Quantification of dioxin in the sieved fraction of river sediment

H. Ozaki*, S. Taniguchi**, R. Takanami*, N. Shimomukai*, T. Hamasaki***, M. Sugahara*** and R.R. Giri**

*Department of Civil Engineering, Osaka Sangyo University, Japan

**New Industrial Research and Development Centre, Osaka Sangyo University, Japan

***Department of Cultural Environment, Osaka Sangyo University, Japan

Abstract Dioxin pollution of aquatic sediments has been one of the important environmental problems in Japan. Grain size distribution and organic constituents may play important roles in dioxins contents in sediments, which have not been well investigated. This paper aims to quantify dioxins (PCDDs/Fs and co-PCBs) in sieved surface sediment fractions obtained from Kizu and Sumiyoshi Rivers in Osaka, Japan. The samples were prepared and analyzed following the 'Manual of the Survey and Measurement of Dioxins in Sediment' (Environment Agency of Japan, 2000). The results showed that TEQ concentrations of dioxins increased with decreasing grain size in sediment fractions. Sediment fractions with less than 20 μm grain size showed the highest dioxin contents. Dioxins with five and six chlorine atoms dominated other congeners in less than 20 μm fractions. The dioxin TEQ concentrations increased with total organic carbon (TOC), total carbon (TC), ignition loss (IL), total sulphur and nitrogen contents in the sediment fractions. Thus, reporting dioxin contents in sediments without considering grain size distribution may be erroneous, and conventional sedimentation and separation techniques might not be useful for treating contaminated sediments. This information can be useful for effective remediation of dioxin-contaminated sediments.

Keywords Dioxins; quantification; sediment fraction; surface sediment

Introduction

Dioxin represents a group of primarily anthropogenic chemical compounds as unintended by-products of a number of human activities including combustion, certain types of chemical production, chlorine bleaching of paper and other industrial processes. Dioxins are almost insoluble in water, very slowly broken down in the environment and do not leach into deep soil once bonded to organic carbon.

Environmental pollution due to dioxins in Japan dates back to the 1950s (Masunaga, 2001; Sakurai *et al.*, 2000; Yao *et al.*, 2002). Studies have shown that use of agrochemicals in paddy fields and municipal solid waste incineration have been the two major dioxin sources to soil and aquatic environments in Japan (Masunaga, 2001; Sakai *et al.*, 2002; Masunaga *et al.*, 1999). An investigation of dioxin sources in the sediments from Lake Shinji showed drastic increases in total dioxin and furan concentrations from 1945 to 1970 (Masunaga *et al.*, 1999) which corresponded to the period of extensive use of agrochemicals in Japan (Yao *et al.*, 2002). Now, dioxins and dioxin-like impurities in Japanese agrochemicals have been removed and waste incinerators have been improved to prevent dioxin pollution. However, the environmental survey of dioxins in Japan pointed out that concentrations in water and sediments in public water areas exceeded both the environmental quality standards and the past recorded survey values (Environment Agency of Japan, 2000). This could have been the result of runoff from agricultural lands with agrochemical-derived polychlorinated dibenzo-p-dioxins/furans (PCDDs/Fs) to aquatic environments including sediment (Yao *et al.*, 2002).

Sediment is one of the most dioxin-contaminated components in the environment (Kadokami *et al.*, 2002). Several investigations have been conducted to date on dioxin-contaminated aquatic environments, including sediments, in Japan (Masunaga *et al.*, 1999; Naito *et al.*, 2003; Ogura *et al.*, 2002; Sakai *et al.*, 2002; Sakurai *et al.*, 1998, 2000; Yao *et al.*, 2002). Most of these studies focused on quantifying dioxin concentrations, their sources and contamination history. It may be possible that certain sediment fractions (based on grain size distribution) have more dioxin content than the others, and this information could be very useful in remediation of contaminated sediments. However, it is not yet known which sediment fractions contain more dioxins. This paper aims to investigate whether sediment fractions based on grain size distribution have influence on their dioxin contents, and which fractions are likely to contain higher dioxin contents, if so. The investigation was carried out in surface sediment samples from Kizu River (Ochiai Ferry) in Osaka, which flows through one of the most industrialized cities in Japan. Surface sediment samples from Sumiyoshi River, in Osaka, were also analyzed to verify the results obtained from Kizu River sediments.

