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LEVELS OF PCDD/FS AND DL-PCBS IN WATER SAMPLES OF TAIWAN

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (dioxin-like PCBs) are classified as persistent organic compounds (POPs). These contaminants have received much public concern worldwide due to their persistent properties and toxic responses in humans including immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine functions (Papadopoulos et al., 2004). The presence of these compounds in environmental matrix including soil, sediment, air and food has been studied by many authors (Ren et al., 2009; Li et al., 2010; Zhang et al., 2010; Nunes et al., 2011; Dömötörová et al., 2012; Colombo et al., 2013). Nevertheless, investigation of these compounds in water is still scarce, regardless of water as the primary path way that can enhance the risk of human exposure to these toxic pollutants through drinking water. Therefore, the quality of primary water drinking sources as surface water in reservoirs and groundwater need to be addressed.

In this study, several groundwater and surface water samples throughout Taiwan were collected to evaluate the presence of PCDD/Fs and 12 coplanar PCBs in water sources affected by discharges nearby. The characteristics of PCDD/Fs and PCBs distribution in suspended solid/dissolved phase in groundwater are also determined.

2. Materials and methods

2.1. Sample collection

11 groundwater samples were collected around Taiwan (Fig. 1), while two raw surface water samples were collected at two supply water treatment plants in northern Taiwan, which supplies fresh water for Taipei city and New Taipei city.

The sampling system consists of a sampler made of stainless steel, centrifuge (Scientific Methods Inc., 10,000 rpm), two glass fiber filter cases (GFF: Advantech Co. GC-50, 142 mm ID, 3μm and 0.5μm pore size), polyurethane foam holder (PUF: Shibata Chemical Co., 63 mm ID, 3 inch height, density > 0.022 g/cm3), air bubble removal device, vacuum pressure sensor and computer controller. Coarse particles were collected by centrifugal instrument, fine particles were collected by filters and the dissolved phase was adsorbed with PUF. After sampling, coarse particles in the centrifuge was transferred to a glass thimble for storage. All samples were stored in a refrigerator at -50 oC until pretreatment.

2.2. Sample pretreatment and analysis

Three groundwater samples were separately pretreated for different portions including particles in thimble (with the samples collected by centrifugal instrument), GFF and PUF to compare the difference between coarse particles and fine particles or solid phase and dissolved phase together. For other samples, these parts of sample were combined together before treatment.

GFF, PUF and particles in thimble were Soxhlet pre-extracted with toluene for 24 h before sampling to eliminate all organic contaminants. The pretreatment and analysis of samples was carried out following NIEA M 801.11 and NIEA M 803.00B modified from the US-EPA M1613B and US-EPA 1668 for PCDD/Fs and PCBs analysis, respectively. PCDD/Fs recovery standard solutions were added after treatment and PCDD/Fs and PCBs concentrations were determined by a gas chromatograph (GC)/high resolution mass spectrometer (HRMS JEOLJ MS-700) operated in electron ionization and selected ion monitoring (SIM MORDERN) modes with resolution R > 10,000. The gas chromatographic column used is DB-5 MS (60 m × 0.25 mm, 0.2 μm film thickness).

3. Results and discussion

3.1. Dioxin and PCB concentration in groundwater and surface water

PCDD/F and PCB concentrations in two surface water samples are relatively low, with the average concentrations of 0.038 and 0.001 pg TEQ/L (7.474 and 1.862 pg/L), respectively. The average WHO TEQ concentration is 0.394 pg TEQ/L, which is lower than the standard limit of 3 pg TEQ/L set by Taiwan EPA.

On the other hand, the TEQ concentrations of PCDD/F and PCB in groundwater samples varied in a wide range. The concentration of PCDD/F ranged from 0.005 to 3.963 pg TEQ/L. While the concentration of PCBs ranged from N.D to 0.189 pg TEQ/L and the total concentration ranged from 0.005 to 3.963 pg

TEQ/L. Five samples are of low total TEQ concentrations (0.0053-0.0099 pg TEQ/L) that are comparable with the levels of PCDD/Fs reported in previous studies and the concentrations of PCDD/F and PCB of other samples are significantly higher than that of surface water. The samples measured with high PCDD/F and PCB concentrations include GW1, GW2, GW3, GW5, GW9 and GW11, which are collected from the regions affected by sources of PCDD/F and PCB. The highest concentrations of PCDD/Fs and PCBs are found at GW3 and GW1, respectively. The highest TEQ concentration of total PCDD/Fs and PCBs is measured at (3.963 pg TEQ/L) which is higher than the standard for drinking water set by Taiwan EPA, followed by GW9 (0.7572 pg TEQ/L) and GW1 (0.682 pg TEQ/L). The results reflected serious contamination of PCDD/F and PCB in groundwater at these sampling sites.

