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Time-integrated monitoring of dioxin-like polychlorinated biphenyls (dl-PCBs) in aquatic environments using the ceramic toximeter and the CALUX bioassay

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ABSTRACT

Ceramic passive samplers or toximeters (packed with active carbon 1%, w/w, on celite), in combination with the CALUX bioassay have been used as a time-integrated monitoring technique for dissolved dioxin-like PCBs in urban and industrial wastewaters. The technique showed to be reliable during laboratory experiments: (1) PCB-126 amounts extracted from the passive samplers increased linearly with the time of exposure and (2) PCB-126 concentrations calculated from the amounts accumulated by the passive samplers were in agreement with their concentrations in the testing solution. Afterwards the toximeters were applied in the field. Two sampling sites located in Egypt were chosen: the Belbeis drainage canal, and the EMAK paper mill. A total of 18 ceramic toximeters were exposed to the wastewater in both sampling sites for a maximum period of 4 weeks. Two samplers were collected weekly from each site to monitor the increase in target analytes over time. Extracts were analyzed using the CALUX bioassay and the total dioxin-like PCB toxicity was reported for the aqueous phase (water column), as well as the solid phase (sediment and sludge) in both sampling sites. The time-weighted average concentration (TWA) of dl-PCBs in wastewater of the paper mill during the sampling period ranged between 7.1 and 9.1 pg-BEQ L^{-1}, while that of the drainage canal ranged between 9.5 and 12.2 pg-BEQ L^{-1}. The dl-PCBs in the fibrous sludge (paper mill) and bottom sediment (drainage canal) were 0.5 and 0.4 pg-BEQ g^{-1} dry-weight, respectively. The organic-carbon normalized partition coefficients between sediment and water (log K_{oc}) for the paper mill and the canal were 2.4 and 4.3, respectively.

1. Introduction

The thermal and chemical stability of polychlorinated biphenyls (PCBs), among other properties, led to a widespread use in transformers, capacitors, hydraulic fluids, as well as plasticizers, and numerous other industrial applications [1]. Amongst the 209 possible PCB congeners, only 12 have dioxin-like toxicity, since they bind to the Ah-receptor [2,3]. Like most of the other PCB congeners, these dioxin-like PCBs have the potential to cause adverse effects on human and animal health [4]. In fact, the combined effect of their bioaccumulation in the trophic chain and the action of sediments as a reservoir of PCBs make the direct discharge of these compounds into the aquatic system problematic [5]. Their half-life time in these matrices can be as long as several decades [6,7]. Since the major pathway of human exposure to dioxin-like compounds (over 90%) is through the diet [8], especially fish consumption [9,10], it is highly important to monitor dioxin-like PCBs in aquatic systems on a regular basis.

Ceramic-based passive sampling devices have been previously used for monitoring dissolved polychlorinated dibenzo-ρ-dioxins and polychlorinated dibenzofurans (PCDD/Fs) [11,12], polycyclic aromatic hydrocarbons (PAHs) and volatile organic contaminants (VOCs) in surface and ground water [13,14], and flame retardants in river water [15]. The ceramic toximeter is based on the free flow of analyte molecules from the sampled medium through a ceramic diffusion membrane towards a suitable receiving phase, under the effect of a chemical-potential difference [16]. This diffusion-controlled collection of analytes allows for calculating the time-weighted average (TWA) concentration of the target chemicals in the sampled medium during the sampling period depending on Fick's first law of diffusion. In this study a novel, time integrated monitoring method for dl-PCBs was validated. The analytical

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procedure, which is much faster and easier than earlier used methods, involves the in situ pre-concentration of dl-PCBs on activated carbon and their subsequent quantification by the CALUX bioassay. After validation, the toximeters were deployed in different wastewaters in Egypt.

