Accurate quantification of freely dissolved organochlorine pesticides in water in the presence of dissolved organic matter using triolein-embedded cellulose acetate membrane

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Abstract A novel method is described using triolein-embedded cellulose acetate membrane (TECAM) for accurate determination of the freely dissolved fraction of organochlorine pesticides (OCPs) in waters rich in dissolved organic matter (DOM). The performance of the method was tested with an air-bridge system for extracting OCPs from aqueous solutions with and without humic acid. In addition, the partition coefficients between humic acid and water (K_{doc} s) for 20 OCPs were determined by TECAM with negligible depletion extraction. Results show that TECAM predominantly extracts the freely dissolved compounds and its extraction efficiency decreases significantly with an increase in concentration of humic acid in water. The proposed methodology is suitable for facile laboratory K_{doc} measurement for moderate to high hydrophobic compounds ($\log K_{\text{ow}} > 4$). The linear relationship between $\log K_{\text{ow}}$ and $\log K_{\text{doc}}$ obtained in this study agrees well with the results reported earlier. The kinetic uptake rate constants (k_{u} s) and TECAM–water partition coefficients (K_{TECAM} s) for the 20 OCPs were obtained using the controlled laboratory continuous-flow and static exposure system, respectively. These calibration parameters were

used in the field experiment to estimate the freely dissolved concentrations of OCPs in the water of Taihu Lake in China. Our results show that TECAM can be used successfully to determine the freely dissolved OCPs in aquatic environments containing DOM, and the method is particularly suited for long-term water sampling.

Keywords Organochlorine pesticides · Dissolved organic matter · Humic acid · Passive sampling · Freely dissolved concentration

Introduction

The freely dissolved concentration of hydrophobic organic compounds (HOCs) determines the main processes involved in determining their environmental fate, such as transport, distribution, and bioaccumulation [1], and thus exhibits their potential toxic effects [2]. It is generally assumed that only freely dissolved chemical is available for uptake by fish or invertebrates in an aquatic environment [3]. Therefore, from a toxicological and pharmacological point of view, it is of considerable interest to quantitatively determine the freely dissolved fraction of chemicals in order to evaluate and characterize their bioavailability. Natural surface waters usually contain dissolved organic matter (DOM), such as humic materials, and adsorption of HOCs by DOM may significantly reduce their freely dissolved fraction [4, 5]. The compound–DOM interaction is considered one of the most important processes governing the fate of HOCs in aquatic systems. The differentiation between compounds freely dissolved and those bound with DOM is therefore particularly important. Several new techniques have been developed for this purpose in recent years and the triolein-containing semipermeable membrane device (SPMD) [6] and solid-

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phase microextraction (SPME) [7] are the two outstanding representatives among them.

SPME was successfully used as an equilibrium sampling device owing to its relatively short equilibration time (hours to days) [8] and SPMD was generally used as an integrative sampler as it needs a long time to reach equilibrium (days to months) [9]. In aquatic systems where chemical concentrations often vary over time, it is particularly important to obtain time-weighted average (TWA) contaminant concentration as a fundamental part of the ecological risk assessment process. Grab samples may fail to account for episodic contamination events and it is often impossible to excise sufficiently large water samples to achieve detection of the extremely low levels of organic contaminants in aquatic environments. The TWA concentration, using a single sample, would provide a more accurate picture of prevailing contaminant levels than grab samples. For these reasons, it is necessary to develop an integrative sampler which would integrate exposure over time and concentrate chemicals to levels above the limits of detection. Although SPMDs are successfully used as a TWA sampler, it often suffers from a time-consuming dialysis procedure (48 h) and complex cleanup procedures [10]. Therefore, there is a need for developing methods that would combine time-weighted sampling of freely dissolved pollutants with a simple and widely available detection method that could preferably be operated in the field.

Recently a novel membrane-based extraction technique was developed in our laboratory for in situ passive sampling of waterborne hydrophobic organic pollutants involving triolein-embedded cellulose acetate membrane (TECAM) [11, 12]. In TECAM, the triolein drops embed in the matrix of cellulose acetate polymers and closely adhere with the polymers. Thus, the TECAM consists of two immiscible phases: an outer hydrophilic membrane and inner hydrophobic triolein drops. Only the freely dissolved molecules of organic compounds pass through the membrane and accumulate in the triolein (Fig. 1). This extraction process is based on lipid–water partitioning. In contrast to the similar SPMD technique, the unique configuration of TECAM provides the larger ratio of membrane surface area to lipid volume. Furthermore, the use of cellulose acetate as barrier membrane makes it more accessible for waterborne chemicals to pass from the aqueous phase into triolein [11]. The use of TECAM as an extraction technique appears to have several advantages over conventional methods including low cost, simple preparation, less solvent-consumption, and simple pretreatment procedures [11]. Although the applicability of TECAM has been demonstrated for the analysis of OCPs and PAHs in aqueous samples [11, 12], the intrinsic characteristic of TECAM for selectively extracting freely dissolved compounds has not yet been verified.

