water exceeding a million—conditions far removed from those in chemical processes. Chemicals thus tend to seek out phases in which they have high Z values. This largely explains the bioaccumulation phenomena first brought to public attention by Rachel Carson in 1962.

Rather than use fugacity in such contexts, environmental chemists tend to use empirical or estimated partition coefficients such K_{AW}. In this case it can be shown that K_{AW} is $H/(RT)$ or $P^S{}_L M/(C_S RT)$, or $v_S\gamma_i f_{Ri}/(RT)$ where R is the gas constant (8.314 $Pa \cdot m^3 \cdot mol^{-1} \cdot K^{-1}$), M is molar mass ($g \cdot mol^{-1}$), and T is absolute temperature (usually 298 K in data compilations).

Applying the basic fugacity equation (eq 6) shows that the octanol—water partition coefficient K_{OW} is equal to $v_W\gamma_W/(v_O\gamma_O)$ where v_O is the molar volume of water-saturated octanol ($126.6 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$,[16]) and γ_W and γ_O are the activity coefficients. The activity coefficient of benzene in octanol is thus 2.57, which is fairly close to ideality. The K_{OW}, and thus chemical hydrophobicity, is largely controlled by the activity coefficient in water and is a valuable metric of partitioning into near-ideal phases.

The relatively high value of K_{AW} of benzene and other nonpolar organics is clearly controlled by their relatively high vapor pressures and the low solubilities. It is often not appreciated that even low vapor pressure substances such as hexachlorobenzene (HCB), DDT, or polychlorinated biphenyls (PCBs) can have high K_{AW} values by virtue of their low solubilities in water that cause very large aqueous phase activity coefficients.

Most high molar mass organic contaminants are solids; thus it is essential to estimate the reference fugacity or liquid state vapor pressure from the experimentally accessible solid vapor pressure using the fugacity ratio F. For example, for HCB with a melting point of 229 °C, F is estimated to be approximately 0.010. This constrains the maximum achievable activity to F. An important environmental and toxicological implication is that it may be impossible to establish short term or acute lethal concentrations to organisms such as fish in aquatic toxicity tests. Attempts to determine the aquatic toxicity of HCB may thus be futile, as discussed by Reichenberg and Mayer.[17] This is often not appreciated by aquatic toxicologists and highlights the need for a sound understanding of the underlying physical chemistry during the design and interpretation of toxicity tests.

These general principles are widely appreciated and applied in chemical engineering practice, but to apply the concepts of fugacity and activity to environmental partitioning also requires addressing ill-defined solvent phases such as humic organic matter or organisms such as fish and indeed humans.

■ ILL-DEFINED SOLVENT PHASES

In principle, relating fugacity to concentration requires a knowledge of the solvent molar volume v and the activity coefficient γ of the chemical in that solvent since, as shown earlier Z is $1/(v\gamma f_R)$. The simplest expedient is to lump all three parameters in the single quantity Z and estimate it using an empirical partition coefficient for the solute from the ill-defined "solvent" to air or water. Environmental chemists thus rely heavily on partition coefficients between organic matter or organic carbon and water K_{OM} or K_{OC} for estimating partitioning to soils and sediments, these coefficients having units such as $L \cdot kg^{-1}$. For example for nonpolar organics, K_{OC} is often approximately $0.35 \cdot K_{OW}$. The proportionality constant 0.35 has units of $L \cdot kg^{-1}$. Partition coefficients are also used to express partitioning from water into biota (bioconcentration factors or BCFs; $L \cdot kg^{-1}$) and for sorption from air to aerosol particles.

Octanol is generally used as a surrogate for organic phases such as lipids, organic matter, and organic carbon. A fugacity analysis shows that such correlations are successful because for a wide range of organic substances the ratios of activity coefficients in octanol and in the solvent phase are relatively constant.[18−20]

Invaluable insights into partitioning into such phases can thus be obtained by a fugacity analysis exploring the fundamental determinants of each Z value. It is likely that greater correlation accuracy can be achieved by treating the two solvent phases (e.g., OM and water) individually rather than in combination. This avoids problems of autocorrelation as occurs in correlations between aqueous solubility and K_{OW} in which both quantities are largely determined by the activity coefficient in water.