2. Materials and methods

2.1. Reagents and materials

The ceramic cylinders were manufactured by ATECH Innovations (Germany) [12]. The XCARB (activated carbon 1%, w/w, on celite) was from Xenobiotic Detection Systems (USA). 3,3′,4,4′, 5-Pentachlorobiphenyl (PCB-126, 99.4%) was from Chem Service (USA). Acetone (Pesti-S grade, minimum 99.9%), *n*-hexane (for dioxins and PCBs, minimum 96%) and toluene (for dioxins and PCBs, minimum 99.8%) were purchased from Biosolve (The Netherlands). Neutral alumina (activated, 150 mesh), silver nitrate (5 wt % on silica gel 60), ethyl acetate pestanal and silica gel 60 were purchased from Sigma–Aldrich (Germany). Anhydrous sodium sulfate was purchased from Boom (The Netherlands). Sulfuric acid (95–97%, ACS reagent), DMSO and glass wool were from Merck (Germany). Standard solution of 2,3,7,8-tetrachlorodibenzo-ρ-dioxin (50 μg/ ml, in nonane) was from Campro Scientific (The Netherlands). The mouse hepatoma H1L7.5c1 cell line used in the CALUX bioassay was provided by Michael Denison (University of California, USA).

2.2. Conditioning of materials

The XCARB and glass wool for the toximeters were conditioned by fluxing in toluene as described previously [12]. The ceramic cylinders were sintered at 750 °C for 24 h to eliminate possible organic traces. PTFE caps and stainless steel cages were rinsed with acetone and Milli-Q deionized water. Silica gel was baked at 200 °C for 48 h prior to use. Glassware and sodium sulfate were baked for 4 h at 450 °C.

2.3. Laboratory testing of toximeters

A generated aqueous solution of PCB-126 was used as a stock solution in the laboratory testing experiments of the toximeters. Fifty micrograms of 3,3′,4,4′,5-pentachlorobiphenyl (PBC-126) were dissolved in 2 mL acetone, and then completed to 1000 mL with deionized water in a light-shielded glass bottle. The solution was shaken for 48 h at 40 rpm. The bottle cap was then removed under the hood for 72 h to allow a slow but full evaporation of acetone. A diluted PCB-126 testing solution was prepared for laboratory testing of the toximeters. Therefore, a 1 L glass bottle was filled with the testing solution for 48 h (prior to applying the toximeters) in order to equilibrate the PCB-126 between the solution and the glass wall. The drained solution is then replaced with a fresh amount of the same concentration. This, in turn, shall reduce the effect of PCB partitioning due to partial saturation of the bottle wall. At the start of the experiment ($t=0$ h), 8 toximeters were immersed in 1 L of the testing solution and after 12, 24, 48, and 96 h of exposure, 2 toximeters were removed from the solution. The bottle containing the toximeters was kept on a shaker (at 40 rpm) for the whole period of exposure.

To measure the concentration of this solution, 10 mL of the PCB solution was extracted 4 times with solvent (10, 10, 5, and 5 mL toluene, respectively). Toluene was evaporated and the extract was redissolved in 10 mL *n*-hexane and analyzed with the CALUX bioassay technique. Concentration of the testing solution at the start of the experiment ($t=0$ h) amounted to 0.78 ($\pm$0.09) μg L^{-1} while at the end it decreased with about 50%. These concentrations were calculated from full dose–response curves (Fig. 1) of the PCB-126 testing solution and of 2,3,7,8-TCDD standard using a CALUX-REP value of 0.038 [17].

2.4. Field application of toximeters

Two wastewater sites located in Egypt were chosen as field sites: (1) the Belbeis drainage canal (N: 30°26′25.88″, E: 31°34′23.16″), which is heavily polluted and frequently used to convey raw industrial and municipal wastewater and (2) the EMAK Paper Manufacturing Company (N: 29°41′50.12″, E: 32°18′13.30″), Ain El-Soukhna, Suez. More details about the sampling locations can be found elsewhere [12]. Wastewater effluents of the paper mill were sampled by applying the toximeters before the primary wastewater treatment process inside the factory. Toximeters exposure continued for 4 weeks in October 2011. Every 7th day, two samplers were removed from each site. Bottom sediment from the drainage canal and fibrous sludge from the paper mill were analyzed to calculate the partitioning coefficient for dioxin-like PCBs in both sampling sites. The whole extraction, cleanup and analysis procedure is schematically presented in Fig. 2. More details are given below.

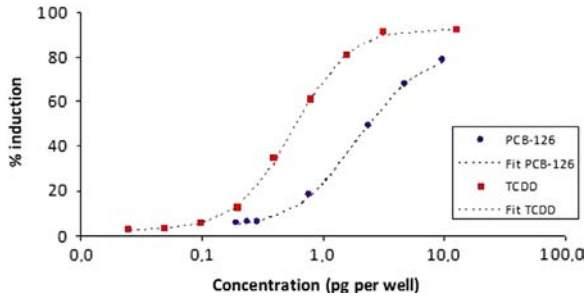

Fig. 1. Dose–response curves of a PCB-126 solution and a TCDD standard calibration curve.