Fig. 1 Schematic diagram of water sampling with a triolein-embedded cellulose acetate membrane (TECAM)

The work described in this paper is a continuation of our ongoing research on TECAM and demonstrates the adaptation of this technique to differentiate freely dissolved chemicals from humic-bound chemicals and thereby estimate partition coefficients. In the case when the role of DOM was evaluated, commercial sources of DOM were used. The laboratory studies were conducted to exploit the characteristic of TECAM to extract the freely dissolved analytes and to obtain uptake kinetic calibration parameters for field applications. Finally, to test the performance of TECAM in an environmental situation, a preliminary field study was also conducted.

Experimental

Principle of TECAM accumulation

If the amount of a chemical which is extracted by TECAM during the measurement is very small compared to the total amount in the solution, the uptake of the chemical by the TECAM (membrane plus triolein) can be simply described by a first-order, one-compartment model:

$$C_{\text{TECAM}} = C_w \frac{k_u}{k_e} (1 - \exp[-k_e t]) \quad (1)$$

where C_{TECAM} is the concentration of analyte in the TECAM (ng g^{-1}), C_w is the concentration of analyte in water (ng L^{-1}), k_u is the uptake rate constant ($\text{L day}^{-1} \text{g}^{-1}$), k_e is the overall elimination rate constant (day^{-1}), and t is uptake time.

When $k_e t$ is small (i.e., $k_e t \ll 1$), chemical uptake is linear and integrative, and Eq. (1) reduces to:

$$C_{\text{TECAM}} = C_w k_u t \quad (2)$$

and when $k_e t \gg 1$, Eq. (1) reduces to an equilibrium model:

$$K_{\text{TECAM}} = \frac{C_{\text{TECAM}}}{C_w} = \frac{k_u}{k_e} \quad (3)$$

with K_{TECAM} being the steady-state TECAM–water partitioning coefficient. The chemical uptake into TECAM remains linear and integrative approximately until the ratio of C_{TECAM}/C_w reaches half-saturation according to Huckins et al. [13]. When calibration kinetic parameters, i.e., K_{TECAM} and k_u , are available, the maximal exposure time in which TECAM accumulates integratively under field conditions can be estimated according to:

$$t_{1/2} = 0.693 K_{\text{TECAM}} / k_u \quad (4)$$

where $t_{1/2}$ is the first-order half-time of the uptake curve and a time of $4t_{1/2}$ is needed to exceed 94% of steady-state concentrations [9].

If a matrix such as humic acid is present in the solution in a dissolved state, the uptake of the chemical by TECAM will be reduced due to the reduced freely dissolved fraction in the water phases, and considering that k_u and k_e are not affected by the presence of humic acid [14], Eq. (1) changes to:

$$C_{\text{TECAM}} = F C_w \frac{k_u}{k_e} (1 - \exp[-k_e t]) \quad (5)$$

The fraction of freely dissolved analyte (F) is given according to Suffet et al. as [15]:

$$F = \frac{1}{1 + K_{\text{doc}} C_{\text{doc}}} \quad (6)$$

where K_{doc} is a dimensionless partitioning coefficient of analyte between humic acid and water, and C_{doc} is the concentration of humic acid in water (carbon based).

When TECAM is used to measure freely dissolved concentration of analyte, the concentration in TECAM is proportional to the freely dissolved concentration in water. Therefore, when humic acid is present, we have:

$$\begin{aligned} \frac{C_{\text{TECAM},t,\text{doc}}}{C_{\text{TECAM},t,0}} &= \frac{C_w F (k_u/k_e) (1 - e^{-k_e t})}{C_w (k_u/k_e) (1 - e^{-k_e t})} \\ &= \frac{1}{1 + K_{\text{doc}} C_{\text{doc}}} \end{aligned} \quad (7)$$

with $C_{\text{TECAM},t,\text{doc}}$ and $C_{\text{TECAM},t,0}$ being the analyte concentration in the TECAM (ng g^{-1}) after a t -hour exposure to water in the presence and absence of humic acid.