A common approach is to correlate logarithms of partition coefficients such as K_{OC} and K_{OW} using a one- or two-parameter linear regression. Another approach is to use a group contribution method to correlate partition coefficients and chemical properties with the presence and number of molecular fragments. For example, the EPI Suite software developed by US EPA and Syracuse Research Corporation contains both databases and quantitative structure−activity (property) relationships (QSARs or QSPRs) to predict key chemical properties such as partition coefficients and environmental reaction processes such as metabolic biotransformation rates in fish from chemical structure.[21]

Whereas partition coefficients for nonpolar organics are well-described by K_{OW}, these correlations can be less successful for polar substances with extensive hydrogen bonding and dissociation properties. This has led to the application of poly parameter linear free energy relationships methods pioneered by Abraham[22] in which more parameters can be included to describe these solute−solvent interactions. More recently, molecular computation calculations have been applied such as the CoSMOtherm method.[23] These estimation methods are very attractive given the need to evaluate the partitioning and reactivity characteristics of some 100 000 chemicals of commerce.[24]

■ ILLUSTRATIONS OF THE FUGACITY CONCEPT APPLIED TO ENVIRONMENTAL PROCESSES

Five brief illustrations are given below to describe how the fugacity concept can be applied environmentally. It must be emphasized that identical results can be obtained using concentrations, rate constants, and mass transfer coefficients. An advantage of the fugacity approach is that the equations become simpler, more transparent, and may be more easily derived and interpreted.

Level I Calculation. The first illustration is an extension of the equilibrium partitioning of benzene presented earlier and is a Level I calculation as deduced using the EQC (EQuilibrium Criterion) model.[25] In this case more environmental media are treated, and the relative concentrations and the relative mass distribution of a quantity of a specified chemical can be deduced. The standard EQC evaluative environment is 100 000 km^2 and is about the area of Ohio. The assumed volumes of air, water, soil, and sediment are respectively 10^{14}, $2 \cdot 10^{11}$, $9 \cdot 10^{9}$, and 10^{8} m^3, and suspended particles and fish are also present in the water phase. Hexachlorobenzene (HCB) is also considered as a more hydrophobic substance and phenol as a more polar, water-soluble, and less volatile substance. The phases and basic partition coefficients are listed in Table 1. The amount in each phase is VZf mol, where V is volume (m^3). Assuming a total amount of chemical (e.g., 100 tonnes), the overall fugacity can be calculated, followed by each concentration (which is proportional to the corresponding Z) and each amount and percentage (which is proportional to VZ). It is not always intuitively obvious where the high amounts reside as distinct from the high concentrations.

Table 1. Level I Equilibrium Partitioning of 100 000 kg of Three Chemicals in the EQC Environment of 100 000 km^2 Showing the Fugacity, Activities, Percentages in Each Phase, and the Bioconcentration Factors (BCF)

substance	benzene	HCB	phenol
K_{AW}	0.225	0.0529	0.00002
K_{OW}	135	316 000	28.8
fugacity (μPa)	31.4	0.73	0.26
activity $\cdot 10^9$	2.47	3000	3.8
air %	99.0	8.42	0.974
water %	0.881	0.319	96.5
soil %	0.105	89.2	2.46
sediment %	0.0023	1.98	0.055
suspended particles %	$7 \cdot 10^{-5}$	0.06	0.0017
fish %	$6 \cdot 10^{-6}$	0.005	$1.4 \cdot 10^{-4}$
BCF	6.7	15800	1.44

In this illustration virtually all of the benzene partitions into the air because of the large air volume and the relatively high K_{AW}. In contrast, HCB with a similar K_{AW} partitions primarily to soil and sediment because of its large K_{OW}. Phenol partitions mainly into water because it has a low K_{AW} and a low K_{OW}. Only for HCB are the fractions associated with suspended particles in water and fish significant. Chemical analyses of water samples are usually of the bulk phase and include suspended matter. Thus in the example for HCB, the fraction of the total concentration analyzed that is dissolved in solution and available for uptake from the water by fish is about 84 %. For more hydrophobic substances this fraction can be even lower. The bioconcentration factor of HCB is, as expected, relatively large.

