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Time-integrated Monitoring of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans (PCDD/Fs) in Urban and Industrial Wastewaters Using a Ceramic Toximeter and the CALUX Bioassay

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Abstract

The ceramic toximeter as a passive sampler in combination with the CALUX bioassay was utilized as a time-integrated pollution-assessment technique for dioxin-like PCDD/Fs in wastewaters. Toximeters filled with XCARB and enclosed in stainless steel cages were submerged in wastewater of Belbeis drainage-canal and EMAK paper-mill, located in Egypt, for 28 days. Two samplers were removed every week from each site. Extracts from toximeters, from bottom-sediments, and from paper-mill sludge were analyzed by the CALUX. Results showed a regular increase in the amounts of PCDD/Fs trapped by the toximeters as sampling time increased. Time-weighted average concentrations (TWA) of PCDD/Fs in the wastewaters of the drainage-canal and paper-mill were 231 (214–281) and 26 (24.1–32.6) pg-BEQ L⁻¹, respectively. Compared to literature data, this means a high pollution level for the drainage-canal water, while the pollution level in the paper-mill wastewater is similar to that reported for other paper mills. The PCDD/Fs levels in the drainage-canal bottom-sediments and in the paper-mill sludge were 8.3 and 14.6 pg-BEQ g⁻¹ dry-weight, at the lower end of internationally reported values in similar compartments. The sampling rate of the tested toximeters for dissolved PCDD/Fs was about 3.6 mL d⁻¹. Sediment/water partitioning coefficient $\log K_d$ of PCDD/Fs in the drainage-canal and the paper-mill was 1.42 and 2.70 respectively. The organic-carbon normalized partition coefficient $\log K_{oc}$ was 4.17 and 3.19 respectively, and is lower than the reported values for other sites.

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Keywords

Passive sampling; Ceramic toximeter; CALUX; PCDD/Fs; Wastewater monitoring; Partitioning coefficient

1. Introduction

A wide variety of synthetic chemicals are continuously released into the environment during production, usage, and disposal of products. Physicochemical properties of these man-made chemicals are wide-ranging, and so are their effects. Amongst them, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), pose significant threats to human health and the environment (Kassim and Barceló, 2009). They have been found in all compartments of the ecosystem, including water, although their aqueous solubility is very low (Van den Berg et al., 2006). In addition to their environmental hazards, PCDD/Fs accumulate in the fat tissue of animals and humans causing potent carcinogenic effects, endocrine-disruption, reproductive, developmental and neurotoxic effects (Wikoff et al., 2012). Monitoring the presence and quantity of these compounds in the environment on a regular basis is therefore not a question of choice, but merely a necessary action for better health protection (Seethapathy et al., 2008).

Passive sampling techniques are gaining an increasing interest in pollution assessment in several environmental compartments. A passive sampler is able to acquire a sample without any active media transport induced by pumping or purging techniques. Based on transport process differences through the housing and the receiving phases, two types of passive samplers can be classified: (1) equilibrium and (2) non-equilibrium based passive samplers (Kot-Wasik et al., 2007). Equilibrium samplers are characterized by a rapid achievement of equilibrium state between contaminants in the water to be sampled and contaminants inside the passive sampler. One consequence of achieving the equilibrium rapidly is that contaminants are also capable of diffusing back into the surrounding water when the aqueous concentrations of contaminants decline. Non-equilibrium samplers are those that do not reach equilibrium with the surrounding water within the sampling period. These samplers are characterized by a high capacity for collecting the contaminants of interest, which in turn ensures that contaminants can be enriched continuously throughout the sampling period (Kot-Wasik et al., 2007). The ceramic toximeter belongs to the latter ones and is the subject of this research.

The ceramic toximeters are based on the free flow of analyte molecules, from the sampled medium through a ceramic diffusion membrane, towards a suitable receiving medium under the effect of a chemical-potential difference (Weiß et al., 2007). This flow of analyte(s) continues until equilibrium is established in the system or until the desired sampling period is reached. The receiving phase should be selectively chosen depending on the analytes of interest. It must act as a perfect sink, which means that it must not release the trapped molecules even if the concentration of the analytes around the sampler decreased to zero (Weiß et al., 2007). The scientific validity and cost effectiveness of using this technique for volatile organic compounds (VOCs) in water had been previously documented (Bopp et al., 2005; Verreydt et al., 2010). In a recent laboratory study, we validated the use of this

sampler for dioxin-contaminated water (Addeck et al., 2012). While the relatively low sampling rate necessitates long sampling times when the concentrations are low, it does enable in a simple way (only one analysis is necessary) the assessment of TWA concentrations over long periods (Weiß et al., 2007).

We have used the CALUX (Chemically Activated LUCiferase gene eXpression) bioassay for determining the PCDD/Fs levels trapped in the toxiometers as well as their levels in the sediments and sludge collected from the sampling sites. The CALUX technique makes use of a reporter gene expressed by recombinant mammalian cells. The genetically-modified cells used contain a stably transfected AhR-responsive firefly luciferase reporter gene, which responds to dioxin-like chemicals by the induction of luciferase in a time-, dose-, and AhR-dependent manner (He et al., 2011). The CALUX signal (gene-induced light intensity) is quantified through a BEQ-value; a Biochemical Equivalent expressed relative to the most toxic dioxin congener 2,3,7,8-TCDD. The advantage of CALUX is to assess directly the PCDD/Fs level present in the sample in “Toxic Equivalent Quantity” without going through calculations based on analysis of complex chemical and toxic equivalency factors (Campbell et al., 2006).

