



Lipid–water partition coefficients and correlations with uptakes by algae of organic compounds



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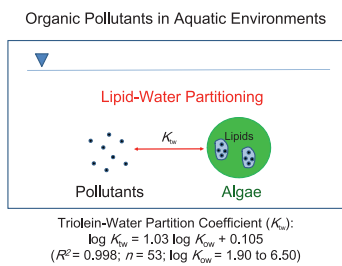
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HIGHLIGHTS

- Partition coefficients of contaminants with lipid triolein (K_{tw}) are measured.
- Measured K_{tw} values are nearly the same as the respective K_{ow} .
- Sorption of the contaminants to a dry algal powder is similarly measured.
- Algal uptake of a compound occurs primarily by partition into the algal lipid.

GRAPHICAL ABSTRACT



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ABSTRACT

In view of the scarcity of the lipid–water partition coefficients (K_{tw}) for organic compounds, the $\log K_{tw}$ values for many environmental contaminants were measured using ultra-pure triolein as the model lipid. Classes of compounds studied include alkyl benzenes, halogenated benzenes, short-chain chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides. In addition to $\log K_{tw}$ determination, the uptakes of these compounds from water by a dry algal species were measured to evaluate the lipid effect on the algal uptake. The measured $\log K_{tw}$ are closely related to their respective $\log K_{ow}$ (octanol–water), with $\log K_{ow} = 1.9$ to 6.5. A significant difference is observed between the present and early measured $\log K_{tw}$ for compounds with $\log K_{ow} > \sim 5$, which is attributed to the presence and absence of a triolein microemulsion in water affecting the solute partitioning. The observed lipid-normalized algae–water distribution coefficients ($\log K_{aw/lipid}$) are virtually identical to the respective $\log K_{tw}$ values, which manifests the dominant lipid-partition effect of the compounds with algae.

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1. Introduction

There is good evidence that the uptake of a sparingly water-soluble organic chemical from water by a biotic organism (e.g., fish) is driven essentially by the chemical's propensity to partition into the biotic lipid phase. This notion is corroborated by the finding that when the fish bioconcentration factor (BCF) (i.e., the equilibrium fish–water distribution coefficient) of a nonionic compound [1,2] is normalized to the fish lipid content, the resulting lipid-based (BCF)_{lipid} value is practically equal to the compound's triolein–water partition coefficient (K_{tw}) [3], where triolein is adopted as the model lipid. By analogy, the contamination of other aquatic organisms by nonionic organic pollutants should proceed by the same lipid-partition

process. In this sense, K_{tw} is a basic parameter for assessing the water-to-biota transfer and fate of organic compounds in aquatic environments.

Algae are organisms widespread in natural water often in massive quantities that may significantly affect the water quality because of their enormous uptake and release of various chemicals and contaminants. By this time, the role of lipids relative to other components in algae on contaminant sorption has not been well defined in current transport/fate studies. Although one expects the algal uptake to be predominated by the lipid-partition process for sparingly soluble compounds, there has so far been no experimental confirmation. In addition to the contaminant uptake and release, some microalgae are artificially cultivated to produce high lipid contents to serve as potential biodiesel fuels [4,5] and as biological substrates to sequester and degrade organic contaminants in wastewater treatment [6,7]. In latter applications, lipids in algae are expected to play a crucial role on biofuel production and contaminant sequestration.

Previous studies indicate that sparingly water-soluble organic compounds are readily absorbed by fresh algae or phytoplankton to yield relatively large BCFs [8–16]. Research on algal uptakes of organic compounds has been conducted with equilibration times ranging from a few hours to days and weeks, with the algal-lipid-normalized BCFs, i.e., the $(BCF)_{lipid}$, of the compounds showing no definitive relations with the octanol–water partition coefficients (K_{ow}) [10–14,16]. For example, the $\log BCF_{lipid}$ of compounds with $\log K_{ow} < 5$ (e.g., 4-chloroaniline and phenanthrene) are comparable in value with their $\log K_{ow}$ but for compounds with $\log K_{ow} > 6$ (e.g., PCBs), the $\log BCF_{lipid}$ are less than the $\log K_{ow}$ [12]. It appears that uptakes of some high- K_{ow} compounds by live algae might have difficulties reaching the equilibrium levels (relative to values in water) due to insufficient contact times.