Materials and methods

Sediment sampling

An Ekman grab sampler (15 × 15 cm size, stainless steel) was used for surface sediment sampling (10–15 cm depth) from Kizu and Sumiyoshi Rivers, in Osaka, in August 2003. The samples were immediately transferred to stainless steel containers and stored at 0°C until sample preparation and analyses started.

Sample preparation

The sediment samples were first sieved to obtain the following fractions: <1 μm, 1–10 μm, 10–20 μm, 20–38 μm, 38–53 μm, 53–75 μm, 75–150 μm, 150–425 μm and >425 μm. The samples were prepared and analyzed following "The Manual of the Survey and Measurement of Dioxins in Sediment" (Environment Agency of Japan, 2000). About 25 g of air-dried sediment samples were extracted with toluene in a Soxhlet apparatus for 16 h after the addition of ^{13}C-labeled internal standards (16 ^{13}C-labeled standards for PCDDs/Fs and 14 ^{13}C-labeled standards for coplanar PCBs). The extracts were then treated with concentrated sulphuric acid. Sulphur contained in the samples was removed using 1 mm diameter copper wires during the extraction process. The extracts were then further purified using multi-layered Silica gel column chromatography. The extracts were divided into two parts for PCDDs/Fs and coplanar PCBs (co-PCBs) analyses. Further purification of the extracts was obtained using alumina column chromatography and activated carbon-impregnated Silica gel column chromatography. The final PCDDs/Fs and co-PCBs fractions were spiked with ^{13}C-labeled recovery standards and concentrated to 50 μL.

Five grams of air-dried sediment sample was thoroughly homogenized/shaken with 50 g of double-distilled water and filtered through 1 μm pore size filters. The filtrates were used for the determination of total organic carbon (TOC) concentrations in the sediment fractions. Air-dried sediment samples were used for carbon, hydrogen, nitrogen and sulphur analyses.

Analyses

PCDDs/Fs and co-PCBs were analyzed using HRGC/HRMS (JEOLJMS-700D). SP-2331 columns (60 m × 0.32 mm ID × 0.25 μm, SPELCO) were used for the separation of tetra to hexachlorodibenzo-p-dioxins/furans and DB-17 columns (30 m × 0.32 mm ID × 0.25 μm, J&W) for hepta to octachlorodibenzo-p-dioxins/furans. The temperature

programs for SP-2331 column were: 100°C for 1 min, 20°C/min to 200°C, 2°C/min to 260°C and hold for 24 min. Similarly, the temperature programs for DB-17 column were: 100°C for 1 min, 20°C/min to 280°C and hold for 15 min. Seventeen PCDDs/Fs congeners were separated from the samples. HT-8 columns (50 m × 0.22 mm ID × 0.25 μm, SGE) were used in co-PCBs quantification. The temperature programs for this column were: 130°C for 1 min., 15°C/min to 220°C, 2°C/min to 300°C and hold for 1 minute. Twelve co-PCB congeners (4 non-ortho and 8 mono-ortho) were separated in the analysis.

TOC measurement was carried out with the filtrates of sieved sediment fractions using TOC Analyzer-810 (SIEVER). Ignition loss (IL) of each sediment fraction was calculated by igniting oven-dried fraction (at 105°C overnight) in a muffle furnace at 600°C for 30 minutes. Carbon, hydrogen, nitrogen and sulphur contents of air-dried sieved sediment fractions were determined using CHNS/O Analyzer-2400 (PerkinElmer).