The ceramic toxiometer in combination with the CALUX bioassay was previously validated as an analytical tool for the determination of PCDD/Fs in solution (Addeck et al., 2012). However, concentrations of dissolved PCDD/Fs in real aquatic systems are very low which makes their in situ determination a real challenge. Hence, the first goal of this research was to apply the passive sampler in aquatic systems that could be contaminated by PCDD/Fs and to determine their concentrations: for that purpose a drainage-canal system and a paper mill effluent, both impacted by industrial and municipal activities (see sampling sites here below) were selected. In addition, the amount of PCDD/Fs accumulated by the passive sampler should increase linearly with the period of exposure. This has been verified too.

2. Materials and Methods

2.1. Sampling Sites

2.1.1. Drainage-canal system—Sampling was carried out during October 2011 at a selected point in Belbeis drainage-canal (N: 30° 26' 25.88", E: 31° 34' 23.16"), east side of the Nile delta, (Egypt). The surrounding area consists of cultivated and inhabited land (Fig. 1). The canal is frequently used to convey raw industrial and municipal wastewater. The entire system is heavily polluted, mainly by sewage. The drainage system and its mouth at Lake El-Manzala are identified as “black spots” starting from 1992 (DRI, 2005) and are still representing a big environmental challenge. During the sampling period, water temperature ranged between 23 – 25 °C. The water-stream flows at 1.7 km/h at the sampling point, the basin depth was about 2 m and its surface width is about 35 m. The color of the water was black and its bad smell likely drives from its very high concentration of sulfides (23.5 mg L⁻¹) (EAA, 2011). Illegal burning of rice-straw was observed nearby the drainage-canal shores and in surrounding farms. This act is a major source of air and water pollution in the area (MSEA, 2011).

2.1.2. Paper-mill effluents—Sampling in effluents of the EMAK paper-mill (N: 29°41'50.12", E: 32°18'13.30"), Ain El-Soukhna, Egypt, was carried out during October 2011. The mill produces 60,000 tons/year of double-coated duplex paper board. About 95% of the raw materials in production consists of recycled paper of all kinds, while the remaining percentage is new pulp from other suppliers. The toximeters were tested at two points inside the factory: (1) Main collecting pool: contains water mixed with fine fibers produced from the milling process. (2) Biologically-treated wastewater pathway. Water temperature ranged between 24–26 °C during the sampling period.

2.2. Chemicals and materials

The ceramic cylinders were obtained from ATECH Innovations (Germany). Acetone (Pestis grade, minimum 99.9%), hexane (for dioxins and PCBs, minimum 96%) and toluene (for dioxins and PCBs, minimum 99.8%) were from Biosolve (The Netherlands). The XCARB (activated carbon/celite 1% w/w) was from Xenobiotic Detection Systems (USA). Neutral alumina (activated, 150 mesh), silver nitrate (5 wt % on silica gel 60), ethyl acetate pestanal and silica gel 60 were from Sigma–Aldrich (Germany). Sulfuric acid (95–97%, ACS reagent), DMSO and glass-wool were obtained from Merck (Germany). Anhydrous sodium sulfate was from Boom (The Netherlands). Glass-fiber filters for ASE were from Whatman (UK). Standard solution of 2,3,7,8 TCDD (50 ng ml⁻¹) was from Campro Scientific (The Netherlands). The mouse hepatoma H1L7.5c1 cell line was provided by Michael Denison (University of California, USA).

2.3. Conditioning of materials

The ceramic cylinders were sintered at 750 °C for 24 hours to eliminate possible organic traces. Glassware was baked for 4 hours at 450 °C. XCARB and glass-wool were conditioned by fluxing in toluene in an ultrasonic bath for 1 hour. Toluene was decanted and the materials were rinsed twice with fresh amounts of toluene before drying. Silica gel was baked at 200 °C for 48 h. PTFE caps and stainless steel cages were rinsed with acetone and deionized water.

2.4. Sampling kits and exposure scenario

A total number of 18 toximeters were used to sample PCDD/Fs for a total period of 28 days. Weekly, 2 toximeters (for duplicate samples) were removed from each sampling site to test the linearity between the exposure period and the mass of trapped PCDD/Fs. Each toximeter consists of a ceramic cylinder of alumina (α -Al₂O₃) lined with a 5 µm coating of titania (TiO₂). The cylinders were 8 cm length (only 7 cm are exposed for diffusion), 0.2 cm wall thickness, 1 cm external diameter, and 30% porosity. The mean pore diameter of the alumina membrane was 0.4 µm and that of the titania coating was 0.05 µm. The titania coating serves as a diffusion barrier limiting the movement of analytes to molecular diffusion only (Fig. 2) (Addeck et al., 2012). The pore diameter was small enough to prevent crossing or growth of microorganisms, as the most dominant bacteria in water systems are 0.5–5.0 µm (Sigeo, 2005). A mass of 1.15 g of pre-conditioned XCARB was packed in each cylinder and small plugs of pre-cleaned glass-wool were inserted in both ends. PTFE caps tightly closed both ends of the cylinders. Toximeters were kept in light-shielded glass bottles

filled with Milli-Q deionized water till the time of deployment. The bottles were vacuumed to ensure full saturation of toximeters with water. Cages of stainless-steel grids were used to enclose and protect the fragile samplers (4 samplers/cage) (Fig. 2). The cages' grid reduces accumulation of the suspended particles on samplers' surface. Cages were loaded with toximeters just before application, and suspended in the water column in both sites. Bottom-sediments and fibrous sludge were collected from the drainage-canal and the paper-mill at the end of sampling period. Sediments, sludge and toximeters were light-shielded and preserved at -20 °C till the time of extraction. Two full toximeters were kept in deionized water as blanks.

