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Distribution of Polychlorinated-dibenzo-*p*-dioxins/-dibenzofurans in Soil from Changsha-Zhuzhou-Xiangtan Urban Agglomeration, China

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The concentration levels and distribution patterns of polychlorinated-dibenzo-*p*-dioxins and -dibenzofurans (PCDD/PCDFs) in soil/sediment sampled from Changsha-Zhuzhou-Xiangtan urban agglomeration were preliminarily investigated. The results showed that the concentrations of PCDD/PCDFs in surface soil samples ranged from 267 to 7509 pg/g with 2175.00 pg/g mean concentration. The I-TEQ concentrations were ranged from 0.92 to 10.21 pg/g with mean 4.82 pg/g concentration. The level of PCDD/PCDFs concentration were higher compared with other area of China. The concentrations of PCDD/PCDFs in sediment samples were ranged from 876.17 to 497759.30 pg/g with 160765.91 pg/g mean concentration and the I-TEQ concentrations were ranged from 2.63 to 1031.21 pg/g with mean 332.55 pg/g concentration. The observation that the toxic equivalent concentrations in 50% of sediment samples were over 80 pg/g, indicated that there had posed a threat to some species. Moreover, the distributions of toxic equivalent concentration of 17 single isomers of PCDD/PCDFs in samples were analyzed and the potential pollution sources were discussed. Further researches should be done to get more information about the sources and the distributions of the PCDD/PCDFs.

Key Words: Dioxins, Soil, Homologue distributions, I-TEQ.

INTRODUCTION

Polychlorinated-dibenzo-*p*-dioxins and -dibenzofurans (PCDD/PCDFs) are well-known toxic environmental contaminants with great concern due to their characteristics of environmental persistence and their tendency to bioaccumulate through the food chain as well as their toxicity[1]. They are released into the environment from numerous sources including municipal and industrial waste incineration, forest fires, as unwanted by-products from chlorinated chemical manufacturing and from automobile exhaust, though they have been never produced for industrial purposes. Due to their physical chemical properties[2-7], PCDD/PCDFs are hydrophobic and in the absence of UV light, resistant to both environmental and biological breakdown and as a result tend to accumulate in both soils and sediments[8,3]. The toxic potencies of PCDD/PCDFs present in complex mixtures can range over several orders of magnitude and can be modulated by interactions among them. Therefore, the ecological relevance of contaminants in matrices is complicated to be assessed, which has led to the conceptual development of toxic equivalency factors or relative potency. Accordingly, the total dioxin-like toxic potency of a compounds mixture can be expressed as a single toxic equivalency (toxic equivalency). The toxic equivalency value has been proven to be a significant indicator in risk assessment for human and wildlife.

It is well known that the soil quality has always been important for soil microbial, plant and animal life, including humans. Soil pollutants can pass to vegetation and enter food chains. Furthermore, the soil has high affinity for hydrophobic organic pollutants and can act as a natural sink[9]. Therefore, it is very important and necessary to study the soil of dioxin-like material to understand the status of soil pollution. Over the past 20 years, the pollution of the soil and sediment in certain district of China are very serious with the rapidly developing industrial and agricultural activities, municipal development, increased usage of chemicals and insufficient recognition of environmental protection. Liu and Liu[10] summarized the distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) and dioxin-like polychlorinated biphenyls (dioxin-like PCBs) in the soil in a typical area of eastern China. The principal component analysis demonstrated that the PCDD/PCDFs and dioxin-like PCBs in major part of contaminated sediment and soil samples derived from the correlative matrix. Yet the different distribution patterns of them in part of sediment samples strongly indicate that other potential sources may be exist. Kiguchi *et al.*[11] analyzed the polychlorinated dibenzo-*p*-dioxins and dibenzofurans in paddy

soils and river sediments in Akita, Japan. The results indicated that the PCDD/PCDFs concentrations in paddy soils were much higher than those in the non-agricultural soils and much higher than those found in other parts of Japan. Although PCDD/PCDFs were ubiquitous in sediments from river sources to mouths of the respective river basins, those concentrations were much lower than those from paddy soils and non-agricultural soils and from other parts of Japan.