In view that triolein is a good surrogate for biological lipids, availability of reliable K_{tw} data is crucial to estimating the lipid effect on the equilibrium uptake of an organic compound by an aquatic organism. Currently, measured K_{tw} values are available for about only 50 compounds, mainly substituted benzenes and polychlorinated biphenyls (PCBs) [3,17]. No K_{tw} values are accessible for other important classes of pollutants, such as polycyclic aromatic hydrocarbons, short-chain chlorinated hydrocarbons, and refractory organochlorine pesticides. Although unavailable K_{tw} data of compounds might be estimated via the reported $\log K_{tw}$ – $\log K_{ow}$ correlation derived with certain compounds, the estimated K_{tw} may suffer a high degree of uncertainties, unless the selected $\log K_{tw}$ – $\log K_{ow}$ correlation has been validated to be applicable for a wide variety of compounds over a certain range of K_{ow} or water solubility (S_w).

Using triolein (99% pure) as the model lipid, Chiou [3] measured the $\log K_{tw}$ values of 38 organic compounds; the method consisted of shaking vigorously the triolein–water mixtures of individual solutes and separating the two solution phases by centrifugation. The measured $\log K_{tw}$ were highly linearly correlated with the respective $\log K_{ow}$ for substituted benzenes of $\log K_{ow} < \sim 5.0$, beyond which the $\log K_{tw}$ for other compounds (e.g., DDT and a few PCBs) exhibited an asymptotic trend with increasing $\log K_{ow}$. The cause of this effect remains unclear. Such effect complicates the $\log K_{tw}$ estimation for compounds with high $\log K_{ow}$ (> 5). On the other hand, Jabusch and Swackhamer [17] measured the $\log K_{tw}$ of 12 PCBs using practical-grade triolein (65% in purity), with the triolein–water mixture being slowly equilibrated; the resulting $\log K_{tw}$ were virtually linear with the respective $\log K_{ow}$ (4.7–8.1). However, it was unclear to what extent the measured $\log K_{tw}$ with 65%-pure triolein were affected by the sample impurity. To ensure the $\log K_{tw}$ data quality, it is pertinent to explore the potential impacts of impurities in triolein and sample equilibration/phase separation methods on the $\log K_{tw}$ values (and on the resulting $\log K_{tw}$ – $\log K_{ow}$ correlation) of the test compounds.

With above considerations, we set out to measure the K_{tw} data for a number of important pollutants encompassing a large range of $\log K_{ow}$. The experiment was carried out with ultra-pure triolein (99.5% in purity) as the model lipid, following basically the procedure of Chiou [3]. The classes of compounds studied include short-chain chlorinated hydrocarbons (SCCHs), alkyl benzenes (ALBZs), halogenated benzenes (HABZs), polycyclic aromatic hydrocarbons (PAHs), PCBs, and organochlorine pesticides (OCPDs), with a total of 53 compounds. Some compounds measured previously by Chiou [3] were reexamined in this study for cross-checking the data.

In addition to acquiring the K_{tw} data, the lipid-normalized distribution coefficients of these compounds with a dry algal powder ($K_{aw/lipid}$) were also determined for examining the lipid effect on the organic-pollutant uptake by algae. The use of dry rather than live algae for this investigation was to assure that the algae–water slurry is well equilibrated and the sample is homogeneous to produce reliable experimental data. The measured $\log K_{tw}$ values of the compounds were regressed against the respective $\log K_{ow}$ to examine the fitness of the $\log K_{tw}$ – $\log K_{ow}$ correlation for estimation of $\log K_{tw}$ from $\log K_{ow}$. The measured $\log K_{aw/lipid}$ values were compared with the corresponding $\log K_{tw}$ to assess the effect of algal lipids on the chemical uptake.

2. Materials and methods

2.1. Materials

The organic chemicals used for lipid-partition and algal-uptake experiments (see the list in Table 1) were purchased

Table 1

Water solubilities (S_w), K_{ow} , and measured partition coefficients of ALBZs, HABZs, PCBs, SCCHs, OCPDs, and PAHs with triolein and algae.