Caution must, however, be exercised when interpreting such results, for example it is likely that the partitioning of phenol to organic matter in soils and sediments is poorly estimated from K_{OW} and as a dissociating substance phenol partitioning can also be affected by pK_a and pH. The activities are all low, thus narcosis is unlikely, but benzene is of concern because of its carcinogenicity and risk is assessed on the basis of lifetime exposure. Phenol is a corrosive and selective toxicant thus narcosis may not be as relevant. The fugacities are in the range (0.2 to 32) μPa, but the activity of HCB and thus its potential for narcosis is about a factor of 1000 larger because of its very low reference fugacity. These results, although approximate, show the wide range of partitioning behavior that can be expected of organic contaminants and highlight the need for accurate physicochemical data.

Whitman Two Resistance Model of Evaporation. The second illustration is of evaporation rate from a pond and employs the Whitman two resistance approach which is routinely applied to gas absorption simulations.[26] The conventional concentration equations applied in chemical engineering are:

$$N = k_{OL}A(C_W - C_A/K_{AW}) \tag{7}$$

where

$$1/k_{OL} = 1/k_L + 1/(K_{AW}k_A) \tag{8}$$

where N is the evaporation rate (mol $\cdot$ h^{-1}), A is area (m^2), C_W and C_A are respectively the concentration in water and air (mol·m^{-3}), k_L, k_A, and k_{OL} are the water-side, air-side, and overall water-side mass transfer coefficients. The ratio of water-side to air-side resistances is $K_{AW} \cdot k_A/k_L$. When K_{AW} is large, k_{OL} is approximately k_L, and the most resistance is in the water phase. For many contaminants K_{AW} is relatively small, that is, ~0.01 but k_A is approximately 100 k_L so both resistances can play a role in determining the flux. Although these equations are simple, it can be intuitively difficult to determine the controlling factors, especially when K_{AW} is small. For example when $K_{AW} < 0.005$, its value becomes unimportant, and paradoxically the evaporation rate is apparently independent of the chemical's volatility.

The corresponding fugacity expressions using D values are simpler and more readily understood.

$$N = D_{OL}(f_L - f_A) \tag{9}$$

where

$$1/D_{OL} = 1/D_L + 1/D_A \tag{10}$$

where D_L is $k_L A Z_W$ and D_A is $k_A A Z_A$. The D values are conductivities and their reciprocals are resistances. The ratio of water-side to air-side resistances is D_A/D_L. Obviously the net flux is zero when f_L equals f_A.

It is relatively simple to add other transport terms, for example, D_P for deposition of the chemical in association with precipitation and atmospheric particles. The net flux is then

$$N = D_{OL} f_L - (D_{OL} + D_P) f_A \tag{11}$$

and a steady-state may be reached with no net flux, but at a nonequilibrium condition, that is, $f_L > f_A$.

Fugacity then acts not only as a driving force toward diffusive equilibrium, but it can address nonequilibrium conditions in which processes such as deposition, advection, and reaction also occur. For many persistent substances the monitored air and water fugacities are similar. The direction of net transport is not obvious when there is unidirectional deposition as well as bidirectional air—water diffusion. In some cases seasonal temperature swings cause reversal of the direction of net transfer; thus there is a need for accurate data not only on the mass transfer and partition coefficients but also on their temperature dependence.

Bioconcentration and Bioaccumulation in Fish. The third example is uptake of chemical by a fish from water (bioconcentration) or from water and food (bioaccumulation). The general steady-state equation when rate of input equals the rate of loss is:

$$f_W D_R + f_D D_D = f_B(D_R + D_E + D_M + D_G) \tag{12}$$

where f_W, f_D, and f_B are the fugacities in the water, food (diet), and the fish, respectively. The uptake D values are D_R for respiration of water and D_D for food consumption. The loss D values are D_R for respiration (a reversible process), D_E for fecal egestion, D_M for metabolic biotransformation, and D_G for growth dilution. High bioconcentration of substances such as DDT and PCBs is ultimately driven by the solute's high activity coefficient in water and relatively low activity coefficient in organic phases such as lipids in biota. Lipids and octanol have fairly similar solvent properties for many hydrophobic organic substances.[18] For exposure to a nonmetabolizing substance only by respiration f_B will approach f_W, that is, thermodynamic equilibrium. The steady-state partitioning between the fish and the water, or bioconcentration factor (BCF), is measured as C_B/C_W. The BCF for hydrophobic chemicals correlates well with K_{OW} because the solvation properties of lipid dominate the partitioning process to the whole organism and the BCF is essentially Z_B/Z_W and is approximately proportional to Z_O/Z_W and thus to $(\nu_W\gamma_W)/(\nu_O\gamma_O)$. It follows that for poorly metabolized neutral organic chemicals with a log K_{OW} between 1 and 6, the BCF can be approximated as $0.05 \cdot K_{OW}$ where 0.05 is a typical volumetric lipid fraction in fish.[18]

When exposure is both from respiration and diet, the proportions of each route can be readily ascertained by inspection of D_R and D_D and the prevailing fugacities in the water and the diet, respectively. For highly hydrophobic substances (log $K_{OW} > 5$), bioaccumulation in fish is largely controlled by D_D (dietary intake) and D_E (egestion) and the ratio f_B/f_D approaches D_D/D_E. The biomagnification factor from diet to organism C_B/C_D depends on f_B/f_D and can be substantial achieving values of typically 3 to 5 for fish and much higher values of 30 to 100 for air breathing mammalian and avian species.[27,28] In elegant experiments, Gobas and colleagues have measured the fugacity increase in the gastro-intestinal tract which results from hydrolysis and absorption of the dietary lipids with a resultant drop in Z.[29,30] High concentrations are thus expected environmentally and biologically under conditions of solvent "switching" when the solvent phase has a high Z value (corresponding to a relative low activity coefficient) and especially under conditions of solvent "depletion" when Z in a solvent phase drops by virtue of reaction or mass transport. The generalities of these processes have been reviewed elsewhere.[31]

Comprehensive Exposure and Risk Assessment. The fourth example of fugacity models illustrates their application in chemical risk assessment. The Risk Assessment IDentification And Ranking (RAIDAR) multicompartment, mass balance model estimates chemical partitioning, mass transport, and reaction at a steady state between compartments of air, water, soils, sediments, and a variety of natural and agricultural organisms and humans.[32,33] The compartment fugacities differ because of variation in input and loss rates by degradation reactions and mass transport. The model can be used to screen large numbers of chemicals to identify those that pose the greatest potential for exposure and risk to humans and the environment. The model requires two chemical partition coefficients (i.e., K_{OW} and K_{AW}), reaction half-lives in air, water, soil, sediment, and vertebrates (e.g., fish), for exposure assessment and additionally toxic effect information for risk assessment. These data can be obtained from databases or from chemical structure (i.e., SMILES notation) using models such as EPI Suite.[21] The model output includes traditional concentrations and fugacities. The fugacities can be converted to chemical activities as described earlier, that is, $a_i = f_i/f_{Ri}$. Figure 1 shows the chemical activities derived from fugacities calculated by the RAIDAR model in comparison to chemical activities derived from monitoring data from various compartments of the Great Lakes environment for HCB.[12] Also shown in Figure 1 is the range of activities at which toxic effects are likely to occur, assuming a narcotic mechanism of toxic action. Figure 2 shows the same data in terms of modeled and measured concentrations.

These figures provide the following insights into the environmental behavior of this substance: (1) the monitored concentrations vary greatly, by a factor of 10^8, and thus simple inspection and interpretation of concentrations can be difficult; (2) the agreement between monitored and estimated concentrations is satisfactory and suggests that the model is adequately simulating the processes of environmental fate and bioaccumulation; (3) the fugacities and activities vary over a narrower range of about 10^3 and the relative equilibrium status is easy to interpret (e.g., the

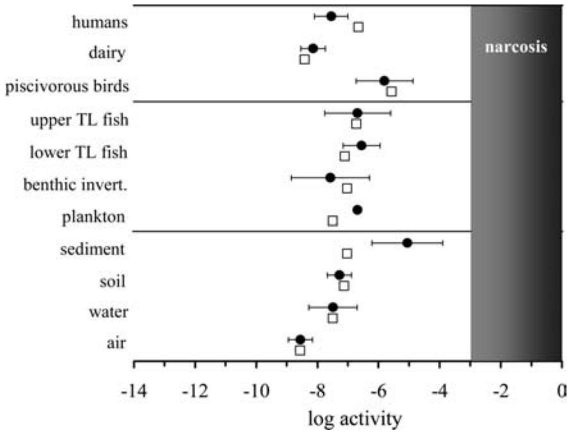

Figure 1. Measured (closed circles) and modeled (open squares) chemical activities for hexachlorobenzene from the Great Lakes Basin compared with chemical activities associated with narcotic toxicity.[12] The error bars reflect the range of measured data from ca. 1990−2005.

