

Atmospheric Deposition of Polychlorinated Naphthalenes in Dongjiang River Basin of Guangdong Province, South China

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Abstract—Atmospheric deposition of polychlorinated naphthalenes (PCNs) was investigated at 10 sites in Dongjiang River basin of Guangdong Province South China, during the winter and summer of 2010. The average daily deposition flux of total PCNs was 828 pg/(m²·d), and the corresponding TEQ was 0.14 pg/(m²·d). Based on these values, the presumed average annual deposition of total PCNs was 8.5 kg for Dongjiang River basin within Guangdong province, and the corresponding TEQ was 1.3 g. Tri-CN_s dominated the deposition fluxes in all samples and contributed to more than 50% of total PCNs. In addition, high contents of higher chlorinated PCNs (penta-CN_s to octa-CN_s) implying the source areas were discovered in Guangzhou and Dongguan instead of Huizhou. Spatially, the average daily deposition fluxes of PCNs in Guangzhou city and Dongguan city were much higher than those in less developed Huizhou city. Seasonally, the fluxes were generally higher in summer than in winter, while the corresponding TEQ fluxes were the reverse. The results indicated the PCNs emissions in the Dongjiang River basin could be ascribed to both the combustions and other sources, while to contemporary PCNs the combustion sources was becoming important.

Keywords: polychlorinated naphthalenes, South China, atmospheric deposition, source, daily deposition flux

INTRODUCTION

Polychlorinated naphthalenes are a group of chemicals consisting of naphthalene substituted with 1–8 chlorine atoms, yielding 75 possible congeners. Historically, they were used for their thermal stability in dielectric fluids and insulators (Falandysz, 1998). PCNs have been identified as persistent, toxic, and bioaccumulative substances. Production figures for PCNs are unavailable, but have been estimated to be around 150,000 tonnes (Falandysz, 1998). PCNs are no longer commercially produced ever since 1977, but they are still routinely observed in air (Helm *et al.*, 2004; Mari *et al.*, 2008), soil (Nadal *et al.*, 2007), and sediment (Castells *et al.*, 2008). Evaporation from old or in-use products containing

PCNs and PCBs, and release during waste, residential, commercial, agricultural, and other combustions are still the sources of PCNs to the environment (Falandysz, 1998). In addition, several studies suggested that the contributions of combustion related PCNs to the total PCNs in environmental media had increased over the past a few decades (Meijer *et al.*, 2001; van der Gon *et al.*, 2007).

The present study was carried out in Dongjiang River basin of Guangdong Province, South China. Dongjiang River (or the East River), a tributary of the Pearl River, supplies potable water for lots of cities including Guangzhou, Dongguan, and Hong Kong etc. Highly developed industries such as electronic and mechanical processing industries in Dongguan city may pose a potential pollution to the Dongjiang River. The purpose of this research is to investigate the fluxes of the atmospheric deposition and sources of PCNs within Dongjiang River basin, and to evaluate the potential effects of PCNs to the Dongjiang River.

MATERIALS AND METHODS

Deposition sampling

As shown in Fig. 1, atmospheric depositions at 10 sites within Dongjiang River basin and 1 control site in Guangzhou city (GZ) were collected every month during the winter (January and February) and summer (July and August) of 2010. The collection of wet and dry deposition samples was achieved together using a stainless steel barrel (Diameter, 25 cm; High, 45 cm). All of the samplers were placed on the top roofs of buildings about 20 m high. Deionized water (4 L) and a few algaecides were added into the sampler. At the end of sampling period, water was collected using amber glass bottles, while particles inside the sampler were wiped with cleaned absorbent cotton (extracted with DCM for 72 h). All of the samples were transported to the laboratory and analyzed immediately.

Sample extraction and analysis

Deposition sample was first passed through glass-fiber filter (GF/F; diameter, 14.2 cm) to divide into water phase and particle phase.