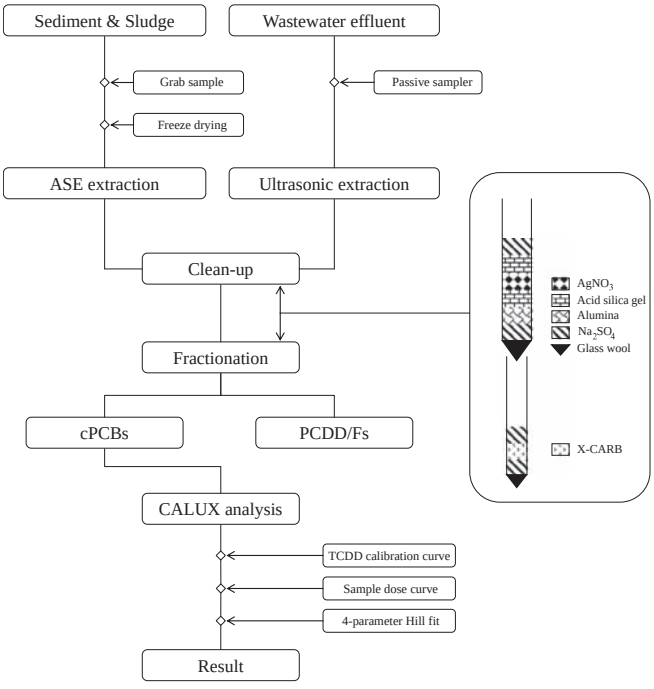

Fig. 2. Extraction, cleanup and analysis scheme of the CALUX bioassay procedure for dl-PCBs.

2.5. Extraction of toximeters, sediment, and sludge

Toximeters, sediment, and sludge were light-shielded and preserved at −20 °C till the time of extraction. The applied toximeters as well as blank toximeters (immersed in Milli-Q water) were rinsed with deionized water and left to dry. The PTFE caps were removed and the XCARB was ejected into glass vials. Toluene was used as the extraction solvent. First, 15 mL of toluene was added to the vials. Then, the samples were ultrasonicated for 1 h, centrifuged to settle down the suspended particles, and the liquid phase was transferred into new glass vials through pre-cleaned glass wool filters. This step was repeated 3 more times for all samples using 9, 9, and 6 mL of fresh toluene in each extraction cycle [11].

The drainage canal sediment and paper mill cellulosic sludge were freeze-dried for 72 h, and then homogenized with a pestle and mortar. Liquid nitrogen was added to the paper mill sludge to assist the breakup of the fibrous blocks. The homogenized powders were then sieved (35 mesh) to remove the larger grains such as pebbles and blocks. Five grams of both sediment and sludge were extracted using Accelerated Solvent Extraction (ASE 200, Dionex Sunnyvale, CA, USA) equipped with 33 mL stainless steel extraction cells. A mixture of *n*-hexane/acetone (1/1, v/v) was used as an extraction solvent. The operating conditions were set to 125 °C, 2 cycle extraction mode, 6 min heating time, 10 min static period, 1500 psi pressure, and 60% flushing volume. Afterwards, the extracts were evaporated and the residues were dissolved in 10 mL *n*-hexane.

2.6. Cleanup of extracts

Extracts from laboratory deployed toximeters did not undergo a cleanup process, since a single PCB congener was used. Extracts from field-deployed toximeters as well as sediment and sludge were pretreated with 4 mL sulfuric acid. The cleanup was carried out through a multi-layer silica gel column, coupled in series with a carbon column to remove compounds that might interfere during the CALUX bioassay analysis, as described by Croes et al. [18]. After loading the samples, the columns were rinsed with 45 mL *n*-hexane, and then the silica columns were removed. The carbon columns were first rinsed with 8 mL *n*-hexane/acetone (9/1) and the coplanar PCBs were eluted with 15 mL *n*-hexane/ethyl acetate/toluene (80/10/10). Finally, the PCDD/Fs were eluted with 20 mL toluene (for other experiments). The PCB extracts were centrifuged under vacuum (40 °C) till dryness, and the deposits were redissolved in 5 mL *n*-hexane. A number of dilutions were made for each sample prior to the CALUX analysis.