In this paper, a preliminary study about the formation of PCDD/PCDF in from Changsha-Zhuzhou-Xiangtan Urban Agglomeration of China was described. Their homologues and isomer-specific concentrations and compositions of PCDD/PCDF in soils and sediments were investigated. The PCDD/PCDF homologue and isomer compositions were compared to those of putative sources. Furthermore, the isomer-specific data through statistical analyses to elucidate the relationship between the samples and possible sources were analyzed.

EXPERIMENTAL

Soil sampling: As shown in Fig. 1, 55 surface soils samples (0-20 cm) and 5 sediment samples were collected from 55 locations in Changsha-Zhuzhou-Xiangtan Urban Agglomeration during May 2008, according to the different land use function. Soils and sediments collected from 60 locations, respectively, with different land uses from Changsha-Zhuzhou-Xiangtan Urban Agglomeration China during the spring of 2008 (Table-1) were analyzed for PCDD/PCDFs.

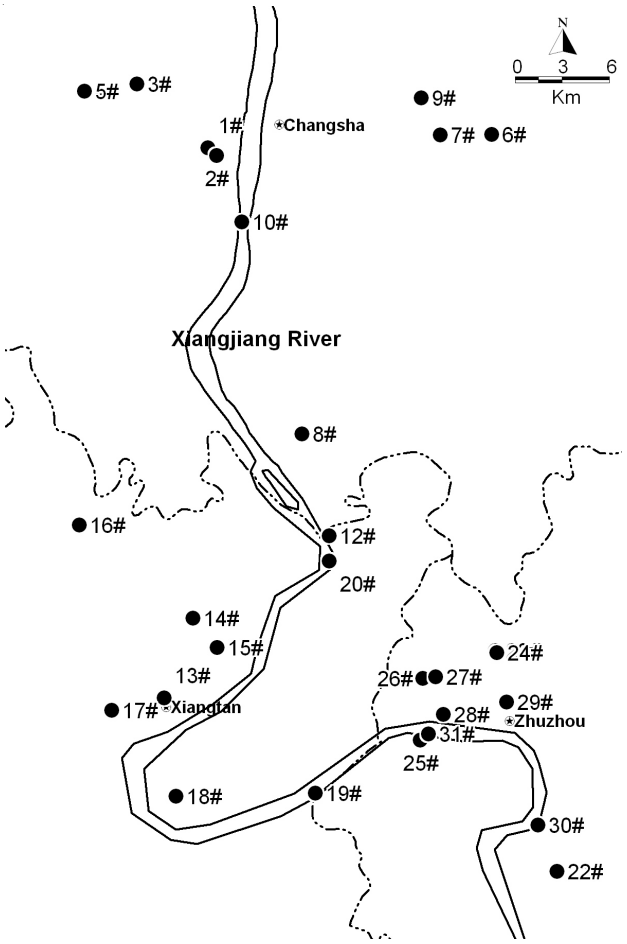

Fig. 1. Distribution of sampling locations

Sediments were collected along the xiangjiang river using a stainless steel scoop at a depth of 0-10 cm. After collection, pebbles and twigs were removed. All samples were transported on ice at 4 ºC to the laboratory and were frozen at -20 ºC until analyses. Samples were freeze-dried and ground with a mortar and pestle, prior to analysis.

Sample preparation: Soil samples were freeze dried and ground with a mortar and pestle, sieved through a 1 mm sieve. Samples (20 g) were then Soxhlet extracted for 48 h with 200 mL high purity acetone/hexane (1:1, v/v). Activated copper was added to remove sulfur. The extracts were concentrated to approximately 2 mL by rotary ecolourator (Büchi R-200, Switzerland) and were solvent-exchanged to hexane. The concentrated extracts were ecolourated to near dryness under a gentle stream of nitrogen gas, re-dissolved in 0.5 mL of dimethyl sulfoxide and stored at -20 ºC prior to the EROD bioassay.