Water phase: The water phase was added with surrogate standards (¹³C-trans-Chlordane and PCB 209) and adsorbed by XAD (Purified by Soxhlet extracting with methanol, acetone, DCM, methanol each for 24 h). After adsorption, the XAD was eluted with 150 ml of methanol, followed by 150 ml of DCM. The methanol within the elution was separated from the DCM by liquid-liquid extraction with 300 ml deionized water, and the rest water was extracted 5 times with 50 ml of DCM. The DCM portions were combined and dried with anhydrous sodium sulfate.

Particle phase: Absorbent cotton and glass fiber filter were Soxhlet extracted with DCM for 48 h. The extract and the elution of XAD resin were combined, exchanged into hexane, and evaporated to approximately 1 ml. The extract was first fractionated by a sulfuric acid-silica gel column, and then purified with a multi-layer column filled with anhydrous Na₂SO₄, florisil (2% deactivated),

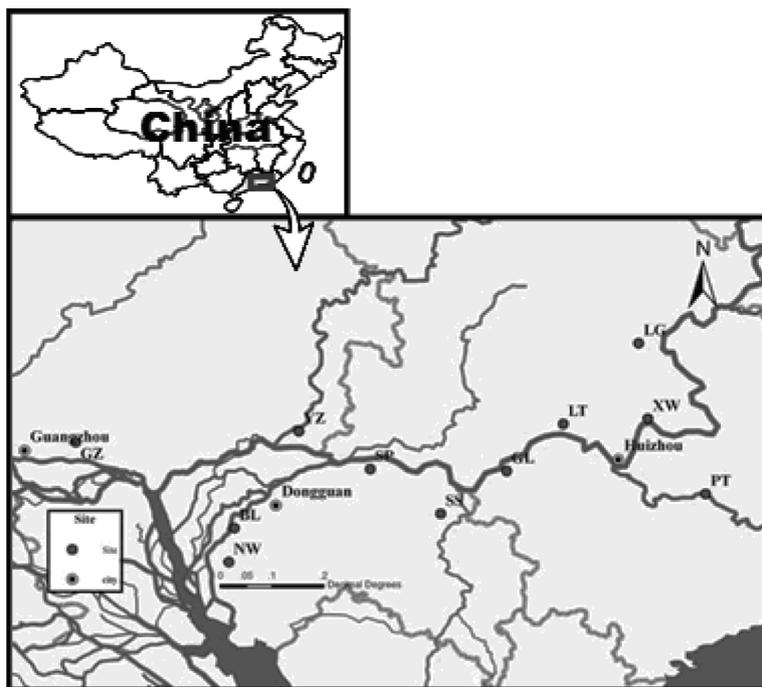


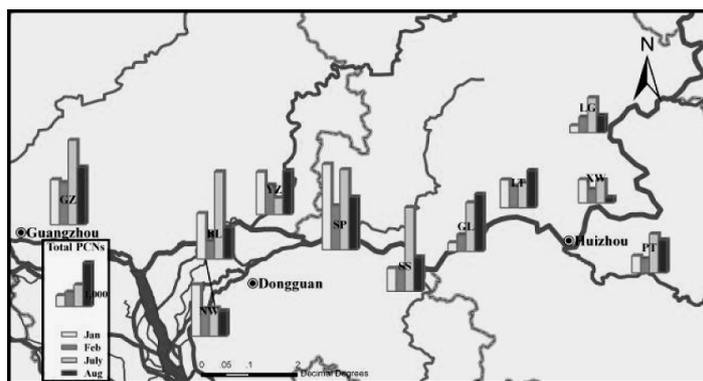
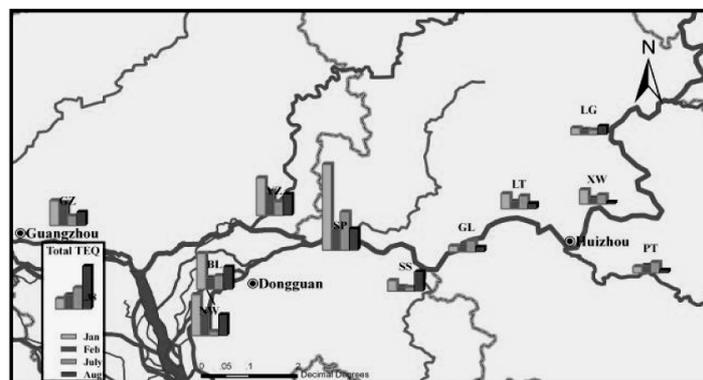
Fig. 1. Map of sampling locations.