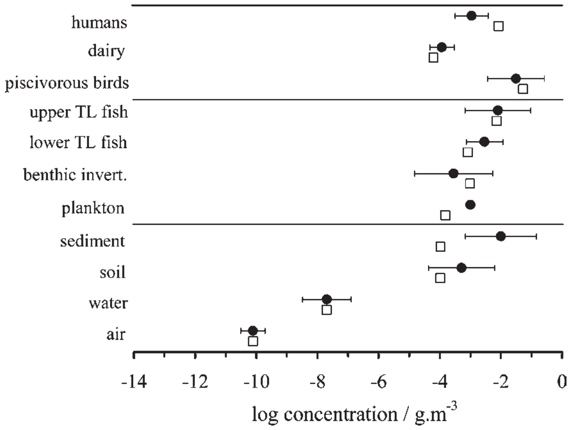

Figure 2. Measured (closed circles) and modeled (open squares) chemical concentrations for hexachlorobenzene from the Great Lakes Basin.[12] The error bars reflect the range of measured data from ca. 1990−2005.

biomagnification and fugacity increase from fish to avian species); and (4) the compartments and species that are highest in activity and thus closest in proximity to activities associated with toxic levels are clearly indicated (i.e., identifying species at risk).

Modeled or measured chemical concentrations can be used to determine a rate of total human exposure from air, water, and diet and this exposure can be compared with estimates of tolerable intake rates (e.g., $\mu g \cdot d^{-1}$ or $\mu g \cdot kg^{-1} \cdot d^{-1}$). Further, an "intake fraction", the fraction of the rate of emission or discharge that is taken up by a human population or individuals, can be estimated.[34−37] Such model calculations can be used to compare chemicals for exposure (using estimates of actual chemical emission rates) and comparative exposure potential (using assumed and equivalent emission rates for all chemicals).

Global Distribution of a Persistent Chemical by Long-Range Transport. The GloboPOP model is used to illustrate the utility of fugacity models in understanding and predicting the global distribution and long-range transport of persistent organic pollutants (POPs). GloboPOP is a nonsteady state, multicompartment mass balance model that includes 10 climatic zones and a two-dimensional treatment of the global atmosphere.[38] It has been used to help understand the global fate of α-hexachlorocyclohexane (αHCH).[39] The ability of the model to reproduce the measured latitudinal variability in seawater concentrations[40] is illustrated in the top two panels of Figure 3. The model also reproduced the steady decline in seawater concentrations that occurred during the 1990s in response to a global phase-out of this substance which was an ineffective byproduct in the pesticide comprising a mixture of HCHs. The calculated ratio of fugacities in water and air, shown in the lower left panel, reveals that the water was generally under-saturated with respect to the atmosphere and α-hexachlorocyclohexane was diffusing from air to the oceans. A reversal of equilibrium status then occurred during the early 1990s in the Arctic, when air concentrations declined much faster than those in seawater and there was diffusive evaporation. These model simulations are in agreement with observations.[41] Overall, the flux of α-hexachlorocyclohexane was still downward, even in the Arctic as shown in the lower right panel of Figure 3 because of wet deposition processes that are advective rather than diffusive in nature.