Experimentally, K_{doc} is calculated from $C_{\text{TECAM},t,\text{doc}}$, $C_{\text{TECAM},t,0}$, and C_{doc} , as follows:

$$K_{\text{doc}} = \frac{\frac{C_{\text{TECAM},t,0}}{C_{\text{TECAM},t,\text{doc}}} - 1}{C_{\text{doc}}} \quad (8)$$

Materials and methods

Reagents and materials

The standard mixture solution of 20 studied OCPs shown in Table 1 was purchased from Supelco (Bellefonte, PA). Although all the OCPs studied in this experiment are hydrophobic, they cover a wide range of molecular size, water solubility, and other physicochemical properties. In this respect, they are considered to be representative of a wide spectrum of the organic pollutants of significance in environmental toxicology. Humic acid was purchased from Fluka (Steinheim, Germany). Although commercial humic acids showed some differences from the natural aquatic humic substances, they do possess the similar property of associating with the HOCs [17]. Triolein (1,2,3-tri-*cis*-9-octadecenyl)glycerol) of 95% purity was obtained from Sigma-Aldrich (St. Louis, MI). The organic solvents were of HPLC or pesticide analytical grade and obtained from Fisher (Fair Lawn, NJ) and J. T. Baker (Phillipsburg, NJ). All other chemicals were of analytical grade or above, and the ultrapure water used in this study was purified by a Milli-Q Gradient system (Millipore, Bedford, MA).

Stock humic acid solutions were prepared by dissolving humic acid in 0.01 M sodium hydroxide solution (pH=12). The solution was stirred for about 24 h and centrifuged at 27,100 average relative centrifugal force (20 °C) for 1 h to remove most of the particles, and then filtered to 0.45- μm with prerinsed cellulose acetate nitrate membrane filters (Whatman, Clifton, NJ) to remove any remaining particulate material. The dissolved organic carbon (DOC) content of the humic acid stock solution was measured with a total organic carbon (TOC) analyzer (phoenix-8000, Tekmar-Dohrmann, USA). Humic acid concentrations are expressed as kilograms of organic carbon per liter of water. The solution was stored in the dark at 4 °C until use.

TECAMs preparation

The TECAMs were prepared in a clean room to reduce vapor-phase contamination. The procedure for preparing TECAM was the same as described previously [11]. TECAMs were constructed in the same configuration: 40- to 50- μm thick, 12-cm wide, and 18-cm long, embedded with 7.5 wt% of triolein. Small pieces of TECAM (4 cm $\times$ 6 cm, average wet weight 0.159 g) were used for all

Table 1 Selected physicochemical properties of the 20 organochlorine pesticides (OCPs), analytical performance of triolein-embedded cellulose acetate membrane (TECAM) sampling, and comparison of mean concentration of the studied OCPs in TECAMs exposed in air-bridge system solutions

OCP	Physicochemical property		Analytical performance				
	Aqueous solubility		Detection limit (ng L ⁻¹)	Precision (RSD %, n=3)	Extraction recovery (%) ^c	C_{TECAM} (ng g ⁻¹ , mean±s, n=3)	
	Log K_{ow} ^a	(μg mL ⁻¹) ^a				0 mg L ⁻¹	15 mg L ⁻¹
α-Endosulfan	3.62	0.53	0.5	19	85	51.5±6.0	50.1±4.6
Endosulfan sulfate	3.66	— ^b	0.2	15	97.3	77.3±6.7	74.2±6.2
γ-HCH	3.70	7.3	0.3	18	77.5	54.6±6.6	54.8±6.0
β-HCH	3.80	0.7	0.5	16	79	82.4±10.6	81.4±9.9
α-HCH	3.81	1.63	0.3	18	75	49.0±5.8	48.6±5.9
β-Endosulfan	3.83	0.28	0.7	14	92.5	54.2±3.2	53.5±5.4
δ-HCH	4.14	10.7	0.1	15	74.6	235.4±18.5	231.4±21.2
Endrin aldehyde	4.80	—	1.5	17	87.6	36.4±3.9	35.6±3.6
Endrin ketone	4.99	—	0.5	12	99.4	78.5±8.3	75.3±7.1
Heptachlor epoxide	5.00	0.35	0.6	16	87.2	69.8±7.1	71.3±8.4
Methoxychlor	5.08	0.1	0.4	14	97.4	107.4±8.4	104.8±9.7
Endrin	5.20	0.26	1.0	16	108.4	81.9±7.1	79.4±7.4
Heptachlor	5.27	0.03	0.2	9	97.4	10.8±1.3	10.9±1.3
Dieldrin	5.40	0.14	0.6	13	88.5	67.3±8.1	67.7±7.4
α-Chlordane	5.90	0.056	0.3	12	88.5	48.4±4.4	48.9±3.4
4,4'-DDD	6.02	0.02	0.7	11	105.3	46.4±4.5	45.2±4.2
γ-Chlordane	6.10	0.056	0.2	8	83.3	38.4±3.4	38.2±4.2
4,4'-DDE	6.14	0.04	0.4	10	93.5	23.8±2.8	23.6±2.9
4,4'-DDT	6.36	0.0017	1.3	11	105.5	44.1±4.2	42.1±4.4
Aldrin	6.50	0.18	0.5	12	76.4	34.7±3.6	35.5±2.8