Chemical analysis: Sample preparation for the analysis of PCDD/PCDFs was accomplished according to the US EPA method 1613. About 10 g of each dried fly ash fraction collected was transferred to glass Soxhlet thimbles, spiked with a mixture $13C_{12}$-labeled PCDD/PCDFs internal standard and extracted for 24 h with 250 mL toluene. The toluene-extract was then concentrated to approximately 10 mL by a rotary ecolourator prior to the cleanup process. After the internal standards were spiked, 2 L carrier solution was extracted with toluene to check the dissolved dioxins. The extracts were firstly washed with H_2SO_4 until colourless, subsequently hexane followed by a water rinse were used to neutralize. Sample cleanup was carried out with multi-silica gel column and activated acidic alumina column, respectively. After cleanup the extract was concentrated again then transferred to a vial. Before mass analysis, $13C_{12}$-labeled PCDD/PCDFs-recovery standards were added. The size dependent levels of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) contained in fly ash particle from a municipal solid waste incinerator (MSWI) were characterized by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

The toxic equivalence of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans were calculated by multiplying the detected concentration by the corresponding toxic equivalency factors provided by the world health organization[12]. The calculated toxic equivalency (TEQcal) was obtained as the sum of toxic equivalencys from the individual compounds by assuming an additive effect when dioxin-like chemicals mixed.

Statistical analysis: All the statistical analysis was performed using SPSS software version 13.0 (SPSS Inc., Chicago, USA). One-way analysis of variance (ANOVA) was used for statistical comparisons and Pearson coefficient was used for correlation analysis. A value of $p < 0.05$ was considered to be statistically significant.

RESULTS AND DISCUSSION

Polychlorinated dibenzo-*p*-dioxin/polychlorinated dibenzofurans distribution in soil samples: As shown in Fig. 2, the levels of total polychlorinated dibenzo-*p*-dioxins

TABLE-1
SAMPLE DETAILS INCLUDING GEOGRAPHICAL DESCRIPTIONS OF ALL SAMPLING LOCATIONS, DISTRIBUTION OF SAMPLING LOCATIONS FROM Changsha-Zhuzhou-Xiangtan URBAN AGGLOMERATION

City	Sites	Land uses				Region	Samples	
		Agricultural	Industrial	Municipal	Others		Soil	Sediment
Changsha city	1#				√	Uphill of Yuelu Mountain	√	
	2#				√	Late love Pavilion (Downhill of Yuelu Mountain)	√	
	3#		√			High-Tech Development Zone	√	
	4#	√				Vegetable garden nearby Changsha High-Tech Development Zone	√	
	5#	√				Rice paddy nearby the Changsha High-Tech Development Zone	√	
	6#	√				Rice paddy nearby Longping science and technology zone	√	
	7#	√				Vegetable garden nearby Longping science and technology zone	√	
	8#	√				Vegetable garden nearby Muyun industrial park	√	
	9#		√			Xingsha industrial park	√	
	10#			√		Houzishi bridge sediment		√
	11#			√		The moon island sediment		√
Xiangtan city	12#				√	Zhaoshan (background site)	√	
	13#			√		The Peace Park	√	
	14#				√	Jiuhua economic zone	√	
	15#	√				Rice paddy nearby Jiuhua economic zone	√	
	16#		√			Manganese ore mining	√	
	17#	√				Shanhong Zhongke	√	
	18#		√			Xiangtan Iron and Steel Group	√	
	19#				√	Shuangma industrial park (upstream)		√
	20#				√	Xiangjiang River (nearby Zhaoshan)		√
Zhuzhou city	21#	√				Vegetable garden in Dongjia high-tech park	√	
	22#				√	Dongjia high-tech park (mountain)	√	
	23#	√				Rice paddy nearby Nanche Group	√	
	24#	√				Vegetable garden nearby Nanche Group	√	
	25#	√				Rice paddy nearby Hetang Park	√	
	26#	√				Rice paddy nearby Qingshuitang	√	
	27#	√				Vegetable garden nearby Qingshuitang	√	
	28#	√				Vegetable garden nearby Jinyuan chemical company	√	
	29#		√			Zhuzhou Coal-washing Group	√	
	30#				√	Upstream of Xiangjiang		√
	31#				√	Downstream of Xiangjiang River		√

