Short Communication

Distribution of polychlorinated biphenyls in an urban riparian zone affected by wastewater treatment plant effluent and the transfer to terrestrial compartment by invertebrates

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HIGHLIGHTS

- The distribution of PCBs in an urban riparian zone around a wastewater effluent affected river was investigated.
- Relatively high abundances of PCB-11 and PCB-28 were found for most samples.
- Mid-chlorinated congeners (PCB-153 and PCB-138) were more accumulated in chironomids and dragonflies as well as soil dwelling invertebrates.
- Emerging invertebrates can carry waterborne PCBs to the terrestrial compartment.
- The estimated annual flux of PCBs from emerging chironomids ranged from 0.66 to 265 ng m⁻² y⁻¹.

GRAPHICAL ABSTRACT

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ABSTRACT

In this study, we investigated the distribution of polychlorinated biphenyls (PCBs) in a riparian zone affected by the effluent from a wastewater treatment plant (WWTP). River water, sediment, aquatic invertebrates and samples from the surrounding terrestrial compartment such as soil, reed plants and several land based invertebrates were collected. A relatively narrow range of $\delta^{13}\text{C}$ values was found among most invertebrates (except butterflies, grasshoppers), indicating a similar energy source. The highest concentration of total PCBs was observed in zooplankton (151.1 ng/g lipid weight), and soil dwelling invertebrates showed higher concentrations than phytophagous insects at the riparian zone. The endobenthic oligochaete *Tubifex tubifex* (54.28 ng/g lw) might be a useful bioindicator of WWTP derived PCBs contamination. High bioaccumulation factors (BAFs) were observed in collected aquatic invertebrates, although the biota-sediment/soil accumulation factors (BSAF) remained relatively low. Emerging aquatic insects such as chironomids could carry waterborne PCBs to the terrestrial compartment via their lifecycles. The estimated annual flux of PCBs for chironomids ranged from 0.66 to 265 ng m⁻² y⁻¹. Although a high prevalence of PCB-11 and PCB-28 was found for most aquatic based samples in this riparian zone, the mid-chlorinated congeners (e.g. PCB-153 and PCB-138) became predominant among chironomids and dragonflies as well as soil dwelling invertebrates, which might suggest a selective biodriven transfer of different PCB congeners.

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1. Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that consists of 209 possible congeners and have been prohibited for production and application because of their toxicity, bioaccumulation and high persistence (<http://chm.pops.int>). Wastewater derived from households and industrial activities have been shown to be potential sources of PCBs and can contaminate the surrounding environment through the effluents from wastewater treatment plants (WWTPs) (Blanchard et al., 2004; Wang et al., 2007). In recent years, 3,3-dichlorobiphenyl (PCB-11) has gained increasing interest because this congener is normally not found at significant level in common technical PCB mixtures (Frame et al., 1996). Nevertheless, PCB-11 was found at high concentrations in WWTPs in the New York city area (Litten et al., 2002) and even served as a tracer for wastewater effluents (Rodenburg et al., 2011). Rodenburg et al. (2010) found that PCB-11 was mainly associated with pigment manufacturing. Due to its relatively high volatility, PCB-11 has been prevalently found in Chicago air (Hu et al., 2008) and was even detected at relative high abundance in environmental samples from the Antarctica (P. Wang et al., 2012).

It is generally thought that transport of PCBs is mainly dominated by physical systems such as the atmosphere and ocean currents, but recent studies have revealed that biologically driven transfer through the behaviors and lifecycles of certain animals can also contribute to contaminant movement between compartments (Blais et al., 2007; Walters et al., 2010). Several studies have been carried out to explore the biodriven transfer of aquatic PCBs. For example, spiders which prey on aquatic insects can contribute to the flux of PCBs from sediment to the terrestrial ecosystem (Walters et al., 2010). Mayflies could bioaccumulate PCBs in sediment during the aquatic stage and transfer these to land in large quantities due to high reproduction cycles (Daley et al., 2011). These studies suggested that emerging aquatic insects might be important vectors of contaminants from the aquatic compartment to the terrestrial ecosystem. However, most previous studies focused on sediments contaminated from historical production of PCBs and few studies have shown a direct biomediated transfer of PCBs originated from WWTP effluent in urban areas. Because treated WWTP discharge can provide large amount of nutrients to the recipient environment, there could also be increased presence of invertebrates near by the effluent.