^a Selected values from Mackay et al. [16]^b — values are not obtained^c Calculated by equation: $R = (C_T \times W_T) / ((C_{w0} - C_{w1}) \times V_w) \times 100\%$. R is the ultrasonic extraction of TECAM for each target compounds; C_T is the measured concentration of target compound in TECAM (ng g⁻¹); W_T is the mass of TECAM (g); C_{w0} and C_{w1} are initial and residual concentration of target compound in water before and after TECAM extraction (ng L⁻¹), respectively; V_w is the volume of water (L). The extraction recovery experiments were conducted in static exposure system

laboratory experiments unless otherwise indicated. All the TECAMs were kept in Milli-Q water before use.

TECAM absorption profiles

Since knowledge of the absorption kinetics provides information for TECAM sampling, it is necessary to determine the absorption profiles of OCPs to TECAM in the bottle experiments. Absorption profile experiments were separately conducted by adding TECAM to 1 L of test solution in a conical glass flask. Test solutions were prepared from Milli-Q water to which a methanol solution of the OCP mixture was added to give a concentration of each analyte of 200 ng L⁻¹ for the time-dependent kinetic study and 1–500 ng L⁻¹ for the concentration-dependent study. The maximum concentrations in water were kept below the reported water solubility limits for these compounds (Table 1). The flasks were sealed to prevent loss of

analytes due to volatilization. All the experiments were performed on a constant temperature-reciprocating shaker with controlled conditions (90 rpm, 20 °C). The concentration-dependent study lasted for 1 h and the time-dependent kinetic study lasted for 12 h. During the kinetic study, TECAMs were removed after each hour exposure and placed into a new flask filled with 1 L test solution. Thus there were 11 successive TECAM removals for the 12-h-long kinetic study. The OCPs accumulated in the TECAM were monitored throughout the 12 h of exposure. All the experiments were carried out in triplicate.

Determination of uptake kinetic parameters

For field application, the uptake kinetic calibration parameters (i.e., K_{TECAM} and k_u) were required for calculating the freely dissolved concentration from field-deployed TECAM samples.

Flow-through exposure Landrum et al. proposed that the actual uptake rate constant based on the freely dissolved analyte concentration is the same for both exposures with and without DOM [14]. Hence, it is feasible to obtain k_{us} in a controlled laboratory continuous-flow system which approximately simulates the flow conditions of field exposure.

The dechlorinated tap water (passed through an active carbon column filter and a fine-particle filter) with organic carbon content $<0.4 \text{ mg L}^{-1}$ was used in flow-through exposure study. TECAMs were exposed to the 20 OCPs at nominal concentrations of 20 ng L^{-1} as well as to the control water in the flow-through exposure system. Exposures were conducted at a water temperature of $20 \pm 1 \text{ }^{\circ}\text{C}$. Two 15-L aquaria were used and the solution containing 20 OCPs was pumped into the aquaria at a rate of 3.5 L h^{-1} to obtain relatively stable concentrations of the different OCPs. The effective linear velocity of water in aquaria was approximately 0.1 cm s^{-1} and significant turbulence occurred during water input. In the aquaria, the TECAMs were suspended vertically. The exposure lasted for 192 h. During the experiment, duplicate TECAMs from the aquaria were sampled at 12, 24, 48, 96, and 192 h of exposure. Furthermore, samples of water (250 mL) were also taken at each TECAM sampling time to monitor the concentrations of the OCPs in the exposure waters.

Static equilibrium experiment Multiple conical glass flasks containing 1 L of Milli-Q water and one TECAM each were spiked with the 20 OCPs to give concentrations of individual analyte of 100 ng L^{-1} . The experimental set up of static exposure was the same as described by Xu et al. [11]. According to the previous result [11], the exposure lasted for 16 days to ensure all the 20 studied OCPs could approach the steady state in TECAM. Water samples from the flasks (250 mL) were taken at the time when TECAM were sampled. The experiment was carried out in triplicate.

Validation of determining freely dissolved concentration

Before humic acid binding experiments can be performed, it is necessary to validate the use of the TECAM method to determine the freely dissolved fraction of OCPs in the presence of DOM. For this purpose, the measurements of two solutions with identical free concentration (one with humic acid and the other without) were compared. The solutions were prepared using an air-bridge system as described by van Wezel et al. [18]. The system consists of two round-bottomed flasks connected by a bent tube. One flask was filled up with 1 L of Milli-Q water, the other was filled with 1 L of 15 mg L^{-1} humic acid solution, and both solutions were spiked with 20 OCPs to obtain an aqueous concentration of 200 ng L^{-1} for each analyte. Then the two

flasks were connected by the vapor-tight air-bridge and the flasks were magnetically stirred for 3 weeks to equilibrate the system [18, 19]. The basic principle of this system is that only the unbound chemical diffuses through the vapor phase, and then the free concentration in both flasks will eventually equilibrate after a period of time. After equilibration, one TECAM was put in each flask and sampled for 1 h on the rotatory shaker (90 rpm, $20 \text{ }^{\circ}\text{C}$), and was then ready for analysis.