2.5. Extraction of toximeters, sediments, and sludge

The toximeters were rinsed with deionized water and left to dry. Caps were removed and the XCARB was ejected into glass vials. Toluene was used as extraction solvent as it gives the highest recovery rates for PCDD/Fs from XCARB (XDS, 2008). First, 15 mL of toluene was added to the vials. Then, the samples were ultrasonicated, centrifuged to settle down the suspended particles, and the liquid phase was pipetted 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 (Addeck et al., 2012). The drainage-canal sediments and paper-mill sludge were freeze-dried in a lyophilizer. They were homogenized with a pestle and mortar. Liquid nitrogen was added during paper-mill sludge processing 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 sediments and sludge were extracted using pressurized liquid extraction (ASE 200, Dionex Sunnyvale, CA, USA) equipped with 33 mL stainless steel extraction cells. A mixture of hexane/acetone (1/1, v/v) was used as an extraction solvent because it gave reliable results compared to other solvents for fish, meat, atmospheric deposition and biological samples (Croes et al., 2011). The extraction conditions were 125 °C, 2 cycle extraction, 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 of hexane.

2.6. Clean-up of extracts

All extracts from toximeters, sediments, and sludge were pretreated by adding 4 mL sulfuric acid. The clean-up took place through a multi-layer silica gel column coupled in series with a carbon column to separate PCDD/Fs from dioxin-like PCBs and other compounds that might interfere during the CALUX bioassay analysis. The silica gel column (25 mL) was filled from bottom to top with a glass-wool plug, 1.9 g sodium sulfate, 2.0 g deactivated neutral alumina, 3.0 g of a 33% (w/w) sulfuric acid on silica gel mixture, 1.0 g silver nitrate (5 wt% on silica gel 60), 2.8 g of a 33% (w/w) sulfuric acid on silica gel mixture, and 1.9 g sodium sulfate. The carbon column (10 mL) was filled from bottom to top with a glass-wool plug, 0.7 g sodium sulfate, 0.34 g XCARB, and 0.7 g sodium sulfate (Figure 3). Before loading the samples, the acid silica columns were rinsed with 60 mL hexane, and the carbon columns were rinsed with 5 mL acetone, 20 mL toluene, and 10 mL hexane (Croes et al., 2011). After adding the samples, the columns were rinsed with 45 mL hexane, and then the silica columns were removed. The carbon columns were first rinsed with 8 mL hexane/acetone (9/1) and the coplanar PCBs were eluted with 15 mL hexane/ethyl acetate/toluene

(80/10/10). Finally, the PCDD/Fs were eluted with 20 mL toluene, centrifuged under vacuum (40 °C) till dryness, and dissolved in 4 mL hexane. A dilution series was made for each sample prior to the CALUX analysis. A schematic overview of the sampling strategy, extraction, clean up, fractionation and final measurements is given in Figure 3.

2.7. The CALUX bioassay

The CALUX bioassay was performed using the sensitive mouse hepatoma H1L7.5c1 cell line. The applied protocol was previously described by Van Langenhove et al., (2011) and is based on U.S. EPA method 4435 (XDS, 2008). Briefly, the cells were grown in cell culture plates containing 15 mL RPMI 1640 supplemented with 8% FCS and 1% penicillin/streptomycin (Gibco, UK). After trypsinizing, the cells were counted and diluted to a concentration of $55\text{--}65 \times 10^4$ cells mL⁻¹ (Croes et al., 2011). Each well on the 96-well plate was seeded with 200 µL cell suspension in RPMI. After 24 h incubation at 37 °C with 5% CO₂ and 80% humidity, 188 µL of a standard solution or sample extract in RPMI with 1% DMSO was added to each well. After 20-24 h incubation period, the medium was removed and the wells were rinsed with 75 µL PBS buffer (Gibco, UK). Then the plate was visually inspected under the microscope for any significant defects in cell morphology. 50 µL lysis reagent (Promega, USA) was added and the plate was shaken for 5 min. After a 10 min incubation period in the luminometer (Glomax, Promega, USA), 50 µL luciferine reagent (Promega, USA) was injected into all wells (integration time 3 s, lag time 5.6 s) The measured luminescence was expressed in relative light units (RLU) which were later converted into bioanalytical equivalency value (CALUX-BEQ) by comparing the response of a given sample to a dose-response curve obtained from 2,3,7,8-TCDD standards (Croes et al., 2011). Results from CALUX are expressed in pg-BEQ L⁻¹ while the GC-HRMS literature data (to compare with) are presented as toxic equivalency values (TEQs) and expressed in pg-TEQ L⁻¹.

2.8. Total organic carbon (TOC) content in sediments and sludge

The total organic carbon (TOC) content in bottom-sediments and fibrous sludge samples was measured so that the organic-carbon normalized partition coefficient for PCDD/Fs in both aquatic environments could be calculated. TOC measurements were carried out with a CHN elemental analyzer (Flash 1112 EA Elemental Analyser, Thermo Finnigan, Italy). The organic matter in the dry homogenized samples was quantitatively converted to CO₂, N₂, SO₂, and H₂O by high temperature oxidative combustion at >900°C in an O₂ atmosphere, after 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. TOC quantification was performed by comparing the CO₂ signal with that of an aniline standard.