In this study, we collected river water, soil, sediment, vegetation and invertebrates in a riparian zone around the effluent of a large WWTP. We aimed to investigate and compare the levels of PCBs in all collected samples, study the biodriven transfer of PCBs from WWTP effluent to terrestrial compartment by emerging invertebrates and the potential bioaccumulation of PCBs in this urban riparian zone.

2. Materials and methods

2.1. Sample collection

The sampling was conducted around a river in north Beijing. A portion of this river is continuously receiving treated effluent from a WWTP with a wastewater treatment capacity of approximately 400,000 m³ per day. The river also receives diffuse effluents from households, drainage and small workshops. Sampling was conducted about 0.5 km downstream of the WWTP effluent in the summer of 2010. Several small dams are placed upstream of the WWTP effluent to control the river flow and are sometimes closed off which leads to occasional drying of the river bed upstream of the WWTP. Collection of soil and biota samples in upstream sites was not feasible because the upstream river bank was paved by concrete on both sides, but sediment and common reed samples were collected about 3.5 km upstream of the WWTP effluent. Common reed samples were pooled from about five individual plants. A water sample was collected in the river close to the WWTP

effluent and was stored at 2 °C before pretreatment. Composite sediment and tubifex tubifex samples (~100 individuals) were collected from the same spots using a sediment grabber. Zooplankton was sampled using plankton net with mesh size of 200 µm and transferred to a pre-cleaned glass bottle. Individual butterflies (n = 10), cicada (n = 2), large dragonflies (n = 5), small dragonflies (n = 5), large grasshoppers (n = 4) and small grasshoppers (n = 4) were composited to form a single sample for each species. Emerged chironomids were sampled by sweep net and pooled together to obtain sufficient quantity for subsequent analyses. A soil sample was pooled from five subsamples at a grass plain within 2 m from the stream shoreline where influence from the river water is most significant. Composite samples of earthworms (~50) and larvae of scarabs (also called white grubs, ~40) were collected from the soil sampling sites. These two terrestrial invertebrates are mostly buried under the soil surface, where earthworms feed on organic matter whereas white grubs mainly feed on plant roots.

A total of 21 composite samples were collected and labeled as WWTP effluent (WWTP-E), reed stem-leaf upstream (Reed-SLu), reed root upstream (Reed-Ru), reed stem-leaf downstream (Reed-SLd), reed root downstream (Reed-Rd), sediment downstream (Sed-d), sediment upstream (Sed-u), soil downstream (Soil-d), zooplankton (Zooplan), butterfly (Butt), chironomids (Chir), tubifex tubifex (Tubi), cicada (Cica), large dragonfly [Drag(L)], small dragonfly [Drag(S)], small grasshopper [Gras(S)], large grasshopper [Gras(L)], small scarabaeidae larva [Scar(S)], large scarabaeidae larva [Scar(L)], small earthworm [Earth(S)], large earthworm [Earth(L)]. All the biota, soil and sediment samples were wrapped in aluminum foil, sealed in ziplock bags, transported back to the laboratory within the same day. The different worms and larvae were placed on moist filter paper for 24 h in order to evacuate their gut contents. The plants (common reed) were washed with purified water and divided into roots and stem/leaf.

2.2. Chemicals

Native and labeled PCB standards (purity ≥ 98%, isotopic purity ≥ 99%), were purchased from Wellington Laboratories (Ontario, Canada). PCB surrogate standards (68A-LCS) include ¹³C₁₂-PCB-1, 3, 4, 15, 19, 37, 54, 81, 77, 104, 105, 114, 126, 155, 156, 157, 169, 188, 189, 202, 205, 206, 208 and 209. The internal standards (68A-IS) comprised of ¹³C₁₂-PCB-9, 52, 101, 138 and 194.

2.3. Sample pretreatment and instrumental analysis

The pretreatment and analysis of the different sample matrices is based on the isotope dilution quantification protocol outlined in the US EPA 1668 methods and has been described in our previous studies (Wang et al., 2007; Wang et al., 2010). Briefly, the solid samples were freeze dried, ground, spiked with labeled surrogate standards, extracted by accelerated solvent extraction (ASE), cleaned up by a multilayer silica column and further spiked with labeled internal standards before instrumental analysis.