K_{doc} measurement

For K_{doc} measurements, the sample solutions were produced by diluting the humic acid stock solution with Milli-Q water to reach an organic carbon content of 2 mg L^{-1} and 15 mg L^{-1} , respectively. Artificial organic-free control water was prepared from Milli-Q grade water ($\text{DOC} < 0.1 \text{ mg L}^{-1}$). Before use, the solutions were adjusted to a pH of 7.5 ± 0.2 with 0.1 M HCl and 0.1 M NaOH . One liter of each solution was transferred to each 1-L glass bottle and spiked with 20 OCPs to give a concentration of 200 ng L^{-1} for each analyte. The bottles were kept sealed with Teflon-lined caps and shaken gently on the shaker for 4 days in the dark before TECAMs were added. It was assumed that the equilibrium of OCP partition between water and humic acid was reached after 4 days, since some investigators have shown that the sorption equilibrium between HOCs and humic acid is established very rapidly [20, 21]. One TECAM was then added to each bottle and sampled for 1 h on the shaker (90 rpm, $20 \text{ }^{\circ}\text{C}$), and was then ready for analysis.

Field application with TECAM

To demonstrate the field applicability, nine TECAMs ($12 \text{ cm} \times 18 \text{ cm}$) were deployed at one site of Taihu Lake in China. Each TECAM was placed in a stainless steel mesh cage and submersed in surface water to a depth of 50 cm. The exposure period lasted for 8 days and three replicate TECAMs were taken at 2, 4, and 8 days. Surface water samples (1 L) of the site were also collected at each sampling time, filtered ($0.45\text{-}\mu\text{m}$ Millipore glass microfiber filters) immediately for DOC measurement, and analyzed for OCPs. The water temperature was about $19\text{--}22 \text{ }^{\circ}\text{C}$ during the deployment period, and the average DOC content of lake water at the site was ca. 5 mg L^{-1} . The OCP residues in the surface water were extracted using solid-phase extraction (SPE) with C_{18} cartridges (Envi-18, Supelco).

Sample processing

TECAMs were rinsed with distilled water and wiped up with clean paper tissue. Each TECAM was extracted with the ultrasonic extraction device (SCIENIZ, Shanghai, China)

using 10 mL (for laboratory exposure samples) or 20 mL (for field exposure samples) of *n*-hexane as solvent for 10 min. The procedure was repeated for three times (the extraction recoveries are described in Table 1). After extraction, solutions were combined and pre-concentrated to 1-mL final volume, transferred to a vial, and concentrated to 200 μ L under a stream of nitrogen. The water samples (each 250 mL) from the batch and flow-through exposures were extracted by partitioning with dichloromethane. The C₁₈ cartridges were eluted with 10 mL of dichloromethane each [11]. All the eluates were evaporated under a gentle stream of nitrogen and solvent-exchanged into *n*-hexane (200 μ L). Pentachloronitrobenzene (Supelco), used as an internal standard, was added to all extracts just prior to injection into a GC.

Instrumental analysis

Analysis of OCPs was performed with an Agilent 6890 series GC equipped with a ⁶³Ni electron capture detector and a 7683 autosampler (Agilent, Palo Alto, CA). A 30 m $\times$ 0.25-mm i.d. $\times$ 0.25 μ m HP-5 column (J&W Scientific, USA) was used for pesticides identification and quantification. Nitrogen was used as carrier gas at 1.0 mL min⁻¹ under the constant-flow mode. The oven was programmed from 80 to 180 $^{\circ}$ C (15-min hold time) at a rate of 20 $^{\circ}$ C min⁻¹, then to 240 $^{\circ}$ C at a rate of 4 $^{\circ}$ C min⁻¹, and further to 280 $^{\circ}$ C at a rate of 20 $^{\circ}$ C min⁻¹ holding for 7 min. Split/splitless injection of a 1- μ L sample was performed with a 1.8-min solvent delay time. Injector and detector temperatures were maintained at 250 $^{\circ}$ C and 300 $^{\circ}$ C, respectively. Pesticides were identified by comparing the GC peak retention times with those of authentic reference standards and quantified by peak area using an internal standard method.