2.7. The CALUX bioassay for extracts

The CALUX (Chemically Activated LUciferase gene eXpression) bioassay technique makes use of a reporter gene expressed by recombinant mammalian cell line. The mouse hepatoma H1L7.5c1 cell line was used in CALUX bioassay analysis as described before [18]. Briefly, each well on the 96-well plate was seeded with 200 μL cell suspension in RPMI ($55–65 \times 10^4$ cells mL^{-1}). After a 24 h incubation period, 188 μL of a standard solution or sample extract in RPMI with 1% DMSO was added to each well. After another 24 h incubation period, the medium was removed and the wells were rinsed with 75 μL PBS buffer (Gibco, UK) and visually inspected under the microscope. Fifty microliters lysis reagent (Promega, USA) was added and the plate was shaken for 5 min. After 10 min incubation in the luminometer (Glomax, Promega, USA), 50 μL luciferine reagent (Promega, USA) was injected into all wells (lag time 5.6 s, integration time 3 s). The measured luminescence was expressed in relative light units (RLU) and converted into a bioanalytical equivalency value (CALUX-BEQ) by comparing the dose–response curve of a given sample to a dose–response curve obtained from 2,3,7,8-TCDD standards. In case no full dose–response curve could be obtained, a Box–Cox transformation was applied instead of the Hill function [19,20]. Results are expressed in pg-BEQ L^{-1} (for dissolved dl-PCBs), and in pg-BEQ g^{-1} (for adsorbed dl-PCBs in sediment and sludge).

2.8. Comparison of the proposed protocol with other analytical approaches

The proposed protocol consists of two parts: (1) the sampling of the dl-PCBs with the toximeter and (2) the analysis with the CALUX bioassay.

The classic sampling procedure involves the collection of large volumes of water, because the concentrations of dissolved dl-PCBs are generally very low in natural waters. Zhang et al. [21] for example, collected water samples in the Yangtze River Delta (China) using a stainless steel container and stored these samples in 4-L brown glass bottles at 4 °C. These samples were then transported to the laboratory, spiked with a labeled PCB solution and the PCBs preconcentrated on an appropriate support. In situ pre-concentration by the toximeter avoids all those additional steps and reduces the risk of loss and contamination.

Dioxin-like PCBs were determined in the same extracts of atmospheric deposition samples in Flanders with the CALUX bioassay and with GC-High Resolution MS [22]. dl-PCBs were generally lower with CALUX than with GC-HRMS, except for some of the very low PCB concentrations (close to the limit of quantification). The CALUX/GC-HRMS ratios ranged between 0.2 and 4.4 (median 0.9).

2.9. Organic carbon (OC) content in sediment and sludge

The organic carbon (OC) content in both fibrous sludge (paper mill) and bottom sediment (drainage canal) was measured in order to calculate the organic-carbon normalized partition coefficient for dl-PCBs in both wastewater systems. OC measurements were carried out with a CHN elemental analyzer (Flash 1112 EA Elemental Analyzer, Thermo Finnigan, Italy). The organic matter in the dry homogenized samples was quantitatively converted to CO_2, N_2, SO_2, and H_2O by high temperature oxidative combustion at >900 °C in an O_2 atmosphere, after the removal of the inorganic carbon in the sample by acidification with 5% HCl. The EA analyzer is connected to a gas chromatograph that separates the combustion gases. OC quantification was performed by comparing the CO_2 signal with that of an aniline standard [23].

2.10. QA/QC

On all 96-well plates, a 10-point TCDD calibration curve, three DMSO blanks and three quality control (QC) solutions (a TCDD standard solution with a concentration of 0.125 ng mL^{-1}) were added in duplicate. The minimum detectable value was calculated as the concentration level at the inflection point of the TCDD curve where the slope is significantly different from zero (i.e. different from the lower plateau of the sigmoid curve), using a *t*-test ($p=0.01$) [24].

Also four blank toximeters (saturated with ultrapure water) were analyzed as a quality control for the whole analytical procedure. The blank extracts were spiked with the QC solution before measurement with the mouse cell line to take into account possible antagonistic or synergetic effects. Recovery of the spiked blanks should range between 80 and 120%.