Instrumental analysis was performed on a high resolution gas chromatography/high resolution mass spectrometer (HRGC-HRMS). The HRMS was operated in EI mode at a resolution ≥ 10,000. A total of 26 PCBs including 12 dioxin-like PCBs (PCB-77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189), 6 indicator PCBs (PCB-28, 52, 101, 138, 153, 180) and other 8 PCBs (PCB-3, 11, 15, 19, 202, 205, 208, 209) were quantified.

Stable isotopes were measured using a Thermo DELTA V Advantage isotope ratio mass spectrometer combined with a Flash EA1112 HT elemental analyzer (Thermo Fisher, Waltham, MA).

More details on the sample pretreatment, analysis and quality assurance and control can be found in the Supplementary Materials.

3. Results and discussion

3.1. Stable carbon and nitrogen isotope analysis

Generally, higher $\delta^{15}\text{N}$ values indicate a higher trophic position for an organism in same food web, whereas similarities in $\delta^{13}\text{C}$ signatures indicate same primary carbon source (Jardine et al., 2006). Plotting the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values can provide useful information on the structure and interactions of the food web in our study (Fig. 1). The lower $\delta^{15}\text{N}$ value of downstream sediment (3.4‰) compared with the upstream sediment (4.4‰) might be due to the influence of WWTP effluent. This difference was also reflected in the somewhat higher $\delta^{15}\text{N}$ values in upstream reed plants (Fig. 1, inset). These results are also consistent with previous reports. For example, the $\delta^{15}\text{N}$ values for sediment and biota samples collected in Boston Harbor, which was historically affected by sewage sludge, tended to be lower than those in the adjacent Massachusetts Bay (Tucker et al., 1999). Distinctly different isotopic signatures were observed between reed plants and the other samples. The reeds samples were more depleted in ^{15}N and significantly enriched in ^{13}C compared to the riparian invertebrates, and their $\delta^{13}\text{C}$ signatures ($-13.5 \pm 0.3\text{‰}$) are also typical for C4 plants (Wang et al., 2006).

The $\delta^{13}\text{C}$ values of the invertebrates (except butterflies, grasshoppers) were within a relatively narrow range from -26.2‰ to -23.2‰ , indicating that the invertebrates had a similar energy source. Fry et al. (1978) found that grasshoppers feeding on both C3 and C4 plants showed intervening $\delta^{13}\text{C}$ values. In our study, grasshoppers have higher $\delta^{13}\text{C}$ values (-18.1 and -17.7‰), which approached those found in C4 plants grown in northern China ($-12.1 \pm 2.5\text{‰}$; Wang et al., 2006). These suggested that grasshoppers might be generalists but have a C4-based diet preference. In contrast, the $\delta^{13}\text{C}$ signature in butterfly was relatively lower than the rest and may be explained by C3 based food sources, which generally display higher degree of ^{13}C depletion (Wang et al., 2003).

Riparian particulate organic matter is a major food source for larval chironomids, and emerging adults usually only has a life span of a couple of days. The downstream sediment, chironomids and dragonflies were in a direct sediment based food chain as indicated by the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis.

3.2. Total PCB levels and comparisons among environmental samples

All PCB concentrations are reported on a dry weight basis and normalized to extractable lipid content (lipid weight, lw) for biota/

vegetation and total organic carbon (OC) for soil and sediment samples (Table SI-1). The concentration of $\sum$ PCBs in the WWTP affected river water was 174.0 pg/L. The $\sum$ PCBs in downstream sediment (103.8 ng/g OC) was higher than those in upstream sediment (54.73 ng/g OC). For common reed samples, similar $\sum$ PCB levels were found in upstream and downstream sites, but when normalized with lipid content the $\sum$ PCBs in downstream reeds (root: 30.27 ng/g lw, stem-leaf: 14.07 ng/g lw) were somewhat lower than the upstream reeds (root: 66.20 ng/g lw, stem-leaf: 17.49 ng/g lw).