2.9 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) (Croes, 2012).

Also two 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 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 (Elskens et al., 2011). The mean EC50 value (n=6) yielded 565 pg per well (SE=46 pg per well). The minimum detectable value was 0.046 pg BEQ per well. All quality control solutions and the toximeter blanks yielded recoveries between 80-120%, while the DMSO blanks were at background level (lower plateau of the calibration curve).

3.2. Quantification of extracted PCDD/Fs

The amounts of accumulated PCDD/Fs were found to increase in toximeters with increasing sampling time (Table 1). This increase was linear except for the results obtained during the 4th week with the drainage-canal samplers (Fig. 4 and Eq. 1 and 2).

$$\text{Drainage-canal: } y=0.092x(R^2=0.97) \quad (\text{Eq. 1})$$

$$\text{Paper mill factory:(week1to3): } y=0.936x(R^2=0.996) \quad (\text{Eq. 2})$$

With y =total mass accumulated on the taximeter (pg BEQ/taximeter) and x = exposure time (days)

The lower amount of PCDD/Fs observed in the drainage-canal water during the last week compared to the previous weeks can be due to several causes. The first possibility is that the XCARB (the receiving medium), has become saturated. However, the adsorption capacity of the XCARB towards dioxins is at least 400 times higher than the highest extracted amount per toximeter (capacity is $> 0.1 \mu\text{g-TEQ PCDD/Fs g}^{-1}$) (Chi et al., 2006). Even if other organic pollutants may also be adsorbed to the XCARB, its adsorption capacity is very high and seems to be sufficient. The second possibility is a sudden change in the levels of dissolved chemicals in the drainage-canal water. This could be due to an irregular and momentary discharge of some specific waste from -for example- a gas station close to the sampling area. Wastes from the latter normally contain a variety of petrogenic hydrocarbons that may disturb the water/sediment equilibrium by affecting the distribution ratio of hydrophobic chemicals in the system. Monitoring records show values between 0.2 and $1.7 \mu\text{g L}^{-1}$ of petrogenic hydrocarbons along the drainage system in May and August 2011 (EAA, 2011). The third possibility is a reduction in the adsorption rate of PCDD/Fs onto the XCARB, due to competitive binding in the drainage-canal water by -for example- active-carbon resulting from rice-straw burning alongside the drainage-canal shores which is common during this period of the year.

Overall, the results obtained after one, two and three weeks showed a linear increase in the amount adsorbed by the toximeters and allowed a correct estimate of the PCDD/Fs levels in the drainage-canal water over that period. During the fourth week the adsorption rate in the toximeters decreased for an unknown reason as described above. This observation might be a useful indicator on some momentary events that could be over- or underestimated by the conventional snapshot sampling technique. The effect of environmental conditions, like temperature, was considered insignificant as it had changed only slightly during the sampling period. A temperature increase of 1 °C corresponds to an increase in the diffusion coefficients (D_w) of about 3-4% (Weiß et al., 2007).

3.3. Calculation of the time-weighted average concentration (TWA) of PCDD/Fs (pg-BEQ L⁻¹)

The CALUX analysis yielded the mass M (pg) of PCDD/Fs that passed through the available surface area A (21.98 cm²) of the ceramic membrane over the sampling period t (7, 14, 21 and 28 days) and trapped by XCARB (Table 1). Assuming that the transport of the PCDD/Fs to the inner part of the ceramic membrane through the diffusion path x (0.2 cm) was based solely on molecular diffusion, the time-weighted average concentration of these chemicals in the sampled medium C_w (pg-BEQ L⁻¹) can be derived from Eq. (3), in this case, calibration and frequent snapshots are not necessary (Weiß et al., 2007):

$$C_w = M \Delta x / A t D_e \quad (\text{Eq. 3})$$

Where D_e (cm² s⁻¹), the effective diffusion coefficient, refers to the alteration in the diffusion rate of analytes (PCDD/Fs) in the porous ceramic membrane compared to that of water. It can be calculated from Archie's law Eq. (4) (Weiß et al., 2007):

$$D_e = D_w \varepsilon^m \quad (\text{Eq. 4})$$

Where D_w (cm² s⁻¹) is the diffusion coefficient of PCDD/Fs in water, ε is the porosity of the ceramic membrane (30%), and m is Archie's law exponent, which ranges between 1.5 to 2.5 in laboratory calibration experiments (Weiß et al., 2007). A value of 2.0 was previously determined and used in field applications with ceramic-based passive samplers (Bopp et al., 2005; Martin et al., 2003). Since there are no direct measurements for aqueous diffusivity of PCDD/Fs, we have used an empirical formula Eq. (5) (U.S. EPA, 1987) to calculate the diffusion coefficient in water D_w for all PCDD/F congeners classified by the World Health Organization (WHO) for their dioxin-like toxicity.

$$D_w = 0.00022 \times Mwt^{-2/3} \quad (\text{Eq. 5})$$

Where Mwt (g/mol) is the analyte's molecular weight. Results are shown in annex. The average value for D_e is 3.79×10^{-7} cm² s⁻¹ with a minimum of 3.32×10^{-7} cm² s⁻¹ and a maximum of 4.36×10^{-7} cm² s⁻¹.