3. Results and discussion

3.1. QA/QC results

All TCDD calibration curves were fitted with a 4-parameter Hill Equation, using a Weighted Least Squares (WLSs) regression technique [20]. The mean EC50 value ($n=10$) yielded 679 pg per well (SE=92 pg per well). The minimum detectable value was 0.046 pg BEQ per well. All quality control solutions and the four toximeter blanks yielded recoveries between 80% and 120%, while the DMSO blanks were at background level (lower plateau of the calibration curve).

3.2. Results of laboratory testing experiments

The PCB-126 amounts determined in the toximeter extracts immersed in the testing solution showed a regular increase with time of exposure (Fig. 3). This is expected since the mass of PCB-126 accumulation by the toximeter (M in Eq. (1)) is linearly proportional to the exposure time (t in Eq. (1)). After 12 h of exposure, 36 pg-BEQ was adsorbed by the toximeter while after 96 h of exposure this amount was almost tripled (110 pg-BEQ).

$$C_w = M\,\Delta x/AtD_e \quad (1)$$

We could also calculate the dissolved PCB-126 concentration in our testing solution at the various sampling times (12, 24, 48 and 96 h) using Eq. (1) [13,15], where C_w is the calculated PCB-126 concentration present in the testing solution (pg-BEQ L^{-1}), M (pg-BEQ) is the PCB-126 mass extracted from the toximeters and measured relative to the 2,3,7,8-TCDD standard, Δx is the ceramic diffusion membrane thickness (0.2 cm), A is the exposed surface area of the membrane (21.98 cm^2), t is the sampling time period (12, 24, 48 and 96 h), and D_e ($cm^2\ s^{-1}$) is the effective diffusion coefficient in the porous ceramic membrane compared to that of water. D_e can be calculated from Eq. (2) [16]:

$$D_e = D_w \times \varepsilon^m \quad (2)$$

where D_w ($cm^2\ s^{-1}$) is the diffusion coefficient of PCB-126 in water; ε is the porosity of the ceramic membrane (0.30); and m is Archie's law exponent, which ranges between 1.5 and 2.5 in laboratory calibration experiments [25]. A value of $m=2.0$ was previously determined and used in field applications with ceramic-based passive samplers [12–14], but according to the results obtained on our testing solution of PCB-126, the value of m was set to 2.5. Since in this experiment only PCB-126 is present, a D_e of 2.59 10^{-7} will be used (see also Table 3 for diffusion coefficients of dl-PCBs).

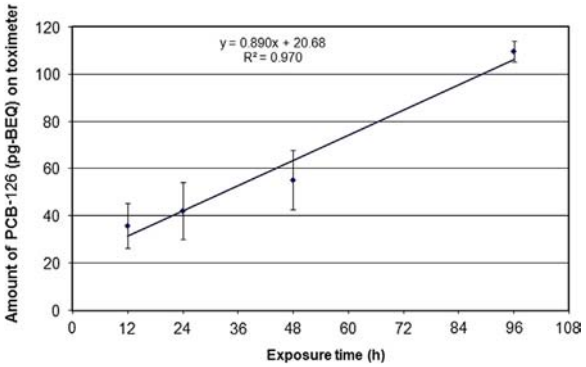

Fig. 3. Accumulated PCB-126 amount versus exposure time (laboratory experiments).

The calculated PCB-126 concentrations at the various sampling times are shown in Table 1. Although the PCB-126 concentration in the testing solution was 0.78 μg L^{-1}, at the start of the experiment, toximeter results were lower and this was also the case for the PCB-126 concentration in the testing solution at the end of the experiment. The reason is that the PCB solution is not stable and that part of the PCB burden in solution adsorbs on the glass wall and a small fraction (a few percent) also on the toximeters, resulting in a progressive decrease of the PCB-126 concentration in the testing solution. The results of the toximeters are, however, in line with the PCB-126 concentration in the testing solution. At the end of the experiment ($t=96$ h) for example, the dissolved PCB-126 concentration in the testing solution was about half that at $t=0$, but compares with the results calculated from the toximeters (see Table 1).

3.3. Results of field application experiments

3.3.1. dl-PCBs amounts extracted from the toximeters

Dioxin-like PCB activities associated with the deployed toximeters (pg-BEQ/toximeter) were quantified from the CALUX measurements, and found to be increasing with exposure time of the samplers at both sampling sites (Table 2).