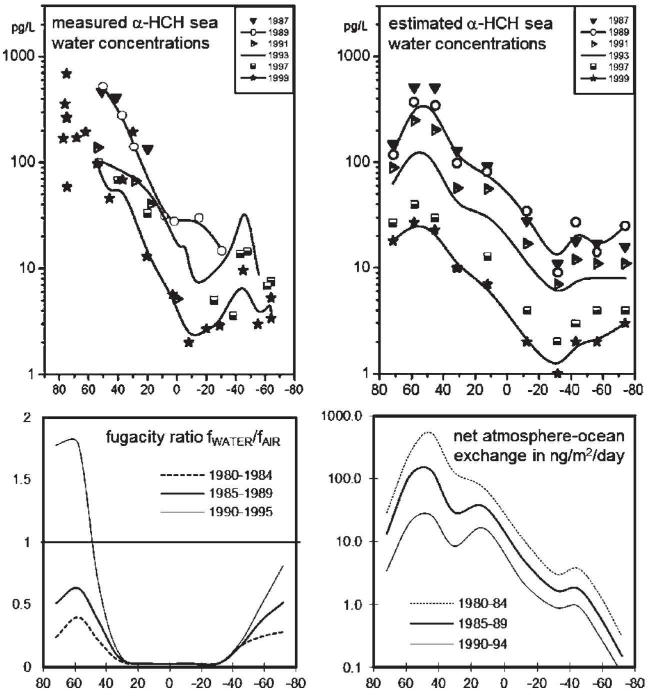

Figure 3. Concentrations of α-hexachlorocyclohexane in seawater as a function of latitude as measured by Lakaschus et al.[40] (upper left) and as predicted with the fugacity-based Globo-POP model (upper right). Also shown are the water/air fugacity ratios (lower left) and the net atmospheric deposition rate (lower right) as predicted by the model.[39]

Clearly αHCH and other substances are capable of being distributed globally. Indeed, the Stockholm Convention on POPs is a global treaty that has been developed to identify and regulate chemicals that are persistent, are transported to regions distant from source regions, are bioaccumulative, and are likely to pose significant adverse effects to humans or the environment.[42] Fugacity mass balance models can improve our understanding of the global distribution process. They can identify the key chemical properties and environmental parameters and assist in the interpretation of monitoring data over spatial and temporal scales. Importantly, models such as GloboPOP can constrain the physicochemical properties that a substance must possess to be subject to transport and accumulation in remote regions such as the Arctic.[43] These models can help to quantify which regions (i.e., countries) are responsible for contributing to global contamination for different chemicals and predict the time required for the environment to respond to regulatory decisions such as banning or restricting production and use.[44]

These selected illustrations demonstrate the versatility and value of fugacity mass balance models, but there are many other examples developed to address a diversity of chemicals and environments. These include the CalTOX model of McKone for assessing exposure from hazardous sites,[45] the indoor pesticide exposure model of Bennett and Furtaw,[46] the model of Coulon et al. of hydrocarbon degradation in constructed biopiles,[47] and the model of Seth et al. addressing chemical fate in sewage treatment plants.[48]

■ CONCLUSIONS

In this contribution we have shown how the concept of fugacity can be applied to describe the fate and transport of organic contaminants in the environment, including partitioning into ill-defined phases such as organisms and humic materials present in soils and sediments. The partitioning and degradation characteristics of a specific chemical of commerce are the primary determinants of where the chemical will accumulate and react, how long it will persist, and by which routes it causes exposure and potential toxic effects to humans and wildlife. Given that there are some 100 000 chemicals of commerce with properties that range in magnitude by up to a factor of about 10^{12}, it is a considerable challenge to obtain the required accurate data for these key fundamental properties. Information on the distribution of chemicals in our complex environment can be obtained from monitoring programs or estimated using mass balance model simulations. Viewing these distributions through the lens of fugacity and activity can assist our understanding of the environmental behavior and effects of these diverse chemicals. The use of the fugacity concept clearly demonstrates the need for accurate fundamental chemical property data. The illustrations demonstrate that describing environmental fate and transport in terms of fugacity and activity can facilitate the assembly of predictive and simulation mass balance models that can range in scale from single organisms to global distribution. Much of the credit for these applications of the fugacity concept beyond the realm of chemical process engineering is attributable to the lifetime contributions of John M. Prausnitz.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 705-740-2911; fax: 705-748-1080; e-mail: dmackay@trentu.ca.

Funding Sources

We are grateful to NSERC for financial support.

■ ACKNOWLEDGMENT

We are grateful to Dr. Frank Wania for constructive comments.

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