By applying all parameters to Eq. (3) and using the mean D_e value, the mean concentrations of PCDD/Fs in water during the sampling period (TWA) of Belbeis drainage-canal and EMAK paper-mill were 231 and 26 pg-BEQ L⁻¹, respectively. Using the minimum and maximum D_e values, we obtain for the drainage-canal concentrations of 214 and 281 pg-BEQ L⁻¹ and for the paper-mill 24.1 and 32.6 pg-BEQ L⁻¹. Since on the international level no concentration limits for PCDD/Fs in aquatic systems were established, we compared our results with those from other studies.

In Newark Bay (New Jersey, USA), dissolved PCDD/Fs concentrations 20 pg-TEQ L⁻¹ were recently observed using polyethylene (PE) passive samplers (Friedman et al., 2012). An earlier study on PCDD/Fs in UK rivers revealed a concentration of 80 pg-TEQ L⁻¹ (Rose et al., 1994). Water samples taken after the 2002 flood in the Elbe River showed PCDD/F levels from 0.1 to 14.7 pg-TEQ L⁻¹ in the Czech Republic (Holoubek et al., 2003) and from 4.4 to 15.5 pg-TEQ L⁻¹ (Wittenberg) and 37.0 to 85.9 pg-TEQ L⁻¹ (Magdeburg) in Germany (Theile et al., 2003). Comparing our PCDD/Fs levels in the Belbeis drainage-canal with those from literature, we must conclude that the canal is heavily polluted with PCDD/Fs.

Regarding PCDD/Fs levels in the wastewater from paper-mills, in Sweden, concentrations between 0.11 and 133 pg-TEQ L⁻¹ with a mean value of 19.1 pg-TEQ L⁻¹ were reported (Buckley-Golder et al., 1999). In China, a study on PCDD/Fs levels in wastewater from a large pulp-mill, showed an average concentration of 315.6 pg-TEQ L⁻¹ (Zheng et al., 2001). The PCDD/Fs levels in the industrial water of the EMAK paper-mill are in accordance with those literature values. The toximeters from the biologically-treated wastewater of EMAK paper-mill did not show a decrease in PCDD/Fs content (data not shown). This was expected because the applied biological treatment process is not basically meant to remove this kind of chemicals.

3.4. Sediments and sludge

CALUX analyses of the bottom-sediments and fibrous sludge yielded PCDD/Fs contents of 8.3 and 14.6 pg-BEQ g⁻¹ dry-weight, respectively. For comparison, the levels of PCDD/Fs in the sediments from 3 industrial areas in Cairo, Egypt, were between 1.8 and 38 pg-TEQ g⁻¹ d.w. (El-Kady et al., 2007). In 2001, PCDD/Fs levels of 1.64 and 1.83 pg-TEQ g⁻¹ d.w., were reported for two regions with industrial sites (Zlín and Beroun) in Czech Republic (E.C., 2004). In the Netherlands, sediments of rivers, lakes, and canals showed PCDD/Fs levels between 1 and 10 pg-TEQ g⁻¹ d.w. (Buckley-Golder et al., 1999). In Belgium, CALUX measurements of PCDD/Fs in sediments of the Yser and the Scheldt Rivers showed values between 10 and 42 pg-BEQ g⁻¹ d.w. (Sanctorum et al., 2007). In general, the typical PCDD/Fs contamination levels of the sediments in the EU member states range from < 1 up to 200 pg-TEQ g⁻¹ d.w. (Buckley-Golder et al., 1999). When comparing these values with the measured PCDD/Fs levels in the Belbeis drainage-canal sediments and EMAK paper-mill sludge, it appears that they are within the typical European levels.

The relatively low PCDD/Fs content in the drainage-canal bottom-sediments compared to their dissolved levels in water column, and to other much less contaminated sites might be attributed to the high content of petrogenic hydrocarbons in the drainage-canal water. The latter compete with the sediments and especially its organic fraction for the PCDD/Fs

present in the system and thus affect their sediment/water partition ratio. The hydrocarbon levels varied from 0.53 to 1.74 $\mu\text{g L}^{-1}$ in May 2011 and 0.20 to 1.24 $\mu\text{g L}^{-1}$ in August 2011, along the drain-mouth, Lake El-Manzala (EAA, 2011).

3.5. Distribution coefficients in the two sampling environments

The sediments/water partitioning (or distribution) coefficient of PCDD/Fs in both sampling sites (a site-specific parameter) was calculated according to Eq. (6) (Suarez et al., 2006):

$$K_{oc} = K_d / f_{oc}; K_d = C_s / C_w \quad (\text{Eq. 6})$$

Where: K_{oc} : organic-carbon normalized partition coefficient (between the solid organic matter phase and the dissolved phase) for PCDD/Fs congeners (annex), K_d : distribution coefficient between the solid phase and the dissolved phase for PCDD/Fs, f_{oc} : measured mass fraction of organic carbon (TOC) in the solid-phase, C_s : measured concentration of PCDD/Fs in dry solid-phase sediments or sludge (pg-BEQ g^{-1}), and C_w : measured concentration of PCDD/Fs in the dissolved phase (pg-BEQ L^{-1}).

Solving Eq. (6), $\log K_d$ amounts to 1.42 and 2.70 for the drainage-canal and paper-mill wastewater, respectively, while using the measured TOC content in bottom-sediments (canal) of 0.18 % and in sludge (paper-mill) of 32.5 %, $\log K_{oc}$ amounts to 4.17 and 3.19, respectively. The value of $\log K_{oc}$ in the drainage-canal is much lower than the values reported for PCDD/Fs congeners in other aqueous environments (annex). This might be attributed to a disturbed sediments/water partitioning due to the reported presence of petrogenic hydrocarbons in the canal water (EAA, 2011).