among nine sampling sites (1#-9#) in Changsha city were ranging from 267 pg/g to 5019.34 pg/g with a mean value of 2205.55 pg/g. The maximum polychlorinated dibenzofuran concentrations were found at locations 6#, where were a vegetable garden nearby Longping science and technology zone. The levels of total polychlorinated dibenzo-*p*-dioxins among seven sampling sites (12#-18#) in Xiangtan city were ranging from 1222.63 pg/g to 7509.61 pg/g with a mean value of 3221.92 pg/g. The maximum polychlorinated dibenzofuran concentrations were found at locations 13#, where were a municipal land used as park. The levels of total polychlorinated dibenzo-*p*-dioxins among seven sampling sites (21#~27#) in Zhuzhou city were ranging from 356.5 pg/g to 2848.48 pg/g with a mean value of 1330.18 pg/g. The maximum polychlorinated dibenzofuran concentrations were found at locations 27#, where were a vegetable garden nearby Qingshuitang.

The total PCDD/PCDFs concentrations in the agricultural area in Xiangtang city were highest than those in othe two cities. The total PCDD/PCDFs concentrations trend was Changsha city > Xiangtan city > Zhuzhou city. Profiles of PCDD/PCDFs composition were similar in all soil samples (Fig. 2). It is interestingly that the polychlorinated dibenzo-*p*-dioxin concentrations in sediments were between 27 and 77 times higher than those of polychlorinated dibenzofurans throughout the samples, whereas in soil samples the polychlorinated dibenzo-*p*-dioxin concentrations were 6.18 to 1778.83 times higher than those of polychlorinated dibenzofurans. The high polychlorinated dibenzofuran concentrations may imply the presence of PCDD/PCDFs source originating from commercial PCBs. Most industrial mixtures of PCBs contain PCDD/PCDFs. Therefore, commercial PCBs are suspected as the source of PCDD/PCDFs in the study area.

Among all of the samples, the dominant polychlorinated dibenzo-*p*-dioxin congeners were OCDD (87.35-99.06 %) and 1,2,3,4,6,7,8-HpCDD (0.56-5.15 %), while the dominant polychlorinated dibenzofuran congeners were 1,2,3,4,6,7,8-HpCDF (20.54-48.65 %) and OCDF (17.24-46.39 %).

Moreover, the levels of total PCDD/PCDFs concentrations in surface soil are closely related with the land use ways. The levels of total PCDD/PCDFs in rice paddys and vegetable