Results

Surface sediment samples obtained from both Kizu and Sumiyoshi Rivers, in Osaka, were analyzed for PCDDs/Fs, co-PCBs and other constituents. Since the natures of the results in both the cases were similar, only the selected results of the former are presented here.

PCDDs/Fs and co-PCBs contents

PCDDs/Fs and co-PCBs concentrations in the various sieved fractions of the surface sediment samples were calculated in toxicity equivalency unit (TEQ). Calculation of TEQ values were based on the Toxicity Equivalency Factors (TEFs) for PCDDs/Fs and co-PCBs established by the WHO/IPCS in 1998.

The results for PCDDs (Figure 1) indicated that sediment fractions with smaller than 20 μm grain sizes contained the highest concentrations. The fraction with less than 10 μm grain size contained the second highest PCDDs concentrations. However, the difference between these two was small. The sediment fractions with less than 38 μm and 53 μm grain sizes followed the first two with respect to PCDDs concentrations. The concentration differences between the first two and the latter were significant.

The results for PCDFs were almost similar to those of PCDDs in terms of TEQ concentrations in different sediment fractions. But the TEQ values for the latter were about threefold the former. Unlike the results for PCDDs/Fs, co-PCB concentrations in the sediment fraction with less than 10 μm grain sizes were the highest. The fraction with less than 20 μm grain sizes showed the second highest. This was followed by ~38 μm
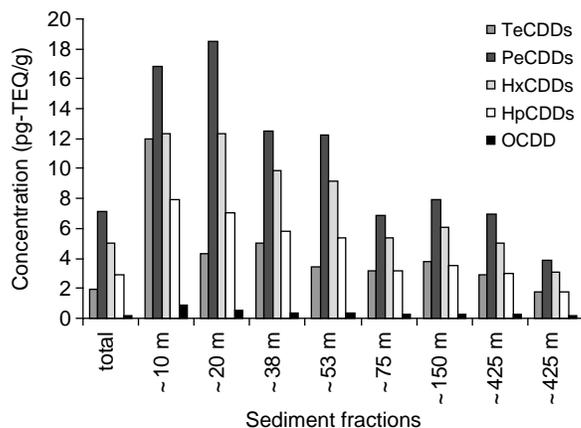

Figure 1 TEQ concentrations of PCDDs

H. Ozaki *et al.*

and ∼53 μm fractions. The difference between ∼10 μm and ∼20 μm fractions was significantly bigger.

The scenario of PCDDs/Fs and co-PCBs contents in sediment expressed in actual concentration (pg/g) was different than with TEQ concentrations. Co-PCB concentration was the highest (≈36,000 pg/g). The maximum PCDD concentration was about 2,000 pg/g while PCDFs concentrations were the smallest (≈400 pg/g), as shown in Figures 2 and 3.

PCDD/F and co-PCB congeners

Among the seven PCDD congeners separated, 1,2,3,7,8-PeCDD showed the highest TEQ concentration (about 40%) in ∼20 μm sediment fraction (Figure 4). Then, 1,2,3,4,7,8-HpCDD and 1,2,3,6,7,8-HxCDD had the second and third highest concentration values (about 16% and 13%), respectively. Other congeners contributing about 10% concentrations were 2,3,7,8-TeCDD; 1,2,3,7,8,9-HxCDD and 1,2,3,4,7,8-HxCDD. 1,2,3,4,6,7,8,9-OCDD had less than 1% contribution. Similar trends were observed in other sediment fractions also (Figure 1).