neutral silica gel (3% deactivated) and neutral alumina (3% deactivated) from top to bottom. After being micro concentrated to approximately $50 \mu\text{L}$, pentachloronitrobenzene (PCNB) was added as the internal standard.

PCNs were analyzed by GC-ECNI-MS in selected ion monitoring mode on a DB-5ms column ($30 \text{ m} \times 0.25 \text{ mm i.d.} \times 0.25 \mu\text{m}$ film thickness) with methane as the reagent gas. The initial oven temperature was set at 80°C for 0.5 min, $15^\circ\text{C}/\text{min}$ to 160°C , $3^\circ\text{C}/\text{min}$ to 240°C , and $6^\circ\text{C}/\text{min}$ to 270°C held for 10 min. PCN congeners were quantified against a technical PCN mixture Halowax1014 containing known amounts of tri- to octa-CNs (Helm *et al.*, 2004).

QA/QC

A procedural blank was run with each batch of 11 samples. The results showed only CN 27/30, 51, 49 were detected in blanks with average values of 0.11, 0.70, and 0.29 ng/g, respectively. The surrogate recovery for ^{13}C -trans-Chlordane and PCB 209 in all samples was 73–109% and 86–108%, respectively. The reported results were corrected by the blanks, but not by the surrogate recoveries.

a- Σ PCNs

b-TEQ

Fig. 2. Distributions of Σ PCNs and TEQ deposition fluxes (a- Σ PCNs, b-TEQ).

RESULTS AND DISCUSSION

Deposition fluxes

The deposition fluxes of Σ PCNs (total PCNs) ranged from 131 to 2,000 $\text{pg}/(\text{m}^2 \cdot \text{d})$ with an average of $828 \pm 503 \text{ pg}/(\text{m}^2 \cdot \text{d})$ (Fig. 2a). The deposition fluxes of PCNs corresponding TEQ in the current study ranged from 0.02 to 0.75 $\text{pg}/(\text{m}^2 \cdot \text{d})$ with an average of $0.14 \pm 0.13 \text{ pg}/(\text{m}^2 \cdot \text{d})$ according to the reference of Noma *et al.* (2004) (Fig. 2b).

The average annual total PCNs deposition and the corresponding TEQ for Dongjiang River basin within Guangdong province were presumed by dividing this area into the upstream and the downstream parts. The upstream part (23,540

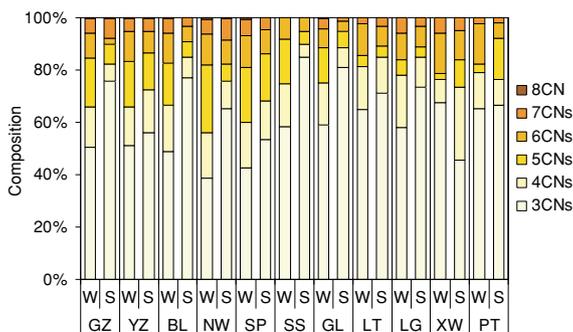


Fig. 3. Compositions of PCN homologues (W: mean of winter samples; S: mean of summer samples).

km²) was less polluted; while the downstream part (8300 km²) was seriously contaminated. According to the locations, LG, PT, XW, LT, GL, SS were used to estimate the annual deposition value of the upstream part, while YZ, BL, NW, SP were used to estimate the downstream one. The average value at each site was employed in this calculation. The annual deposition values of Σ PCNs for the upstream and downstream parts were 5.3 and 3.2 kg, respectively; and the annual deposition values of corresponding TEQ were 0.6 and 0.7 g, respectively.