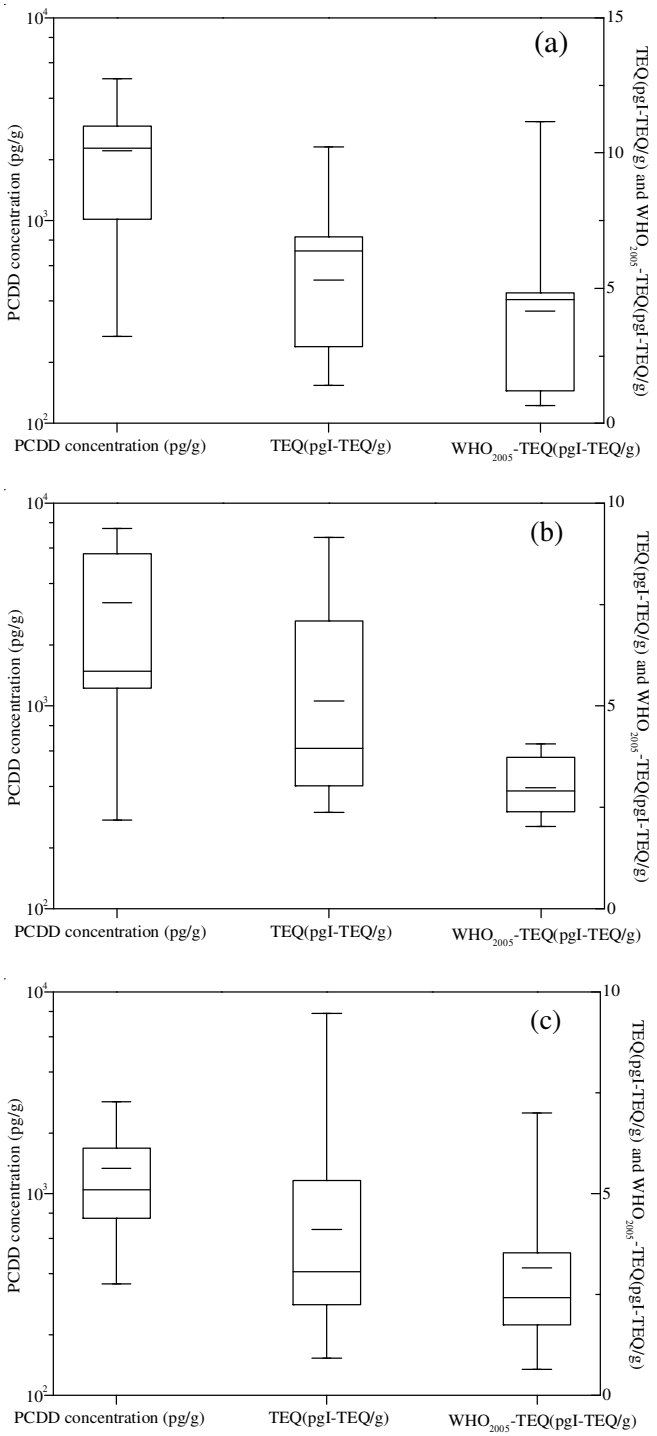

Fig. 2. Concentrations of PCDD/PCDFs in the soil samples (a) Changsha city; (b) Xiangtan city; (c) Zhuzhou city