Altogether ten PCDF congeners were separated in ∼20 μm sediment fraction, and two of them (1,2,3,4,7,8,9-HpCDF and 1,2,3,4,6,7,8,9-OCDF) had less than 1% contributions in TEQ concentration. Among the congeners, 2,3,4,6,7,8-HxCDF and 2,3,4,7,8-
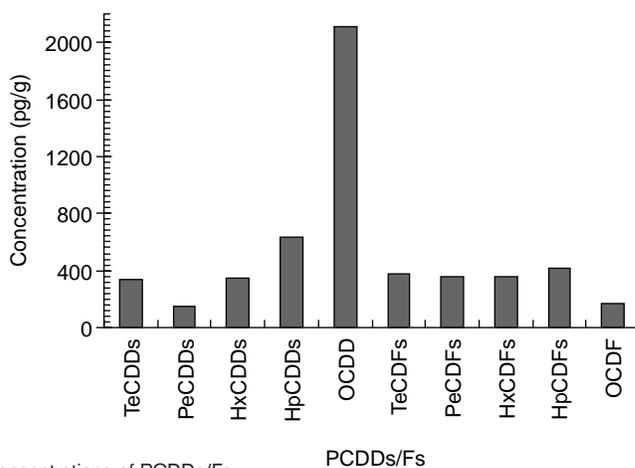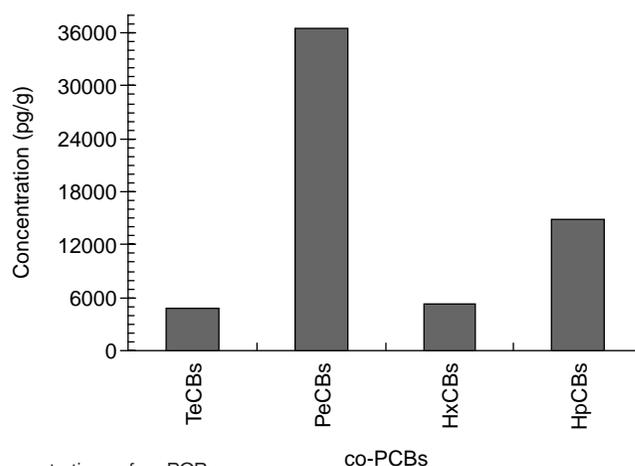
Figure 2 Actual concentrations of PCDDs/Fs
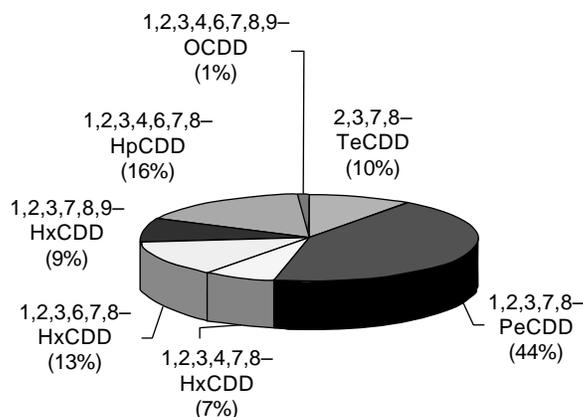

Figure 3 Actual concentrations of co-PCBs

Figure 4 PCDD congeners in ～20 μm fraction

H. Ozaki *et al.*

PeCDF contributed the first and the second highest concentrations (about 39% and 37%), respectively. Concentrations of the remaining congeners (2,3,7,8-PeCDF; 1,2,3,7,8-PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF and 1,2,3,4,6,7,8-HpCDF) ranged between 3% and 6%. Unlike the case in PCDD congeners, PCDF congeners in other sediment fractions were not similar to that in ～20 μm fraction. HxCDF concentration was the highest in ～20 μm fraction while PeCDF concentrations were the highest in other fractions.

Out of twelve, four congeners (3,4,4′,5-TeCB#81; 2′,3,4,4′,5-PeCB#123; 2,3′,4,4′,5,5′-HxCB#167 and 2,3,3′,4,4′,5,5′#189) contributed less than 1% in co-PCB TEQ concentration in ～20 μm sediment fraction. 3,3′,4,4′,5-PeCB#126 contributed the highest (about 69%) to co-PCB TEQ concentration in ～20 μm sediment fraction. Other co-PCB congeners had significantly smaller contributions to TEQ concentration in this fraction. Mainly non-ortho co-PCBs contributed to TEQ concentration in ～20 μm fractions and similar results were obtained in other sediment fractions also.