Few researches have drawn attention on the atmospheric deposition of PCNs. Though Egeback *et al.* (2004) had mentioned the composition of PCNs in the atmospheric deposition; he did not present any solid results somehow. PCNs are structurally similar to polychlorinated biphenyls (PCBs) making the properties of those two groups of compounds alike. The deposition fluxes of PCN-TEQ in Dongjiang River basin (0.02–0.75 pg/(m²·d)) were lower than those (1.5 pg/(m²·d)) of PCB-TEQ in Guangzhou city (Ren *et al.*, 2010), and also much lower than those (0.35–43 ng/(m²·yr), *viz.* 0.96–118 pg/(m²·d)) in Kanto Region, Japan (Ogura *et al.*, 2001). In addition, the deposition fluxes of PCNs in this area (131–2000 pg/(m²·d)) were lower than those (1342–20,362 pg/(m²·d)) of PCBs in Turkey as well (Birgul and Tasdemir, 2011).

Homologue patterns

Among all the PCN homologues, tri-CNs was the most dominant one accounting for more than 50% in most samples (Fig. 3). The relevant abundances of PCN homologues in deposition samples decreased with the increasing of chlorine atom number. It had been reported that each additional chlorine substitution increased the affinity to 1-octanol, but decreased the vapor pressure of PCNs (Lei *et al.*, 1999). This led to the more volatile homologues like tri-CNs showed a much higher abundance than the less volatile homologues (tetra- to octa-CN) in air (Falandysz, 1998). Similar observations were found in air by Helm *et al.* (2003), Lee *et al.* (2005) and Egeback *et al.* (2004).

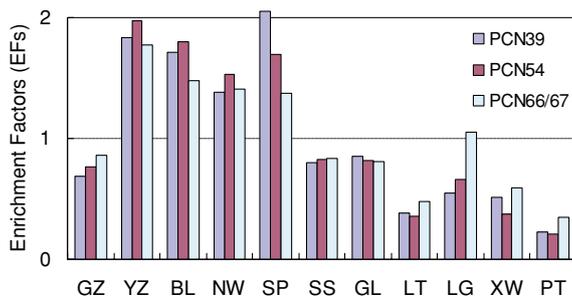


Fig. 4. Enrichment factors of combustion marker PCNs.

However, as shown in Fig. 3, the homologue patterns changed with sampling areas making the relevant abundances of higher chlorinated PCNs (penta- to octa-CN) higher in deposition samples of Guangzhou and Dongguan than those in samples of Huizhou. Higher chlorinated PCNs mainly associate with particles making them difficult to transfer to the areas far from the point source. Hence, the sites where high percentage of higher chlorinated PCNs was observed might be close to the PCNs sources.

Spatial and seasonal trends of PCNs fluxes

For the average deposition flux of total 4 samples, the highest one was in SP site, while the lowest one still in XW site (Fig. 2). Though the deposition fluxes of PCNs varied with the sampling sites, higher flux samples were mainly from eastern part of Guangzhou and northern part of Dongguan. Guangzhou and Dongguan are much more developed than Huizhou with large population, prosperous economy and numerous industry parks. Considering the high developed economy, there might be plenty of sources of POPs like PCNs, such as emissions from historical usage, by-products of various combustions, and metals refining, etc. Other POPs like PBDEs (Wang *et al.*, 2007b) and PCBs (Wang *et al.*, 2007a) were also higher in Guangzhou and Dongguan than in Huizhou.