Results and discussion

Absorption profiles to TECAM

The kinetics of accumulation for the 20 OCPs were measured by exposing TECAMs during 1, 2, 3, 6, and 12 h in sample solutions. For all test substances, the uptake is linear in all exposure studies during the whole exposure period and without any sign of a leveling-off in the uptake curve (Fig. 2). Moreover, it is observed that the TECAM after 1-h exposure accumulated OCP quantity less than 10% of the total OCP quantity in the 1 L exposure water (Table 2) and then met the requirement of “negligible depletion” [20, 22]. For bottles that contained humic acid, the extracted amount was less and proportional to the freely dissolved fraction. Consequently, the equilibrium of the aqueous phase and humic acid is not significantly disturbed under the conditions (90 rpm, 20 $^{\circ}$ C, 1 h) of the bottle experiment.

For all the tested OCPs, the concentrations measured in the TECAM were found to be proportional to the water concentration from 1 to 500 ng L⁻¹ with correlation coefficients higher than 0.99. This is illustrated in Fig. 3 for six selected OCPs with low to high *K*_{ow} values. Limits of detection (LOD) for 20 OCPs were calculated as mean value plus three times the standard deviation of the baseline noise from six blank samples and ranged from 0.1 ng L⁻¹ for the δ -HCH to 1.5 ng L⁻¹ for endrin aldehyde (Table 1). It should be noted that the LOD could be improved by increasing the exposure duration. Relative standard deviations (RSD) calculated for each sample analyzed in triplicates were less than 19% (Table 1).

Determination of uptake kinetic parameters

During the 192 h of flow-through exposure, α -endosulfan, endosulfan sulfate, γ -HCH, β -HCH, and α -HCH were concentrated rapidly by TECAM, covering linear and curved regions of uptake and finally approaching the steady state. Thus, their uptake rate constants (*k*_u) were calculated according to Eq. (1) (Table 2). For other OCPs that were still in the linear uptake phase, the *k*_us were calculated according to Eq. (2) using the slope of the accumulation curves and the average actual water concentration for each OCP (Table 2). The actual concentration of the 20 OCPs ranged from 1.7 to 14.9 ng L⁻¹ in aquaria water. According to Table 2, the data set of TECAM *k*_us showed a generally consistent trend of *k*_u increase with log*K*_{ow}, reaching a maximum near log*K*_{ow}=5.4, and then a reduction can be observed when log*K*_{ow}>6.14. This may be due to steric hindrance of the higher molecular weight OCP in the

Fig. 2 Kinetic uptake of six selected OCPs by TECAMs (4 cm $\times$ 6 cm) exposed for 12 h in Milli-Q water spiked with 200 ng L⁻¹ of OCPs. Sampling was conducted in 1-L bottles on a rotary shaker (90 rpm, 20 $^{\circ}$ C)

Table 2 Concentrations of OCPs in TECAMs after 1-h exposure at different dissolved organic carbon concentration, calculated K_{doc} s, first-order half-time, uptake rate constants in flow-through exposure, and TECAM–water partition coefficients for 20 OCPs

OCP	$C_{\text{TECAM},1 \text{ h, doc}}^a$ (ng g ⁻¹)			Log K_{doc}^b	k_u (L h ⁻¹ g ⁻¹)	$t_{1/2}$ (h)	Log K_{TECAM}
	0 mg L ⁻¹	2 mg L ⁻¹	15 mg L ⁻¹				
α -Endosulfan	47.0	46.8	46.2	3.06	0.138	44	3.94
Endosulfan sulfate	55.7	56.3	53.5	3.44	0.132	58	4.04
γ -HCH	32.1	32.0	31.3	3.26	0.088	26	3.52
β -HCH	38.6	38.7	37.5	3.29	0.132	20	3.58
α -HCH	33.8	33.2	33.0	3.22	0.074	43	3.66
β -Endosulfan	44.8	45.2	41.5	3.72	0.066	109	4.01
δ -HCH	48.4	47.1	41.3	4.06	0.037	100	3.73
Endrin aldehyde	34.9	31.5	26.8	4.30	0.134	144	4.45
Endrin ketone	41.7	35.6	31.0	4.36	0.148	127	4.43
Heptachlor epoxide	63.6	54.4	42.0	4.53	0.113	249	4.61
Methoxychlor	82.1	63.7	44.8	4.74	0.135	215	4.62
Endrin	94.1	81.2	60.5	4.57	0.153	316	4.84
Heptachlor	95.6	68.1	46.3	4.85	0.115	578	4.98
Dieldrin	69.1	51.5	29.2	4.96	0.240	323	5.05
α -Chlordane	92.1	63.9	27.9	5.17	0.195	1,044	5.47
4,4'-DDD	82.3	53.3	20.9	5.19	0.171	938	5.37
γ -Chlordane	54.6	33.4	17.0	5.14	0.181	1,358	5.55
4,4'-DDE	81.6	54.2	23.3	5.29	0.210	944	5.46
4,4'-DDT	53.9	35.1	17.7	5.22	0.149	614	5.21
Aldrin	56.2	36.6	18.2	5.14	0.100	1,527	5.34