When expressed in actual concentrations (pg/g), OCDD had significantly bigger concentration in the sediment samples while HpCDDs showed the second highest concentration (Figure 2). However, OCDF concentration was the smallest, and TeCDFs, HxCDFs and HpCDFs had almost the same concentrations. In the case of co-PCBs, PeCBs showed significantly bigger concentrations compared to other congeners (Figure 3).

TEQ of sediment fractions

Total TEQ concentrations in various sieved sediment fractions and the percentage contribution of each fraction to total TEQ value in the sediment sample were calculated taking into account PCDDs/Fs and co-PCBs together, PCDDs/Fs together and only co-PCBs. Seven sediment fractions (～20 μm, 20–38 μm, 38–53 μm, 53–75 μm, 75–150 μm, 150–425 μm and 425–2000 μm) were selected while calculating the TEQ contribution of each fraction.

While considering PCDDs/Fs and co-PCBs together, the fraction with less than 20 μm particle size contributed the highest (about 41%) to total TEQ concentration. The fractions with 425–2000 μm and 75–150 μm grain sizes showed the second and the third highest concentrations (about 18% and 13%), respectively. Other fractions had less than 12% contributions to total TEQ concentration in the sample.

When PCDDs and PCDFs only were taken into account, the fraction with ～20 μm particle sizes exhibited the highest contribution (about 32%) to total TEQ concentration in the sample (Figure 5). Similar to the earlier case with PCDDs/Fs and co-PCBs, the
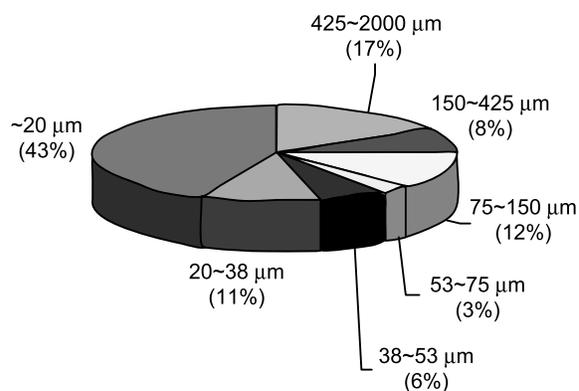
Figure 5 Total TEQ concentration of PCDDs/Fs

fractions with 425–2000 μm and 75–150 μm particle sizes had the second and the third bigger contributions (22% and 17% respectively) to total TEQ concentration. Other sediment fractions contained relatively smaller percentage of TEQ concentrations. Similar results were obtained when contributions of co-PCBs alone to total TEQ concentrations were calculated in various sediment fractions. The total TEQ concentrations of PCDDs/Fs and co-PCBs in sediments from Kizu and Sumiyoshi Rivers were 70 and 54 pg TEQ/g, respectively.

Other components in sediment fractions

Carbon, hydrogen, nitrogen and sulphur contents of various sediment fractions were measured and expressed as the percentage of total sediment weight in each fraction, as shown in Figure 6. Total carbon content increased with the decrease in grain size in sediment fractions in general. Similar trends were observed with the other three elements (H, N and S). However, the differences in results among the sediment fractions with grain sizes 53–75 μm, 38–53 μm and 20–38 μm were very small. Total carbon contents were significantly bigger in each sediment fraction as well as in total sediment sample compared to other three elements measured. Sulphur contents were second highest among the measured elements in each fraction.