Due to different physicochemical properties and sources, there can be a large seasonal variation in the atmospheric deposition fluxes of PCNs. In general, PCN flux was higher in summer than in winter, while the corresponding TEQ was higher in winter (Fig. 2). The main processes contributing to the deposition of PCNs here are dry deposition (most are with particles), wet deposition (by rain scavenging of vapour- and particle-adsorbed chemicals) (Cousins *et al.*, 1999), making the deposition flux relevant with the seasonal precipitation and temperature. PCNs are apt to volatilize to the air in summer when the temperature is getting warmer. In addition, the precipitation as well as the wet deposition of PCNs by in-cloud or below-cloud scavenging or rain-out processes was also high. Meanwhile, the TEQ related PCNs are mostly penta- to hexa-CN. Hence, the deposition fluxes of PCNs corresponding TEQ consisted with higher chlorinated

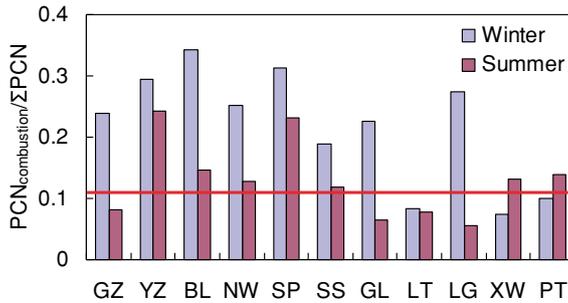


Fig. 5. Fractions of combustion-related PCN congeners to total PCNs (Line: composition of combustion-related PCNs in Halowaxes, 0.11).

PCNs. The deposition value of particles might dominate the TEQ flux for the reason that more than 80% of hexa-CN_s was adsorbed by particles. Particle deposition was higher in winter as a result of the low precipitation making the TEQ deposition increased as well.

Combustion input of PCNs

Relative to technical PCN formulations, combustion-derived PCNs exhibit subtle differences in congener composition and are enriched in what are referred to as “combustion marker” PCNs (Meijer *et al.*, 2001; Takasuga *et al.*, 2004). CN 39, 54, and 66/67 are the most popular and relatively abundant indicator markers. Figure 4 shows the enrichment factors (EFs) for these three combustion markers at each site. EF was calculated via dividing the congener’s mean annual contribution to sum PCNs (i.e., mean of all four samples for each site) by the annual average value for all sites (Harner *et al.*, 2006). EF displays the mass contribution of a PCN congener at the specific site relative to its average contribution in all sites. Generally, the EF values for each of the 3 marker PCNs are consistent. The higher contributions of combustion markers mostly occurred at the developed sites (e.g., BL, NW, SP in Dongguan, and YZ in Guangzhou) where numerous combustion relevant sources of PCNs may be involved. Helm *et al.* (2003) suggested a connection between levels of co-eluting congeners 66/67 with incineration and iron sintering processes. Thus, it is likely that the higher contribution of CN 66/67 at developed sites located in Dongguan and Guangzhou may be due to the high levels of industrial activities in these regions.

The fraction of combustion-related PCN congeners (CN 17/25, 36/45, 27/30/39, 35, 52/60, 50, 51, 54, 66/67) to total PCNs ($PCN_{combustion}/\Sigma PCN$) could provide an evidence for the importance of combustion sources (Lee *et al.*, 2007). This fraction for the Halowaxes is less than 0.11 as estimated from the data provided by Noma *et al.* (2004). Figure 5 shows that YZ, BL, NW, SP, SS have higher compositions of combustion-related PCNs than Halowaxes (0.11) in both winter and summer. This suggested that the contributions of combustion-associated

PCNs to PCNs contaminations in those developed industry areas had become more important than historical emissions. As usage of PCNs had been banned for decades, the combustion-derived PCNs have played a more and more important role than past-use PCNs in the contributions toward PCNs emissions in Dongjiang River basin, especially for the developed industry areas.

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