3.3.2. Dissolved concentrations of dl-PCBs at both sampling sites

Time-weighted average (TWA) concentrations of the dissolved dl-PCBs in the wastewater at both sampling sites were calculated using Eq. (1) too. In this case all dl-PCBs should be considered hence C_w (pg-BEQ L^{-1}) is the total BEQ value of all dl-PCBs present in the sampled media. The sampling time period is also much longer than in the laboratory experiment (7, 14, 21 and 28 days) and D_e ($cm^2\ s^{-1}$) is now the average effective diffusion coefficient of all dl-PCBs and is calculated from D_w using Eq. (2). D_w is the key parameter and is always difficult to determine, since experimental measurements for aqueous diffusion coefficients are unavailable for many organic compounds, including dioxin-like PCBs, and conflicting data have been reported for others [26]. For this reason, two different methods have been used to calculate this parameter for the 12 dl-PCBs: (1) the model suggested by Gharagheizi [27] and (2) the empirical formula in Eq. (3) [28]. Results are shown in Table 3:

$$D_w = 0.00022 \times (\text{molecular weight})^{-2/3} \quad (3)$$

When applying the mean D_e predicted by the model of Gharagheizi [27] (see Table 3) to Eq. (1), the time-weighted average concentration (TWA) of dl-PCBs in the wastewater of the paper mill and Belbeis drainage canal was 7.1 and 9.5 pg-BEQ L^{-1}, respectively. Using the minimum and maximum D_e values calculated by this model, we obtain for the paper mill 7.3 and 6.8 pg-BEQ L^{-1}, and for the drainage canal 9.9 and 9.1 pg-BEQ L^{-1}, respectively.

Table 1
PCB-126 concentrations in solution, calculated from the amount accumulated by the toximeters (pg-BEQ/toximeter) after different periods of exposure using Eq. (1). All samples were analyzed in duplicate.

Sampling period (h)	12	24	48	96
Mean mass of PCB-126 on toximeter (pg-BEQ/toximeter) (SE)	35.9 (9.6)	42.2 (12.1)	55.2 (12.6)	110 (4)
Calculated PCB-126 in solution (μg L^{-1})	0.77	0.46	0.30	0.30

Table 2
CALUX-BEQ levels of dl-PCBs in the dissolved water phase, sediments and sludge of the paper mill wastewater effluents and drainage canal. At both study sites, two toximeters were removed each 7th day.

Sampling period (days)	Paper mill toximeters		Drainage canal toximeters	
	Total measured activity of dl-PCBs (pg-BEQ/toximeter) (SE)	dl-PCB activity, expressed per week (pg-BEQ/toximeter)	Total measured activity of dl-PCBs (pg-BEQ/toximeter) (SE)	dl-PCB activity, expressed per week (pg-BEQ/toximeter)
7	0.17 (0.01)	0.17 (0.04)	0.29 (0.04)	0.29 (0.04)
14	0.25 (0.02)	0.12 (0.06)	0.34 (0.11)	0.17 (0.06)
21	0.34 (0.02)	0.12 (0.01)	0.42 (0.02)	0.14 (0.01)
28	0.56 (0.08)	0.14 (0.05)	0.55 (0.19)	0.14 (0.05)
Sludge/sediment	Paper mill fibrous sludge **0.53 (SE=0.26)** pg-BEQ g^{-1} (dry weight)		Drainage canal bottom sediment **0.37 (SE=0.08)** pg-BEQ g^{-1} (dry weight)	

Table 3
Calculated diffusion coefficients in water (D_w) and effective diffusion coefficient in the porous ceramic membrane (D_e) for dioxin-like PCBs. M.wt. is molecular weight.