   Total organic carbon (TOC) and ignition loss (IL) were also measured in various sediment fractions and compared with total TEQ concentration of PCDDs/Fs and co-PCBs in each fraction, as shown in Figure 7. The results indicated that TOC, total TEQ concentration and IL increased, in general, with the decrease in grain size in sediment fractions.
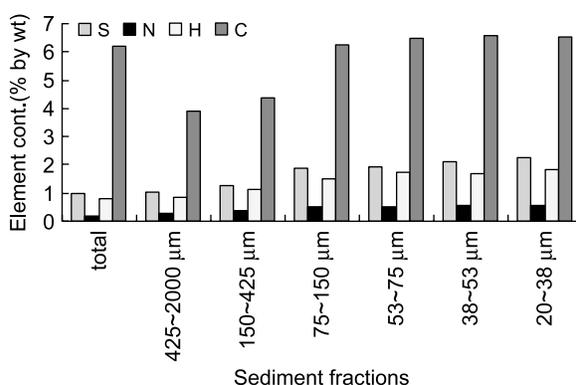

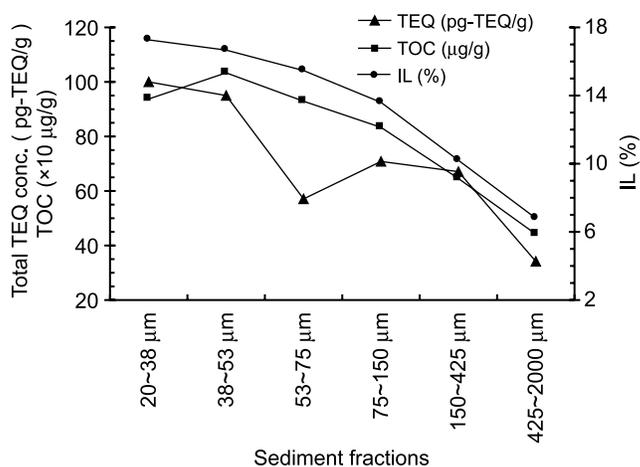**Figure 6** C, H, N and S contents in sediment

Figure 7 Total TEQ, TOC and IL in sediment

However, TEQ concentration value in the 53–75 μm fraction and TOC concentration in the 20–38 μm fraction were smaller than the normal trends observed in the other fractions.

Discussion

Significance of sediment grain size

The results of dioxin quantification in surface sediment samples from Kizu and Sumiyoshi Rivers in Osaka exhibited the importance of grain size distribution in sediment contamination due to non-polar organic pollutants like PCDDs/Fs and co-PCBs. PCDDs/Fs and co-PCBs contents increased with the decrease in grain size in sieved sediment fractions. More specifically, sediment fractions with less than 20 μm grain size contained the highest TEQ concentrations of PCDDs/Fs while co-PCBs content was highest in the fraction with less than 10 μm grain size. In terms of total TEQ concentrations with three different combinations of PCDDs, PCDFs and co-PCBs also, sediment fractions with less than 20 μm grain size contributed the highest percentage values. The results also indicated that the sediment fractions with ∼20 μm grain size contained the biggest percentage of PeCDD and HxPCDDs among the PCDDs/Fs congeners.

Very little information is available on the relation between grain size distribution and contaminant contents in sediments. It is mentioned in "Consensus-Based Sediment Quality Guidelines" (Contaminated Sediment Standing Team (CSST), 2003) that concentrations of trace elements and anthropogenic organic compounds have an inverse relationship with sediment grain size. Results of a special sediment monitoring study for Columbia River conducted in 1995 also showed an inverse correlation between sediment grain size and contaminant concentrations (Blanton *et al.*, 1995). In fact, contents of various organic/inorganic substances in sediments are strongly influenced by sediment grain size that ultimately controls adsorption characteristics and organic pollutant contents of the sediments (CSST, 2003). Thus, the increase in PCDDs/Fs and co-PCBs contents in finer sediment fractions can be explained on the basis of this information.

Coumber *et al.* (2003) mentioned that adsorption of non-polar organic pollutants is strongly influenced by the number of chlorine atoms attached in the compounds. Adsorption of such chemicals decreases with the increase in chlorine atoms. This could be a possible reason for higher contents of PeCDD, HxCDDs and 3,3′,4,4′,5-PeCB in ∼20 μm sediment fractions presented earlier.