3.6. Sampling rates of the ceramic toximeter for freely-dissolved PCDD/Fs

The sampling rate describes the volume of water that is extracted with regard to the chemicals of concern within a certain period of time. In the case of a ceramic membrane, sampling rates are defined according to Eq. (7) (Weiß et al., 2007):

$$R = AD_e / \Delta x \quad (\text{Eq. 7})$$

Applying the calculated mean value of D_e for dioxin-like PCDD/Fs, the sampling rate of the ceramic toximeters for PCDD/Fs is about 3.6 mL d^{-1} . The low sampling rates of ceramic toximeters emphasize their suitability for long-term, time-integrated monitoring. The downside of the low sampling rate is that extended time periods are required to reach the detection limits of the analytical technique, especially in low contaminated environments.

4. Conclusion

In this study, we have applied the ceramic toximeter combined with the CALUX bioassay technique to measure time-weighted average concentration (TWA) (pg-BEQ L^{-1}) of PCDD/Fs in urban and industrial wastewaters. The idea is based on accumulating chemicals of interest (PCDD/Fs) using a suitable receiving phase (XCARB) that maintains a concentration gradient across the diffusion membrane (ceramic). The amounts of

accumulated PCDD/Fs extracted from toximeters were measured by the CALUX semi-quantitative technique.

Results from the Belbeis drainage-canal and the EMAK paper-mill, Egypt, showed a linear intake of dioxin-like PCDD/Fs with time, with an unexplained decrease during the fourth week for the drainage-canal samplers. The average (minimum-maximum) PCDD/Fs levels in both sampling sites during the sampling period (28 days) were 231 (214-281) and 26 (24.1-32.6) pg-BEQ L⁻¹, respectively. The levels of PCDD/Fs observed in the drainage-canal bottom-sediments and the paper-mill fibrous sludge were 8.3 and 14.6 pg-BEQ g⁻¹ dry-weight, respectively. Comparison with data available for other sites was made. It appears that the drainage-canal water is heavily polluted with PCDD/Fs while the paper-mill wastewater is within the reported values for this kind of industry. The low levels of PCDD/Fs in the canal bottom sediments might be attributed to the reported high content of petrogenic hydrocarbons in the canal water, which compete with the sediments for dioxins. Sediment/water partitioning coefficient $\log K_d$ of PCDD/Fs in the canal and the paper-mill was 1.42 and 2.70 respectively. The $\log K_{oc}$ was 4.17 and 3.19, respectively, and lower than previously reported values for other sites.

The sampling rate of the ceramic toximeters for PCDD/Fs was found to be 3.6 mL d⁻¹, which is low compared to other passive samplers. The low sampling rate might also be considered an advantage as it enables long-term and time-integrated pollution assessment for such POPs in aqueous environments, making it a relatively inexpensive method to routinely study the levels, behavior, and fate of these pollutants in aqueous systems.

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Annex

Calculated diffusion coefficients in water (D_w) and effective diffusion coefficient in ceramic membrane (D_e) for dioxin-like PCDD/Fs. *Molecular weight and log K_{oc} data from (Mackay et al., 2006).*

Congeners	Mwt (g/mol)	D_w (cm ² s ⁻¹)	D_e (cm ² s ⁻¹)	$\log K_{oc}$
<i>Dibenzo-p-dioxins</i>				
2,3,7,8-TCDD	321.97	4.68×10 ⁻⁶	4.21×10 ⁻⁷	6.30
1,2,3,7,8-PnCDD	356.42	4.38×10 ⁻⁶	3.94×10 ⁻⁷	8.72
1,2,3,4,7,8-HxCDD	390.86	4.12×10 ⁻⁶	3.70×10 ⁻⁷	6.02
1,2,3,6,7,8-HxCDD	390.86	4.12×10 ⁻⁶	3.70×10 ⁻⁷	9.42
1,2,3,7,8,9-HxCDD	390.86	4.12×10 ⁻⁶	3.70×10 ⁻⁷	9.45
1,2,3,4,6,7,8-HpCDD	425.31	3.89×10 ⁻⁶	3.50×10 ⁻⁷	6.69
OCDD	459.75	3.69×10 ⁻⁶	3.32×10 ⁻⁷	10.96

Congeners	Mwt (g/mol)	D_w (cm ² s ⁻¹)	D_e (cm ² s ⁻¹)	$\log K_{oc}$
<i>Dibenzofurans</i>				
2,3,7,8-TCDF	305.98	4.85×10^{-6}	4.36×10^{-7}	5.18
1,2,3,7,8-PnCDF	340.42	4.51×10^{-6}	4.06×10^{-7}	8.03
2,3,4,7,8-PnCDF	340.42	4.51×10^{-6}	4.06×10^{-7}	5.59
1,2,3,4,7,8-HxCDF	374.86	4.23×10^{-6}	3.81×10^{-7}	7.40
1,2,3,6,7,8-HxCDF	374.86	4.23×10^{-6}	3.81×10^{-7}	7.40
1,2,3,7,8,9-HxCDF	374.86	4.23×10^{-6}	3.81×10^{-7}	9.08
2,3,4,6,7,8-HxCDF	374.86	4.23×10^{-6}	3.81×10^{-7}	6.80
1,2,3,4,6,7,8-HpCDF	409.31	3.99×10^{-6}	3.59×10^{-7}	6.00
1,2,3,4,7,8,9-HpCDF	409.31	3.99×10^{-6}	3.59×10^{-7}	5.00
OCDF	443.75	3.78×10^{-6}	3.40×10^{-7}	6.00
Mean D_w, D_e (cm² s⁻¹) and $\log K_{oc}$		4.21×10^{-6}	3.79×10^{-7}	7.29

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Highlights

Ceramic toxiometers were used as passive samplers for PCDD/Fs in wastewater.