3.2. Congeners distribution

In term of PCDD/Fs, PCDDs constituted a significant fraction (77.3% on average) of total concentration of PCDDs and PCDFs. The contribution of PCDD/F homologues increased with increasing chlorination level. Generally, OCDD is of the highest contribution, followed by HpCDD/Fs and HxDD/Fs. Total contribution of these three congeners are 89.9% and 94.8% in groundwater and surface water, respectively. The increasing trend of PCDD contributions with the increment of chlorination level was more significant than that of PCDFs. The contribution of OCDD in surface water (86.5%) was higher than that in groundwater (67.9%) while the contribution of other PCDDs congeners were lower than that of PCDFs in both groundwater and surface water. The contribution PCDFs to total PCDD/F mass concentration in groundwater (25.3%) was higher than that in surface water (8.9%).

Among 12 coplanar PCBs which were analyzed, PCB 118 was of the highest concentration, followed by PCB 105 and PCB 77. These three congeners made up 74.6 and 86.3% of total PCBs in groundwater and surface water, respectively.

No significant difference regarding the distribution of PCDD/F, PCB congeners between coarse and fine particles was observed. Solid-phase PCDD/Fs generally predominate in water with the higher distribution of PCDDs in comparison with PCDFs (Fig. 2). On the other hand, PCBs are mainly distributed in dissolved phase. Significantly higher distribution of PCBs in dissolved phase is consistent with their water solubilities as reported by Huang and Hong (2002). The increase of PCB solubility follows these orders: #189<#169<#157<#123<#167<#156<#105<#126<#118<#114<#77<#81. However, the result was different from the observation of Kishida (2013) which indicates that PCBs are dominant in solid phase of river water. It is suggested that PCBs distribution may be quite different between groundwater and river water.

3.3. Potential sources of PCDD/F and PCB

Sources of PCDD/Fs have been studied based on homologue profiles and the contribution of each congener to total PCDD/F concentrations by several authors (Kobayashi et al., 2003; Masunaga et al., 2003; Ren et al., 2009; Thuan et al., 2011). Predominance of OCDD in the PCDD/F profile might be related to pentachlorophenate (PCP) contamination (Baker and Hites, 2000). However, Baker and Hites (2000) also indicate that it is difficult to distinguish the PCP source and combustion source. Combustion process generates PCDD/Fs with all tetra- through the octa-homologues whereas PCP primarily generates Hepta and Octa-CDD due to photochemical reaction in the atmosphere. Due to the significantly lower portion of HpCDD compared with OCDD, PCP may not be the major source in water samples analyzed.

Principal Component Analysis (PCA) was conducted to evaluate some possible groupings with similar distribution pattern of PCDD/F and PCB congeners and the results are shown in Fig.3. Three groups of sample that have similar distribution pattern of PCDD/F and PCB are identified i.e., two groups with single sample of GW1 and GW3 and one group consisting all of other samples. It is interesting to note that GW1 and GW3 are collected from the sites located nearby the MWIs.

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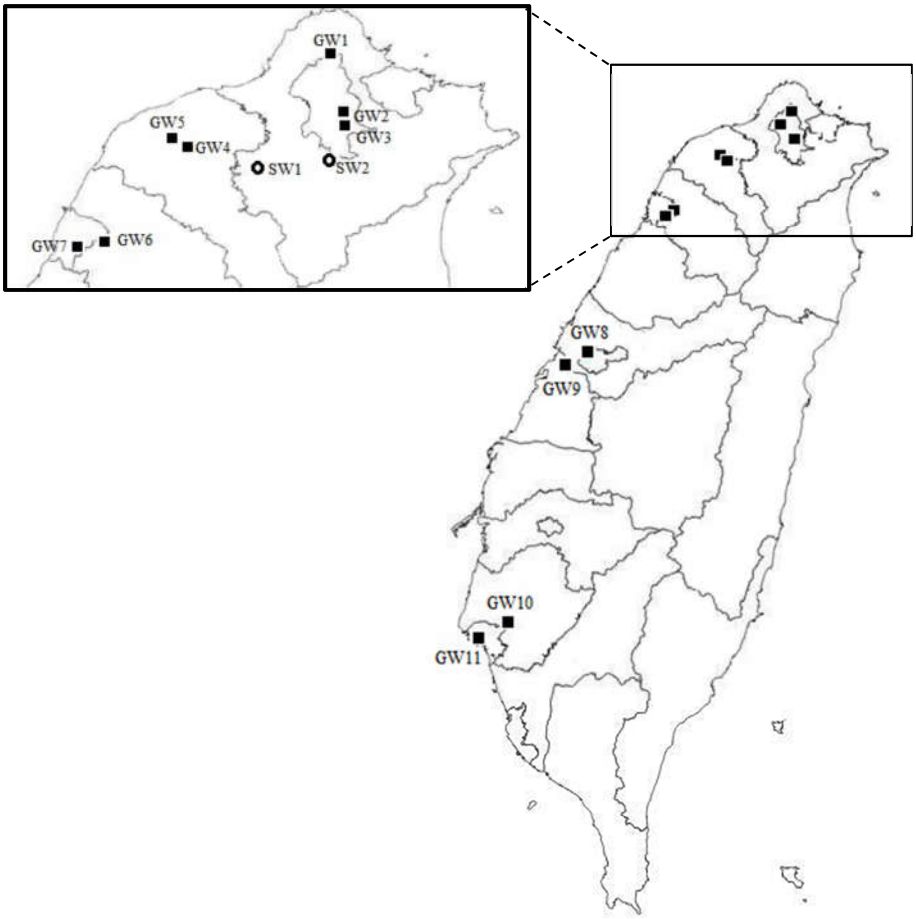