Congeners	M.wt.[a] (g/mol)	Diffusion coefficients[b] ($cm^2\ s^{-1}$)		Diffusion coefficients[c] ($cm^2\ s^{-1}$)		log K_{oc}[a]
		D_w	D_e	D_w	D_e	
Non-ortho						
PCB-77	292	5.0×10^{-6}	2.5×10^{-7}	6.1×10^{-6}	5.5×10^{-7}	5.0
PCB-81	292	5.0×10^{-6}	2.5×10^{-7}	6.1×10^{-6}	5.5×10^{-7}	5.8
PCB-126	326	4.6×10^{-6}	2.3×10^{-7}	5.9×10^{-6}	5.3×10^{-7}	6.2
PCB-169	361	4.3×10^{-6}	2.1×10^{-7}	5.8×10^{-6}	5.2×10^{-7}	6.6
Mono-ortho						
PCB-105	326	4.6×10^{-6}	2.3×10^{-7}	5.9×10^{-6}	5.3×10^{-7}	5.5
PCB-114	326	4.6×10^{-6}	2.3×10^{-7}	5.9×10^{-6}	5.3×10^{-7}	4.9
PCB-118	326	4.6×10^{-6}	2.3×10^{-7}	5.9×10^{-6}	5.3×10^{-7}	6.2
PCB-123	326	4.6×10^{-6}	2.3×10^{-7}	5.9×10^{-6}	5.3×10^{-7}	4.9
PCB-156	361	4.3×10^{-6}	2.1×10^{-7}	5.8×10^{-6}	5.2×10^{-7}	5.4
PCB-157	361	4.3×10^{-6}	2.1×10^{-7}	5.8×10^{-6}	5.2×10^{-7}	5.4
PCB-167	361	4.3×10^{-6}	2.1×10^{-7}	5.8×10^{-6}	5.2×10^{-7}	5.4
PCB-189	395	4.1×10^{-6}	2.0×10^{-7}	5.6×10^{-6}	5.1×10^{-7}	5.8
Mean		$\mathbf{4.6\times10^{-6}}$	$\mathbf{2.2\times10^{-7}}$	$\mathbf{5.9\times10^{-6}}$	$\mathbf{2.9\times10^{-7}}$	**5.6**

[a] Data from Mackay et al. [6].
[b] Based on Gharagheizi [27].
[c] Based on USEPA [28].

Using the mean D_e calculated from Eq. (3), the TWA of dl-PCBs in the paper mill and the drainage canal are 9.1 and 12.2 pg-BEQ L^{-1}, respectively. Applying minimum and maximum D_e calculated using this formula, the dl-PCBs in wastewater of the paper mill amount to 10.1 and 8.3 pg-BEQ L^{-1}, and in the drainage canal to 13.6 and 11.1 pg-BEQ L^{-1}, respectively.

There is little data about dissolved dioxin-like PCBs in aquatic environments, as most studies deal either with total, indicator, or selected PCBs. The dissolved dl-PCB concentrations found in our study fall in the range observed by Khim et al. [29] in Korean rivers (<0.01–238 pg TEQ L^{-1}) and by Chavis et al. [30] in the Yamuna River in India with a mean dl-PCB level of 221 pg TEQ L^{-1} (range: <1–1600 pg TEQ L^{-1}). Lower dissolved dl-PCB levels were observed in rivers in Japan ($n=17$, 2002–2004) and China ($n=5$, 2004–2005), with TEQ-concentrations ranging between 0.0021 and 0.096 pg TEQ L^{-1} and between $<$LOD and 0.0071 (mean 0.0025 pg TEQ L^{-1}), respectively [31,32].

In Egypt, samples taken from Lake El-Manzala on the Mediterranean Sea (mouth of Belbeis drain and some other canals) showed concentrations of 18–48 ng L^{-1} (Σ7 marker PCB congeners) in 1993 [33], between 20.3 and 50.2 ng L^{-1} (total marker PCB) in 2010–2011 [34] and between 1.4 and 17.9 ng L^{-1} (total marker PCB) in May–August 2011 (few months before our sampling campaign) [34,35]. Unfortunately, we cannot compare these to ours because no information about the congener profiles was provided.

3.3.3. dl-PCB concentrations in sludge and sediments at both sampling sites

Dioxin-like PCBs in the sludge and sediment samples in this study amounted to 0.5 and 0.4 pg-BEQ g^{-1} (dry weight) for the paper mill and the drainage canal, respectively. The activities of the toximeters in the drainage canal were quite similar to those in the paper mill wastewater while sediments were less polluted. The lower pollution of the drainage canal sediments can be caused by petrogenic hydrocarbons having a great affinity for PCBs and keeping them in solution. Monitoring records show values between 0.2 and 1.7 μg L^{-1} of petrogenic hydrocarbons along the drainage system in May and August 2011 [32,33] a few months earlier than our monitoring campaign.The continuous presence of these hydrocarbons in the system disturbs the normal sediment/water partitioning of the hydrophobic PCBs.