Activated carbon/celite 1% (w/w) was chosen as a receiving phase to trap PCDD/Fs.

Urban and industrial wastewaters in two sites located in Egypt were tested.

CALUX bioassay was utilized as an analytical technique for extracted PCDD/Fs.

Results were compared to literature data from other sites worldwide.

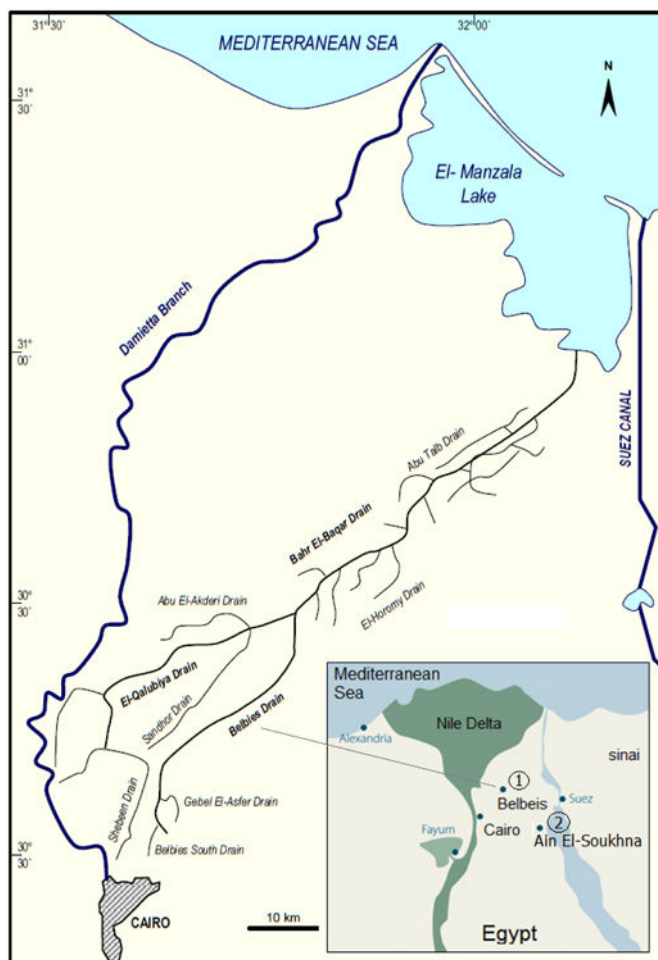


Fig. 1.
Sampling sites: (1) Belbeis drainage-canal and (2) EMAK paper-mill.

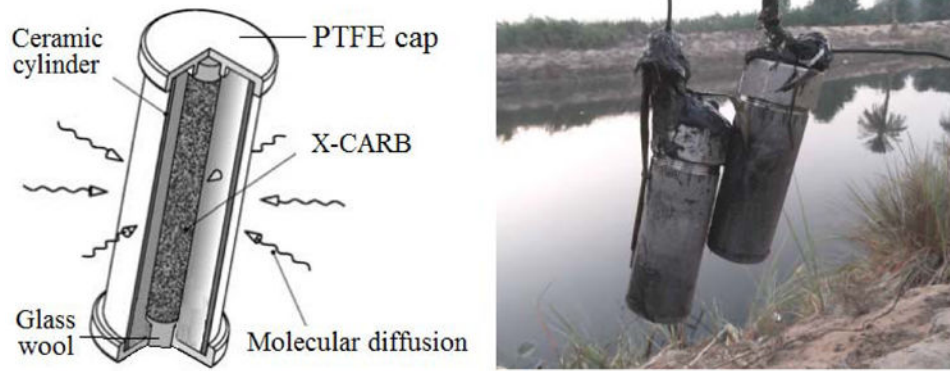


Fig. 2. A linear section of the ceramic toximeter and two stainless steel cages immersed in the drainage-canal water for a duration of 1 week.