$\sum$ PCB concentrations among invertebrates ranged from 7.695 to 151.1 ng/g lw. Among terrestrial invertebrates, earthworms and larvae of scarabs (23.43 to 71.78 ng/g lw) showed higher concentrations than phytophagous invertebrates such as cicadas, grasshoppers and butterflies (7.695 to 26.95 ng/g lw). This might be related to the intimate contact with soil (139.5 ng/g OC) for the soil-dwelling invertebrates. Zooplankton (151.1 ng/g lw) showed the highest $\sum$ PCB concentration among all samples. Emerged chironomids and dragonflies (12.39 to 24.00 ng/g lw) showed lower concentrations than tubifex worms (54.28 ng/g lw). Tubifex tubifex are endobenthic worms and typical bioindicators of wastewater effluents because of their high tolerance towards organic pollution and low oxygen conditions (Bouché et al., 2000). Tubifex worms were not found at upstream sites which further imply the influence of the WWTP effluent to their abundance. These worms are also known to be a food source for some fish species and might therefore further transfer high load of PCBs up through the aquatic food chain. The relatively lower concentrations of chironomids and dragonflies might be due to inter-species differences and the result of biodilution or biotransformation.

3.3. Potential bioaccumulation in aquatic and terrestrial food webs

Biota-sediment/soil accumulation factors (BSAFs) for $\sum$ PCBs were less than unity for relevant downstream invertebrates and reeds indicating that PCBs in this area are strongly sorbed to particulate matter in sediment and soil, or that equilibrium conditions have not been reached (Table SI-2). The BSAFs of earthworms (0.51 and 0.42) were within the range of those found in a typical electronic waste dismantling area in east China (range 0.1–3; Shang et al., 2013). There was also a difference in bioaccumulation potential among the different compartments of reeds, where the roots tended to accumulate more PCBs than the reed stem and leaf. Among aquatic invertebrates, the BSAF for tubifex worms (0.52) was comparable to those of oligochaetes in field samples (0.87) reported by Ankley et al. (1992). However, the BSAF of chironomids (0.18) was significantly lower than chironomids in Crab Orchard Lake (12.19 for male and 0.95 for female; Maul et al., 2006), and also lower than those found in chironomid larvae and adults from a highly contaminated area, the Biesbosch (2.4 and 1.5; Reinhold et al., 1999). These might be explained by the specific individual PCB congeners selected for analysis among different studies, steady state conditions, limnological characteristics and different sources.

In general, chemicals are considered to be bioaccumulative if the bioaccumulation factors (BAFs) exceed 5000 in aquatic organisms (Kelly and Gobas, 2001). In this study, BAFs for $\sum$ PCBs ranged from 71,080 to 870,700 in different aquatic invertebrates (Table SI-2). Significantly higher BAFs were observed in zooplankton and tubifex worms (870,700 and 312,300). If assuming that emerging chironomids and dragonflies have the same concentrations as their larvae, then their BAFs were 71,080 to 138,400, respectively. Significant parabolic correlations were found between $\log$ BAF and $\log K_{ow}$ of individual PCB congeners ($R^2 = 0.24\text{--}0.56$, $P < 0.05$), as shown in Fig. SI-1. The results are consistent with many previous studies which show that mid-chlorinated congeners have higher bioaccumulation potential, such as those in fish species from a WWTP affected lake (Wang et al., 2007).

Fig. 1. The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values among all samples. The inset shows the vegetation samples.

3.4. Congener compositions and correlations among the samples

The contribution of specific homologues to total PCBs (mono-deca) is shown in Fig. 2, whereas individual PCB congener profiles of representative samples can be found in Fig. SI-2. Principal component analysis (PCA) was used on the composition normalized dataset to investigate the similarities in PCB congener profiles among the samples. PCB19 was not detected in the samples and was excluded in this analysis. Three principal components (PCs) were extracted which accounted for 95% of total variance. The first component (PC1, 45%) was significantly correlated with aquatic based samples (Fig. 3). The di- and trichlorinated PCBs (PCB-11 and PCB-28) were most abundant in the WWTP effluent, which respectively accounted for 47% and 29% of Σ PCBs. A relatively high percentage of PCB-11 was also found in downstream soil and sediment (19% and 21%, respectively). Compared to soil, PCB congener patterns in reeds were more consistent with river water, which might indicate direct plant uptake of dissolved PCBs. However, Chu et al. (2006) found that the common reed tended to adsorb higher chlorinated PCB congeners under hydroponic conditions. The discrepancies between the results might be due to the dominance of PCB-11 and PCB-28 in soil pore water in this area. Reed plants might be representative food sources for the phytophagous invertebrates, such as grasshoppers and butterflies in this food web, as similar congener patterns were found. This further indicates that waterborne PCBs could be transferred to the terrestrial food chain by riparian vegetation. The second principal component (PC2, 33%) was positively correlated with most terrestrial samples (soil, earthworms, scarab larvae, chironomids and dragonflies), and showed relationship with high relative levels of the hexachlorinated PCB-153 and PCB-138. This could be explained by the higher bioaccumulation potential of these hexachlorinated congeners compared to most lower and higher chlorinated homologues (Van Praet et al., 2012). The third component (17%) was highly correlated with downstream sediment, tubifex worms and plankton. The similar PCBs congener pattern between tubifex and downstream sediment further support the premise that these worms can be suitable bioindicators of sewage effluent derived POPs contamination.