Compared to other international studies, dl-PCB levels in the sediment and sludge in our study were within the normal range. On the African continent, Nieuwoudt et al. [36] reported mean concentrations ranging between 0.04 and 4.4 pg TEQ g^{-1} dw ($n=11$, 2006, South-Africa), while El Kady et al. [37] found sediment dl-PCB concentrations of 0.19, 0.29 and 0.54 pg TEQ g^{-1} dw on three different sampling points in the Nile River in Greater Cairo ($n=36$, 2003–2004). A recent study in Uganda (2011) yielded slightly lower concentrations, with mean values between 0.02 and 0.21 pg TEQ g^{-1} dw in four different stations in Lake Victoria [38].

3.3.4. Distribution coefficients of dl-PCBs at both sampling sites

The sediment/water distribution coefficient of dl-PCBs in both sampling sites was calculated according to Eqs. (4) and (5) [39]:

$$K_{oc} = K_d / f_{oc} \quad (4)$$

$$K_d = C_s / C_w \quad (5)$$

where K_{oc} is the organic-carbon normalized partition coefficient (between the solid organic matter phase and the dissolved phase) for dl-PCBs (see Table 3), K_d is the distribution coefficient between the solid phase and the dissolved phase for dl-PCBs, f_{oc} is the measured mass fraction of organic carbon (OC) in the solid-phase, C_s is the measured concentration of dl-PCBs in dry sediment or sludge (pg-BEQ kg^{-1}), and C_w is the measured concentration of dl-PCBs in the dissolved phase (pg-BEQ L^{-1}). The measured organic carbon content (f_{oc}) was 32.5% and 0.18% for the paper mill fibrous sludge and drainage canal bottom sediment, respectively. Solving Eqs. (4) and (5), log K_d for the paper mill and the drainage canal were 1.9 and 1.6, respectively. log K_{oc} amounts to 2.4 and 4.3 for the paper mill and drainage canal, respectively.

3.3.5. Sampling rate of the ceramic toximeter

The sampling rate is the volume of water that can be extracted by the toximeter with regard to the target analytes within a certain period of exposure. The sampling rate R (mL day^{-1}) of the ceramic toximeter can be calculated from Eq. (6) [16].

$$R = AD_e/\Delta x \quad (6)$$

Using the mean D_w values from Gharagheizi model [27], and from Eq. (3) [28] (see Table 3), the sampling rate of the ceramic toximeter for the dissolved dl-PCBs in water amounts to 2.7 and 2.1 mL day^{-1}, respectively.

4. Conclusion

In this study, a combined time-integrated monitoring tool for the dioxin-like polychlorinated biphenyls (dl-PCBs) in aquatic environments was tested. The tool is a combination of a ceramic passive sampler (toximeter) and the CALUX bioassay technique. In the laboratory the linear relationship between mass of dl-PCB adsorbed on the activated carbon of the toximeter and exposure time, a basic characteristic of the toximeter, was verified. In addition, using Fick's law, the concentrations of the dl-PCB concentration in the bulk solution were calculated from the mass of dl-PCB measured on the activated carbon. The calculated results compared well with the concentrations directly measured in the bulk solution.

After these laboratory tests, field applications were carried out in two selected aquatic systems located in Egypt: the EMAK paper mill wastewater effluents, and the Belbeis drainage canal. To our knowledge, this was the first study in Africa monitoring dissolved dl-PCBs in aquatic environments. The results showed time-weighted average concentrations (TWA) of dl-PCBs ranging between 7.1 and 9.1 pg-BEQ L^{-1} in the paper mill wastewater, and 9.5 to 12.2 pg-BEQ L^{-1} for the water column of the drainage canal, (depending on the method used to estimate the aqueous diffusivity of dl-PCBs). Cellulosic sludge and bottom sediment from the sampling sites were analyzed using the CALUX bioassay, and the total dl-PCBs amounts to 0.5 and 0.4 pg-BEQ g^{-1} (dry-weight), for the mill and the canal, respectively. The organic-carbon normalized partition coefficient (log K_{oc}) for dl-PCBs in the mill and the canal was 2.4 and 4.3, respectively.

The field results obtained with our toximeters showed that for the determination of dissolved PCB concentrations in aquatic systems, it is no longer necessary to sample large water volumes, transport them to the laboratory where specific pre-concentration techniques should be applied before analysis. In situ pre-concentration by the toximeter avoids all those additional steps and reduces the risk of loss and contamination.

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