Fig.1 Geographical location of sampling sites

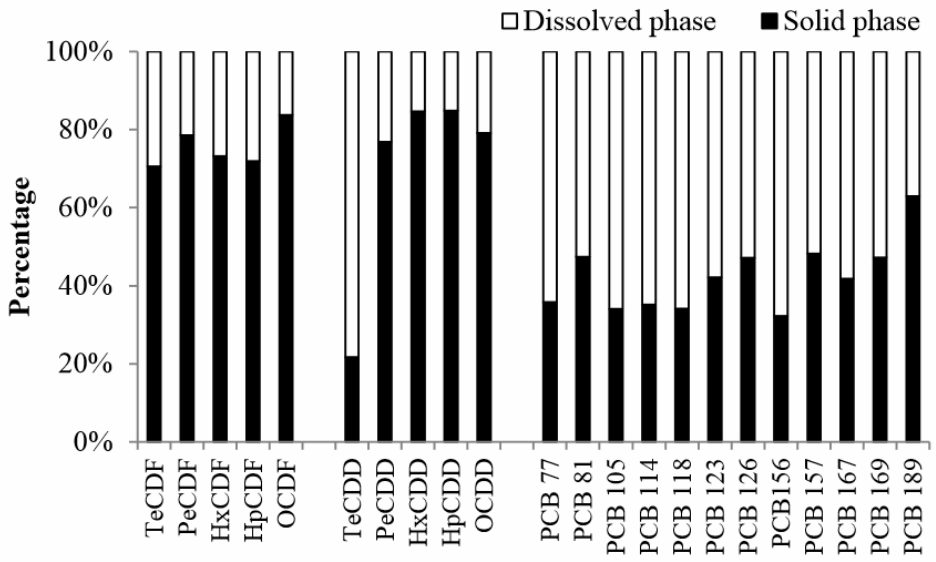

Fig. 2 Distribution of PCDD/F and PCB congeners in solid and dissolved phases of groundwater

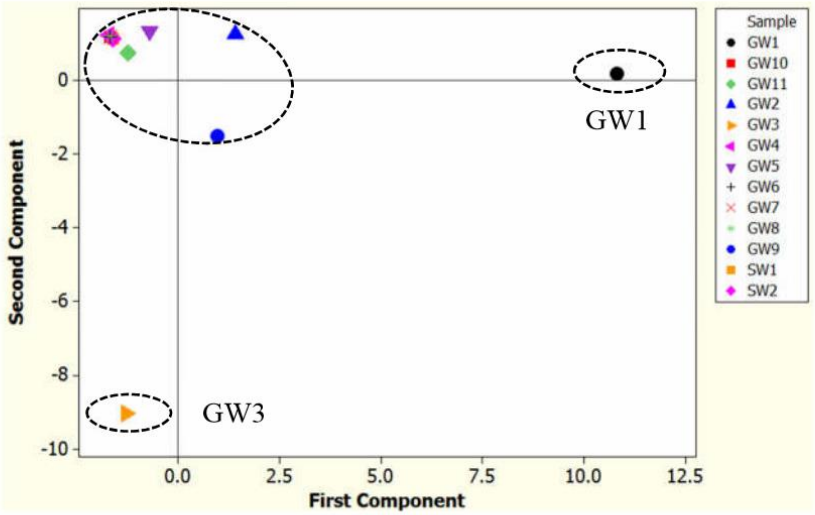

Fig. 3 The score plot of the PCA based on the relative contribution of PCDD/F and PCB congeners