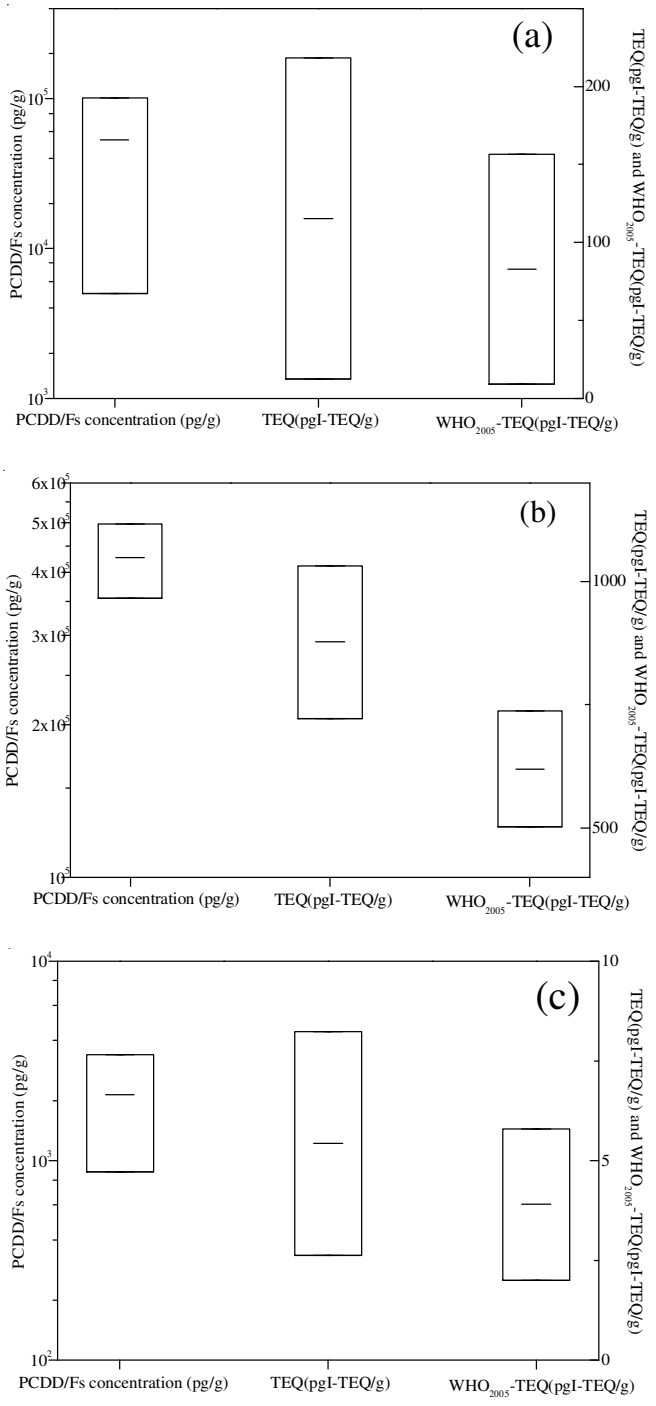

Fig. 3. Concentrations of PCDD/PCDFs in the sediment samples (a) Changsha city (b) Xiangtan city (c) Zhuzhou city

gardens were lower than those in industrial parks. There must be aware when the PCDD/PCDFs concentrations are higher than 5 pg I-TEQ/g. All vegetables from these locations should be cleaned and graze is forbidden.

PCDD/PCDFs distribution in sediment samples: As shown in Fig. 3, the levels of total polychlorinated dibenzo-*p*-dioxins among six sediment samples were ranging from 876.17 pg/g to 497759.30 pg/g with a mean value of 160765.91 pg/g. In sediments samples, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and 1,2,3,7,8,9- HxCDF were most prevalent. When compared with other locations, OCDD at locations 30 and 31 contributed relatively greater to the total polychlorinated dibenzo-*p*-dioxin concentrations, accounting for 97.17 % at site 30 and 97.43 % at site 31, while 1,2,3,4,6,7,8-HpCDD contributed relatively less proportions (2.51 % and 2.37 % respectively). Moreover, the percentages of lower chlorinated polychlorinated dibenzo-*p*-dioxins at Xiangjiang sediments (28# and 29#) were relatively lower when compared with other locations.

The PCDD/PCDFs concentration levels in Changsha-Zhuzhou-Xiangtan Urban Agglomeration China were greater when compared with another areas[13-15]. Changsha city is the down-stream of Xiangtan city. The high PCDD/PCDFs concentration

in sediments in Xiangtan city caused the high PCDD/PCDFs concentration in sediments in Changsha city (10#)?The PCDD/PCDFs concentration in sediments in Zhuzhou city was lower, which indicated that the PCDD/PCDFs pollution mainly occurred in Xiangtan city. There must be attached great importance in the PCDD/PCDFs pollution caused by the sediment in Xiangjiang river.

Distribution of PCDD/PCDFs homologues: Dioxin is a kind of chemical structure and biology with similar characteristics of the third generation (the floorboard of aromatic compound, which including polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and Co-PCBs[16]. The speciation characteristics of PCDD/PCDFs can indicate the pollution source of surrounding soil and sediment. The congener profiles of PCDD/PCDFs of 25 soil samples were shown in Fig. 4. The results showed that 2,3,7,8-PCDD, which known as toxicity strongest PCDD/PCDFs homologues, was detected in 77 % samples. The levels of polychlorinated dibenzo-*p*-dioxin congeners in all samples were greater than polychlorinated dibenzofurans. Moreover, the level of HpC-DD and OCDD were higher, which indicated that the PCDD/PCDFs discharged from burning source accumulated by dry and wet deposition in the soil after long distance transmission in the atmosphere[17,18]. In addition, the PCDD/PCDFs congener profiles in soil samples were dominated by OCDD.