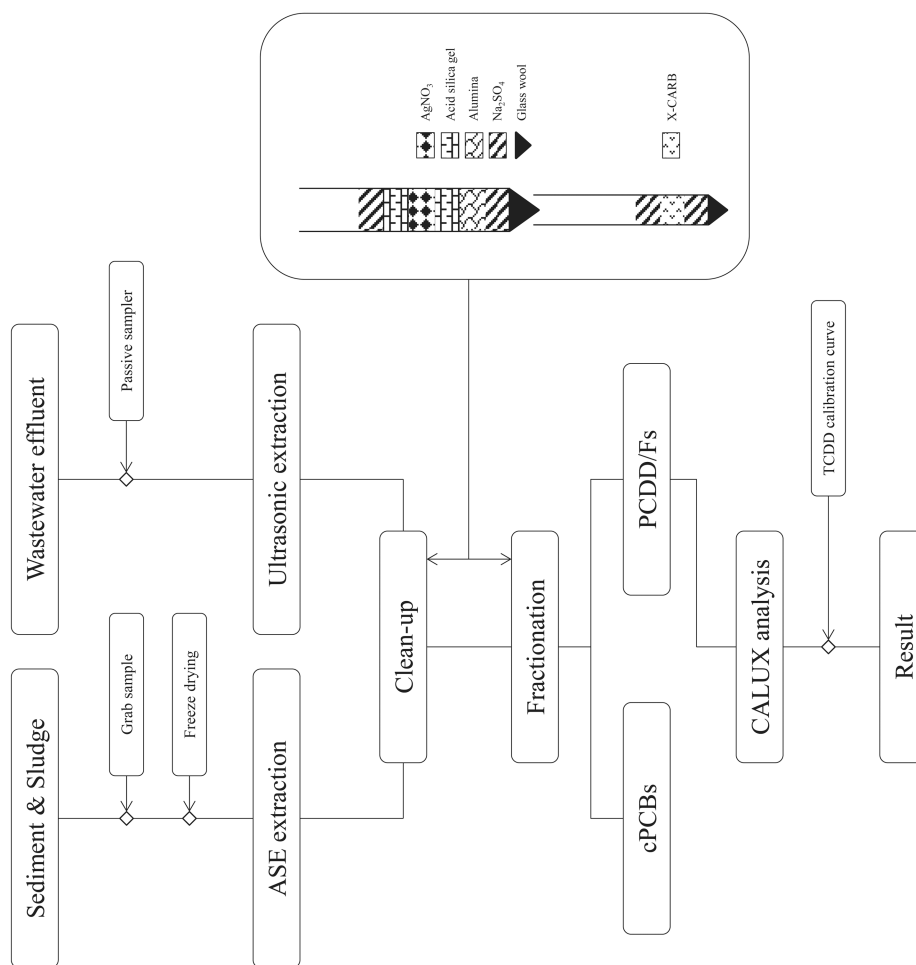


Fig. 3. Sample processing diagram for CALUX analysis.

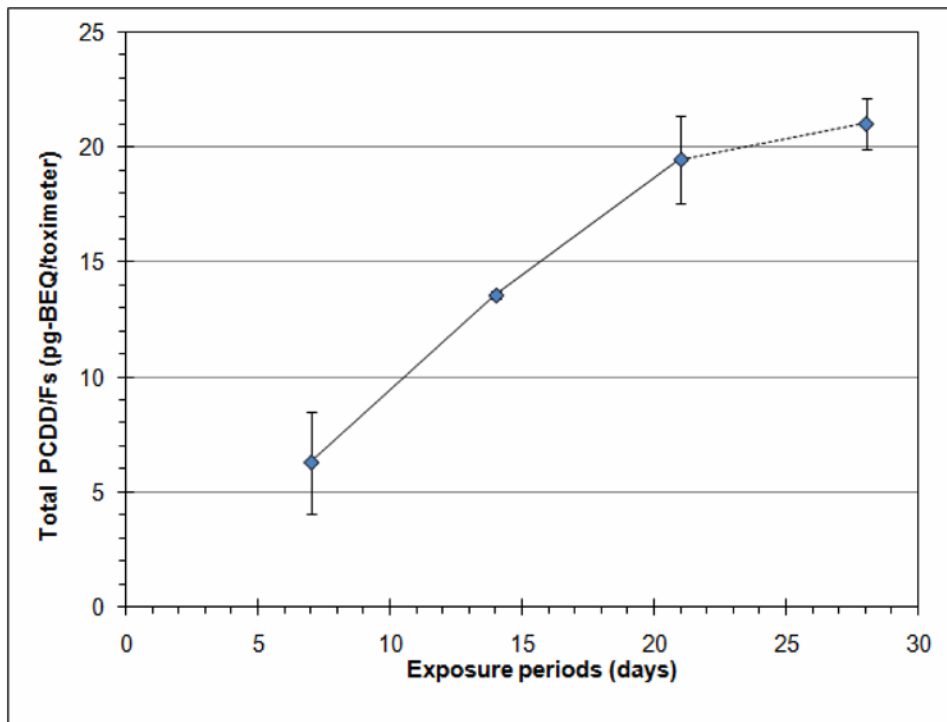


Fig. 4. Increase in accumulated PCDD/Fs with sampling duration (drainage-canal samplers). Each data point is the mean value of duplicate samples.

Table 1

Mass (*M*) of extracted PCDD/Fs from toximeters and CALUX-BEQs for the sediments and sludge samples. Two toximeters were analyzed at each time period (7 days) for both the Belbeis drainage-canal and EMAK paper mill, except for the first time-period at the paper-mill (only one sample could be analyzed):

Time (days)	Drainage toximeters		Paper-mill toximeters	
	M Total PCDD/Fs (pg-BEQ/toximeter) (SE)	Total PCDD/Fs pr week (pg-BEQ/toximeter) (SE)	M Total PCDD/Fs (pg-BEQ/toximeter) (SE)	PCDD/Fs per week (pg-BEQ/toximeter) (SE)
7	6.28 (2.21)	6.28 (2.21)	0.83	0.83
14	13.6 (0.62)	7.27 (0.31)	1.37 (0.001)	0.54 (0.001)
21	19.5 (1.93)	5.91 (0.64)	1.96 (0.04)	0.59 (0.01)
28	21.0 (1.11)	1.55 (0.28)	2.51 (0.05)	0.55 (0.01)
Sediments/sludge	Drainage-canal bottom sediments 8.3 (SE=1.2) pg-BEQ/g dry weight		Paper-mill fibrous sludge 14.6 (SE=2.1) pg-BEQ/g dry weight	