Decachlorobiphenyl (PCB-209) was also found in the WWTP effluent (0.8%) but remained at relative low proportion among the invertebrates (0.6–2.4%), which is likely due to reduced absorption efficiency and bioaccumulation potential of this very hydrophobic congener. PCB-209 is not usually found in technical mixtures but has recently been found at remarkably high levels in some sewage sludge samples from Beijing (Guo et al., 2009) and also in wastewater irrigated farm soils (Wang et al., 2010). The specific sources of PCB-209 are currently not well known but might be related to industrial activities and the use of certain commercial products.

3.5. Transport of PCBs from aquatic to terrestrial compartment by chironomids

Chironomids, dragonflies and other emerging aquatic insects can relocate a considerable amount of aqueous biomass to terrestrial habitats. A rough estimation of the annual flux (F) of PCBs ($\text{ng} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$) transferred by emerging chironomids was conducted using a simplified model:

$$F = P \times E \times C \quad (1)$$

where P is the annual production of chironomids larvae biomass (dry weight) per square meter sediment ($\text{g} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$), E is the proportion of produced biomass that is removed by adult emergence (dimensionless), C is the concentration of PCBs in chironomids (2.653 ng/g dry weight).

A low and high P value (1 and $100 \text{ g} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$) was selected based on the assumptions from Menzie (1980), while E was chosen as 0.25 and 1. The results showed that the estimated annual flux of PCBs for chironomids ranged from 0.66 to $265 \text{ ng} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$. This range is much lower than the estimated PCBs flux of about $20 \text{ } \mu\text{g} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ by chironomids around a sewage treatment plant in Sweden (Larsson, 1984) and in Lake Hartwell (Raikow et al., 2011). This is also lower than the net atmospheric flux (343 – $16200 \text{ ng} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$) of PCBs in a lake at another part of Beijing which also receives WWTP effluent (Y.W. Wang et al., 2012). However, compared to volatilization/deposition processes at the air–water interface, the insect mediated transfer of aquatic pollutants to land could generally be considered a net positive transfer process. The emerging insects could also transfer waterborne PCBs directly to terrestrial predators such as odonata, spiders, insectivorous birds and bats.

4. Conclusion

We found in this study that the investigated urban riparian ecosystem could be affected by PCBs contamination from a river affected by effluents from wastewater treatment plant. The low chlorinated non-Aroclor congener PCB-11 and the indicator congener PCB-28 were the predominant PCB congeners among most aquatic based samples. Chironomids and dragonflies as well as soil dwelling invertebrates showed relatively high accumulation of mid-chlorinated congeners (PCB153 and PCB138), although no apparent biota-soil/sediment accumulation was found for total PCBs. High bioaccumulation factors were however observed in collected aquatic invertebrates. The estimated annual flux of PCBs for chironomids ranged from 0.66 to $265 \text{ ng} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ in this area. This is probably an underestimation of the insect mediated PCBs transport to the

Fig. 2. Contribution of specific homologue to total analyzed PCBs (mono-deca).

Fig. 3. Loading plot of PC1 and PC2 from principal component analysis for the composition normalized dataset. Tubifex, plankton and downstream sediment were highly correlated with PC3 (plot not shown).

terrestrial compartment as other emerging aquatic invertebrates (such as mayflies and caddisflies) could also be abundant in this area. A limitation of this study is the low number of sampling sites and field samples, and more extensive work is needed to further investigate the biodriven transfer of POPs from urban wastewater to the surrounding terrestrial compartment.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.06.006>.

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