Compound	$\log S_w^a$	$\log K_{ow}^a$	$\log K_{tw}$	$\log K_{tw}^b$	$\log K_{aw/lipid}$
ALBZs					
Benzene	−1.64	2.13	2.26	2.25	2.38
Toluene	−2.25	2.69	2.88	2.77	2.90
Styrene	−2.54	2.95	3.10	–	3.20
Ethylbenzene	−2.82	3.15	3.36	3.27	3.39
1,2-xylene	−2.78	3.13	3.30	–	3.38
1,4-xylene	−2.83	3.18	3.33	–	3.39
1,3,5-trimethylbenzene	−3.24	3.42	3.72	3.56	3.86
1-ethyl-2-methylbenzene	−3.21	3.53	3.83	–	3.80
1,2,4,5-tetramethylbenzene	(−4.02)	4.10	4.34	–	4.37
Hexamethylbenzene	(−4.68)	4.61	4.89	–	4.93
HABZs					
Fluorobenzene	−1.79	2.27	2.39	2.33	2.49
Chlorobenzene	−2.38	2.84	3.01	2.97	3.05
Bromobenzene	−2.58	2.99	3.24	3.12	3.28
Iodobenzene	−2.95	3.28	3.58	3.42	3.58
1,2-dichlorobenzene	−2.98	3.38	3.56	3.51	3.65
1,4-dichlorobenzene	(−3.03)	3.37	3.61	3.55	3.67
1,2,3-trichlorobenzene	(−3.79)	4.04	4.18	4.19	4.19
1,2,3,4-tetrachlorobenzene	(−4.59)	4.60	4.73	4.68	4.78
Pentachlorobenzene	(−5.20)	5.03	5.32	5.27	5.35
Hexachlorobenzene	(−5.71)	5.50	5.75	5.50	5.81
PCBs					
Biphenyl	(−3.95)	4.04	4.34	4.37	4.37
4-PCB	(−4.67)	4.61	4.92	–	4.98
2,4'-PCB	(−5.34)	5.10	5.45	5.30	5.58
4,4'-PCB	(−5.56)	5.33	5.57	5.48	5.48
2,4,4'-PCB	(−6.02)	5.62	5.97	5.52	5.98
2,2',5,5'-PCB	(−6.19)	5.81	6.13	5.62	6.17
2,2',4,5,5'-PCB	(−7.01)	6.50	6.81	5.81	6.73
SCCHs					
Chloroform	−1.22	1.90	2.08	–	2.16
Carbon tetrachloride	−2.28	2.73	2.93	–	3.12
Trichloroethylene	−1.99	2.53	2.71	–	2.88
Tetrachloroethene	−2.92	3.38	3.50	–	3.69
1,1,1-trichloroethane	−2.00	2.47	2.56	–	2.55
1,1,2,2-tetrachloroethane	−1.75	2.39	2.53	–	2.61
Pentachloroethane	−2.61	2.89	3.16	–	3.35
OCPDs					
Lindane	(−3.62)	3.72	3.91	–	4.04
Dieldrin	(−5.22)	5.10	5.33	–	5.30
Chlordane	(−6.03)	5.54	5.73	–	5.77
Heptachlor	(−6.05)	5.73	6.00	–	5.97
p,p'-DDE	(−6.15)	5.77	5.99	–	6.10
p,p'-DDT	(−6.79)	6.36	6.52	5.90	6.58
PAHs					
Indane	−3.04	3.33	3.57	–	3.61
Naphthalene	(−3.09)	3.36	3.56	–	3.61
Acenaphthene	(−3.89)	3.92	4.19	–	4.19
Fluorene	(−4.14)	4.18	4.30	–	4.45
2,6-dimethylnaphthalene	(−4.25)	4.31	4.52	–	4.58
1,5-dimethylnaphthalene	(−4.19)	4.38	4.51	–	4.55
Phenanthrene	(−4.48)	4.46	4.71	–	4.82
Anthracene	(−4.63)	4.54	4.82	–	4.91
Fluoranthene	(−5.15)	5.16	5.40	–	5.43
Pyrene	(−4.92)	5.18	5.49	–	5.56
Benz[a]anthracene	(−5.89)	5.61	5.84	–	5.86
Chrysene	(−6.11)	5.73	5.98	–	–
Benzo[a]pyrene	(−6.82)	6.34	6.70	–	–

^a Values from Chiou et al. [19] and Mackay et al. [21], with S_w in mol/L. The $\log S_w$ values with parentheses are for the subcooled liquids.

^b values from Chiou [3].

from various suppliers: Aldrich, Alfa Aesar, Chem Service, Dr. Ehrenstorfer, Fluka, J.T. Baker, Janssen Chimica, Merck, Showa, Sigma–Aldrich, and Supelco. They were of either GC or HPLC grades, or analytical standards, with indicated purities of 99.0 to 99.9%, except 1,1,2,2-tetrachloroethane (97%), pentachloroethane (98.4%), pentachlorobenzene (98%), indane (95%), pyrene ($\geq 97\%$),

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