^a Average values for triplicates, RSD < 22%^b Values were calculated by Eq. (8) for OCP concentration in TECAM after 1-h exposure in sample solutions with 15 mg L⁻¹ humic acid and without humic acid

membrane or increasing water side resistance for high K_{ow} OCP. Analyte aqueous diffusion coefficient and molecular weight are closely related quantities. Worch proposed that aqueous diffusion coefficients decrease with increasing

molecular weight or size [23]. This indicates that TECAM sampling rates can be expected to decrease for some higher molecular weight OCPs. Indeed, our early results have also revealed that the k_u s of PAHs decreased when log K_{ow} exceeded approximately 6.0 [12].

The steady-state partitioning coefficients (K_{TECAMs}) between TECAM and water were determined using Eq. (3) in the static equilibrium experiment (Table 2). The first-order half-time ($t_{1/2}$) was estimated using Eq. (4) and the k_u values from the flow-through exposure study (Table 2). It is observed that, for α -HCH, β -HCH, γ -HCH, α -endosulfan, and endosulfan sulfate, the uptake equilibrium could be quickly reached within several days. For the rest of OCPs taken into the consideration, the uptake equilibrium could not be reached within 2 weeks.

Thus it appears that the TECAM sampling method could be used to measure the freely dissolved fraction of OCPs for in situ field sampling using the K_{TECAM} and k_u calibration values obtained under laboratory conditions.

Validation of determining free concentration

The most important step is to validate that TECAM extracts only the freely dissolved fractions of OCPs in the presence of humic acid. After equilibration, the free concentrations of OCPs in both flasks of the air-bridge

Fig. 3 Calibration curve of TECAMs (4 cm × 6 cm) for six selected OCPs. TECAMs were exposed in Milli-Q waters spiked with OCPs in the concentration range 1–500 ng L⁻¹ and sampled by shaking (90 rpm) for 1 h at 20 °C, $n=3$ for each OCP concentration

system will be equal, since only the free chemical diffuses through the vapor phase. The mean concentration for each OCP in the TECAM samples in the presence and the absence of humic acid were similar (Table 1). The measurements are not significantly different ($P>0.05$), which was expected if the freely dissolved OCPs were equal in both flasks and then TECAM extracts only the freely dissolved fraction. Thus, this result clearly shows that the TECAM method described in this work can be used to measure freely dissolved OCP concentrations in humic acid containing solutions.

Calculation of K_{doc}

The measured $\log K_{\text{doc}}$ values are shown in Table 2. The $\log K_{\text{doc}}$ values were calculated from Eq. (8) based on the OCP concentration measured in TECAM after 1-h exposure in the presence ($C_{\text{TECAM,1h,doc}}$) and absence of humic acid ($C_{\text{TECAM,1h,0}}$). For the more hydrophilic OCPs (i.e., $\log K_{\text{ow}} < 4$), the difference between the concentrations in TECAM after 1-h exposure in the presence and absence of humic acid was found to be small, especially in sample solution with low humic acid concentration (Table 2). Therefore, very reliable partitioning coefficients cannot be calculated. This insignificant difference observed for these compounds reflects relatively low binding affinities with humic acid due in part to their relatively high water solubility (Table 1). As shown in Table 2, it is clear that extraction of OCPs decreased substantially with increasing humic acid concentration, particularly for those OCPs with $\log K_{\text{ow}} > 4$, indicating that in the presence of humic acid OCPs become less available for extraction by TECAM. This strongly suggests that TECAM extracts primarily the freely dissolved fraction of analytes in water leaving behind the fraction adsorbed and/or bound to humic acid. It is noteworthy that $C_{\text{TECAM,1h,doc}}$ and $C_{\text{TECAM,1h,0}}$ values obtained from Eq. (8) were measured with RSD values lower than 22% ($n=3$). This induces a variation of K_{doc} lower than a factor of 3.8 and a corresponding variation of $\log K_{\text{doc}}$ lower than 13%.