Other influencing factors

Assessment of sediment qualities is based on its content of organic matter and other nutrient constituents (sulphur, nitrogen, phosphorus, etc). On the other hand, contents of such constituents depend on sediment grain-size distributions (CSST, 2003; Coumber *et al.*, 2003; Blanton *et al.*, 1995). Some authors found good correlations between decreasing sediment grain size and increasing organic content. The results presented in the earlier paragraphs revealed that content of total carbon, sulphur, hydrogen, nitrogen and total organic carbon (TOC) increased with a decrease in grain size in the surface sediment samples from Kizu and Sumiyoshi Rivers. The total carbon contents of each sieved sediment fractions were significantly higher.

Organic matter content plays very important role in adsorption and bioavailability of non-polar organic chemicals and trace elements in sediment (Parsons, 2004; CSST, 2003). The Consensus-Based Sediment Quality Guidelines (CSST, 2003) mentioned a strong correlation between sediment TOC concentrations and contents of non-polar organic compounds like dioxins. The guidelines also stated that validity of normalization of non-polar organic contaminants' concentrations with TOC contents in sediments covers wide range ($\geq 0.2\%$ TOC) compared to those for trace elements. After investigation of Columbia River sediment, Blanton *et al.* (1995) concluded that river sediments with higher TOC and finer grain size distribution have higher contaminant burdens than sediments with less TOC and more coarse-grained sediments. Parsons (2004) mentioned that dissolved organic constituents in sediment pore-water greatly affect the fate and bioavailability of organic compounds in sediments. Thus, the increasing TEQ concentrations of PCDDs/Fs and co-PCBs with IL (a measure of organic content), TOC and total carbon (TC) contents in sediment fractions from Kizu and Sumiyoshi Rivers in Osaka can be correlated. The highest TEQ concentrations in fractions with $\sim 20\,\mu$m grain size may also be explained on the same basis since they contained the highest TC concentrations.

No specific information could be obtained to correlate higher contents of sulphur, nitrogen and hydrogen with PCDDs/Fs and co-PCBs concentrations in the sediments. Gough *et al.* (2000) found that trace metal contents increased with total sulphur contents in sediments, but the correlation was strong for sediments from brackish water zone. Since sediment sulphur is predominantly organic (King and Klug, 1982) and TEQ concentrations of PCDDs/Fs and co-PCBs increased with total sulphur contents in various sediment fractions from both the rivers, a correlation between these two may be possible. Bigger contents of TC, TOC, sulphur and nitrogen in the surface sediments may indicate fast sedimentation rates and anoxic conditions.

The highest OCDD concentration in sediment samples (Figure 2) indicated pentachlorophenol (PCP) as a possible PCDDs source. Bigger concentrations of TeCDFs, PeCDFs, HxCDFs, HpCDFs and PeCBs (Figures 2 and 3) indicated both incineration and chloronitrofen (CNP) as possible sources of PCDFs and co-PCBs (Masunaga *et al.*, 2001).

Conclusion

The results of this investigation exhibited the importance of grain-size distribution and organic matter content on TEQ toxicity in sediment due to PCDDs/Fs and co-PCBs. The results indicated that fine-grained sediment fractions contained higher percentages of total carbon (TC), total organic carbon (TOC), total sulphur and nitrogen resulting in bigger TEQ concentrations of PCDDs/Fs and co-PCBs. More specifically, the sediment fractions with $\sim 20\,\mu$m grain size contained the highest percentage of TC, TOC, sulphur and TEQ concentrations of PCDDs/Fs and co-PCBs. In terms of total TEQ concentration, PCDDs/Fs and co-PCBs congeners with five and six chlorine atoms dominated in the sediment fractions with $\sim 20\,\mu$m grain size.

Therefore, it may be erroneous to report toxicity of non-polar organic chemicals without considering grain-size distributions in sediments. The results may provide useful information for remediation of contaminated sediments. The conventional sedimentation and separation techniques for treating contaminated sediments might not be efficient since finer fractions contain bigger percentage of contaminants. However, more detailed investigation is needed on the significance of various constituents in sediments on PCDDs/Fs and co-PCBs contents.

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