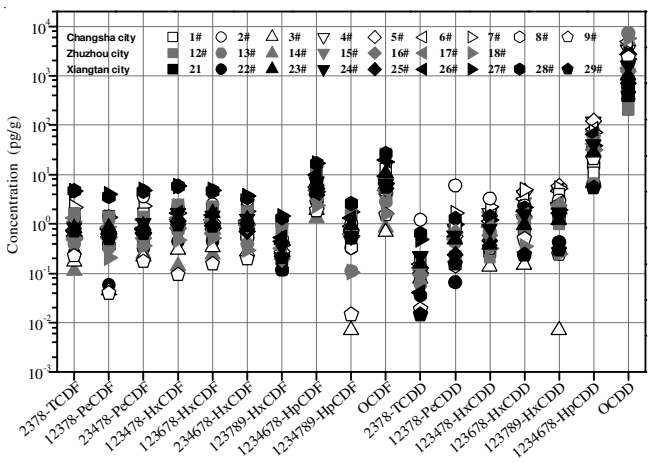

Fig. 4. Concentrations of 17 single isomers of PCDD/PCDFs in soil samples

Toxic equivalency from chemical analysis: The toxic potencies of chemicals present in complex mixtures range over several orders of magnitude. In addition, the ecological relevance of contaminants in matrices is complicated to be assessed, which has led to the conceptual development of toxic equivalency factors or relative potency. Accordingly, the total dioxin-like toxic potency of a compounds mixture can be expressed as a single toxicity equivalency quantity. The toxic equivalency value has been proven to be a significant indicator in risk assessment for human and wildlife.

When compared with soil guiding standards of Canada[19,20], the total PCDD/PCDFs concentrations in the agricultural area in Changsha-Zhuzhou-Xiangtan Urban Agglomeration China were higher. The I-TEQ concentrations in 44 % soil samples were over 5 pg/g compared with Germany soil reference standard[21], where the I-TEQ concentrations in 55 % soil samples of Changsha city, 43 % soil samples of Xiangtan city and 33 % soil samples of Zhuzhou city were over 5 pg/g.The PCDD/PCDFs Pollution Levels were Changsha city > Xiangtan city > Zhuzhou city.

The I-TEQ concentrations in 50 % sediment samples were over 80 pg/g. the results dedicated that there was a much greater risk of death for some species. The I-TEQ concentrations in all two sediments in Xiangtan city were over 80 pg/g. Phenolic is one of the main material of PCDD/PCDFs. The produce of phenolic of coking process in Xiangtan iron and steel company was the main reason to increase the PCDD/PCDFs concentration in sediments of Xiangjiang river in Xiangtan city. So far, the I-TEQ concentration in 19# was 1031.21 pg/g, which was the reported highest concentration. The I-TEQ concentration in sediments samples of Changsha city were 218.15 pg/g.

As shown in Fig. 5, the toxic equivalency of soil samples ranged from 1.39 to 10.21 pg/g and the toxic equivalency of six sediment samples ranged from 2.63 to 1031.21 pg/g, varying greatly among locations.