The $\log K_{\text{doc}}$ values for 4,4'-DDT and γ -HCH from our experiments were selected and compared with earlier published $\log K_{\text{doc}}$ values. However, it was not possible to find comparative data for other OCPs, as only the data of 4,4'-DDT and γ -HCH are available in the literature. The earlier reported $\log K_{\text{doc}}$ values for 4,4'-DDT and γ -HCH ranged from 4.39 to 5.61 and from 1.5 to 2.7, respectively [24]. It will be noted that the $\log K_{\text{doc}}$ value for 4,4'-DDT obtained in our study was in agreement with the published values (Table 2). However, for γ -HCH, our calculated value was somewhat larger than the value reported earlier (Table 2). A possible explanation for this discrepancy results from the low binding affinity between γ -HCH and humic acid. Thus, our method does not appear to be

sensitive enough to obtain very accurate measurements for these compounds in the water samples with low humic acid concentration. Similar observations have been reported in earlier studies [14, 25]. Another possible reason could be the different characteristics of humic acid. The earlier reported K_{doc} values were obtained by using a naturally occurring humic acid while a commercial humic acid was used in the present study. Previous studies have shown that the binding affinity of hydrophobic compounds to commercial humic acid was stronger than natural humic acid [26, 27].

The $\log K_{\text{doc}}$ values for the 20 OCPs obtained from the present study vs. their $\log K_{\text{ow}}$ results in a linear equation,

$$\log K_{\text{doc}} = 0.754 \log K_{\text{ow}} + 0.631$$

and correlation coefficient $R^2=0.93$. This linear relationship between $\log K_{\text{ow}}$ and $\log K_{\text{doc}}$ is similar to that reported by Li et al. [28] and Freidig et al. [29] based on various HOCs.

Application to field sampling

To validate the applicability of TECAM for field sampling, TECAMs were applied to determine the free concentrations of OCPs in lake water containing relatively high organic matter. It was observed that after the 8-day sampling period, seven OCPs including α -HCH, β -HCH, γ -HCH, and δ -HCH were detected (Table 3). They approached the steady state, while 4,4'-DDE, 4,4'-DDT, and α -chlordane remained in the linear uptake region. Therefore, average free dissolved concentrations of OCPs were estimated from Eq. (3) for α -HCH, β -HCH, γ -HCH, and δ -HCH; and Eq. (2) for 4,4'-DDE, 4,4'-DDT, and α -chlordane based on the above-noted kinetic parameters (Table 3).

As shown in Table 3, the OCP concentrations derived by SPE were 1.1–7.2 times higher than TECAM-derived concentrations. The extracted SPE cartridges showed a little brown staining that would indicate adsorption or coextrac-

Table 3 Comparison of the concentrations of seven OCPs in the water of Taihu Lake, China, by solid-phase extraction method and by the proposed TECAM method

Compound	C_{TECAM} (ng g^{-1} , mean $\pm$ SD, $n=3$)	C_{free} (TECAM) (ng L^{-1})	C_{w} (SPE) (ng L^{-1})
α -HCH	8.1 $\pm$ 0.7	1.78	4.79
β -HCH	12.3 $\pm$ 1.7	3.23	7.81
γ -HCH	3.4 $\pm$ 0.6	1.26	4.09
δ -HCH	5.2 $\pm$ 0.7	0.97	1.08
α -Chlordane	1.4 $\pm$ 0.2	0.04	0.16
4,4'-DDE	2.5 $\pm$ 0.4	0.06	0.29
4,4'-DDT	0.4 $\pm$ 0.07	0.014	0.10

tion of DOM-associated chemicals. This finding is in agreement with Qiao et al. [30], who found that the SPE method used for water samples in this study reflected both freely dissolved and parts of the DOM-associated chemicals.

It is noteworthy that although the field exposed TECAM samples were somewhat dirty having a pale yellow coloration, the chromatograms obtained showed well-resolved peaks with no obvious interferences even though the samples were not subjected to any cleanup procedure. This observation further demonstrates the high selectivity of the TECAM sampling method and its suitability for field study.

Conclusions

The novel TECAM sampling method developed in this study provides a viable and facile approach for the determination of the freely dissolved OCP concentration in environmental waters and thus their K_{docS} . This method is based on the principles of partition sampling through membranes and offers significant advantages over the currently used sampling techniques, such as simplicity, reproducibility, and elimination of interferences. The methodology is rather inexpensive, since it is based on easily obtained cellulose acetate and can be prepared in a laboratory easily. The ultrasonic extraction of TECAM samples is time-saving (30 min for per sample) with acceptable recoveries (74.6–108.4%) (Table 1). Moreover, TECAM offers a great potential as a TWA sampler for in situ field sampling to provide information about freely dissolved TWA contaminant concentrations over a long time period.

The results obtained in this study demonstrate the performance of the TECAM sampling method for extracting freely dissolved fraction of OCPs from aqueous solutions. However, it is realized that there are some issues which should to be addressed for further validation of TECAM, including: (1) the effect of biofouling on the uptake kinetics, (2) the effect of water turbulence on the uptake kinetics of analytes during in situ deployment. Research is currently underway in our laboratory to address these issues in order to optimize this technique for field application.

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