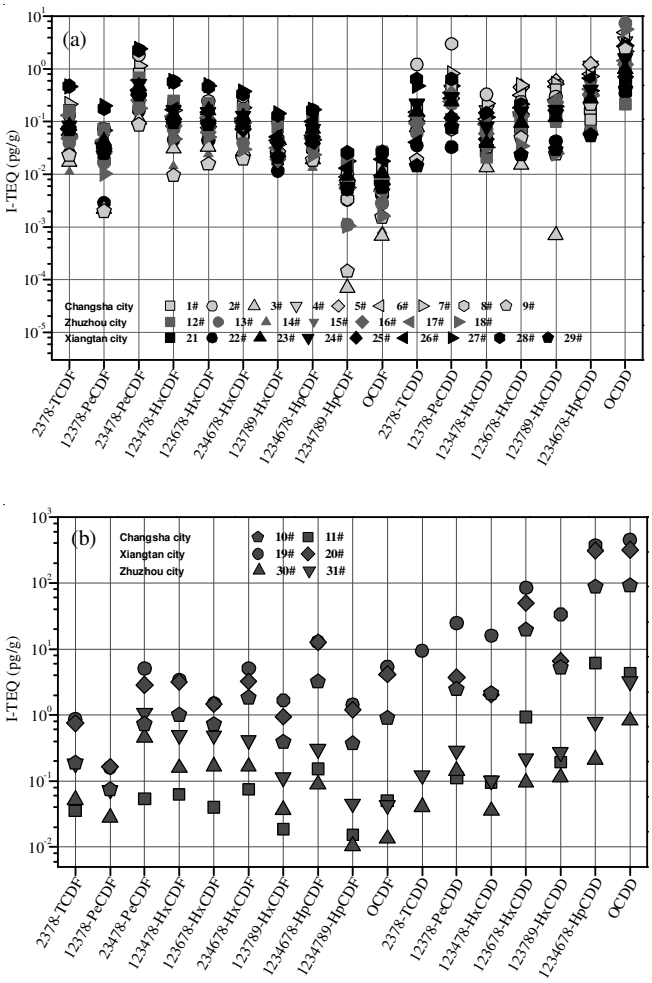

Fig. 5. Distribution of I-toxic equivalency concentration of 17 single isomers of PCDD/PCDFs in (a) soil samples; (b) sediment samples

The average toxic equivalency in 29 soil samples was 4.16 pg/g. The relatively low levels of the toxic equivalency data meant that the pollution of PCDD/PCDFs in main area of the studied district was not obvious. However, the toxic equivalency of the downstream sediment samples was significant higher.

Moreover, some agricultural soil in this area could be judged as polluted by dioxin-like compounds, based on the agricultural soil guidelines of 4.0-10 pg/g dw from Canada, New Zealand and Sweden.

Contributions of PCDD/PCDFs varied among locations, though PCDD/PCDFs were the predominant contributors at most of the locations. polychlorinated dibenzofurans accounted for 2.64-63.09 % of the total toxic equivalency throughout all soil samples and 3.62-44.51 % of the total toxic equivalency throughout all sediment samples. The polychlorinated dibenzofuran congener 2,3,4,7,8-PeCDF accounted for 0.33-30.93 % of the total toxic equivalency at all locations. The predominant contribution of 2,3,4,7,8-PeCDF to toxic equivalency could be due to its great relative potency. In summary, this result suggested that the contributions of PCDD/PCDFs were responsible for the predicted dioxin-like effects derived from chemical analysis in all soil extracts.

Conclusions and future perspectives

The concentrations of PCDD/PCDFs in surface soil samples ranged from 267 to 7509 pg/g with 2175.00 pg/g mean concentration. The I-toxic equivalency concentrations were ranged from 0.92-10.21 pg/g with mean 4.82 pg/g concentration. The level of PCDD/PCDFs concentrationwere higher compared with other area of China. The concentrations of PCDD/PCDFs in sediment samples were ranged from 876.17 to 497759.30 pg/g with 160765.91 pg/g mean concentration. The total PCDD/PCDFs concentrations trend was Changsha city > Xiangtan city > Zhuzhou city.

The levels of polychlorinated dibenzo-*p*-dioxin congeners in all samples were greater than polychlorinated dibenzofurans. Moreover, the level of HpC-DD and OCDD were higher, which indicated that the PCDD/PCDFs discharged from burning source accumulated by dry and wet deposition in the soil/ sediments after long distance transmission in the atmosphere. In addition, the PCDD/PCDFs congener profiles in soil and sediment samples were dominated by OCDD.

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