Passive air monitoring of PCBs and PCNs across East Asia: A comprehensive congener evaluation for source characterization

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Abstract

A comprehensive congener specific evaluation of polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in the atmosphere was conducted across East Asia in spring 2008, applying polyurethane foam (PUF) disk passive air sampler (PAS) as monitoring device. Mean concentrations derived for Japan, China and Korea were 184 ± 24, 1100 ± 118, and 156 ± 20 pg m⁻³ for Σ₂₀₂ PCBs, and 9.5 ± 1.5, 61 ± 6, and 16 ± 2.4 pg m⁻³ for Σ₆₃ PCNs, respectively. Relative to reported data from 2004, the present results suggest that air PCBs concentrations have not changed much in Japan and Korea, while it has increased by one order of magnitude in China. From principal component analysis, combustion emerged highly culpable in contemporary emissions of both PCBs and PCNs across the East Asian sub-region. Another factor derived as important to air PCBs was re-emissions/volatilization. Signals from PCBs formulations were also picked, but their general importance was virtually consigned to the re-emissions/volatilization tendencies. On the contrary, counterpart PCNs formulations did not appear to contribute much to air PCNs.

Keywords:
PCBs, PCNs, Passive air sampling, Principal component analysis

1. Introduction

PCBs and PCNs are organic compounds with remarkable chemical and thermal stability and have been variously applied in industry for many useful purposes, e.g., as insulators, lubricants, plasticizers, flame retardants, dielectric fluids, paint additives, etc. Their production and new use however were prohibited in the 1970s to 1980s following the realization that they are highly toxic, bioaccumulate in biological systems and show great resistance to environmental degradation (IPCS, 2001, 2003; Birnbaum et al., 2000; Yao et al., 2002; Hong et al., 2003; Mai et al., 2005; Wu et al., 2009). There is historical evidence of massive industrialization in this region (Jaward et al., 2005; Pozo et al., 2006, 2009; Lee et al., 2007). With air transport constituting the major pathway by which they are distributed globally, it is presumed that monitoring and understanding their behavior in air should yield valuable information towards their elimination (Jones and de Voogt, 1999; Cousin et al., 2004; Schmidt, 2010).

Presently, the Asian region is recognized as harboring some of the global hotspots of POPs, perhaps a direct consequence of the massive industrialization in this region (Jaward et al., 2005; Pozo et al., 2006, 2009; Lee et al., 2007). There is historical evidence of industrial application of both PCBs and PCNs formulations in East Asian countries such as Japan, China and Korea (Yamashita et al., 2006, 2009; Lee et al., 2007). With air transport constituting the major pathway by which they are distributed globally, it is presumed that monitoring and understanding their behavior in air should yield valuable information towards their elimination (Jones and de Voogt, 1999; Cousin et al., 2004; Schmidt, 2010).

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yield the earliest response when screening for evidence of POPs attenuation (Harner et al., 2006). In the present study, wide-scale air monitoring of PCBs and PCNs was undertaken, applying the polyurethane foam (PUF) disk passive air sampler (PAS). The PUF disk PAS has great utility as air POPs monitoring device (in view of its simplicity to cost effectiveness), especially when the focus is to generate spatially resolved data for insights into the behavior and trends of POPs at the local, national, regional or even global level (Jaward et al., 2004, 2005; Pozo et al., 2006, 2009; Klanova et al., 2007a,b; Lee et al., 2007; Baek et al., 2008; Mari et al., 2008b; Zhang et al., 2008a,b; Li et al., 2009).

The present study utilized environmental chemometric models to characterize pertinent source factors of PCBs and PCNs presently impacting the East Asian region. The objective was to offer an understanding regarding which source factors were most implicated in the spatial distribution of these pollutants, based on statistical evaluation of their congener composition. Appropriate comparisons were made to preceding studies to generate ambient cated in the spatial distribution of these pollutants, based on statis-

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2. Materials and methods

2.1. Study area, sampling process and pre-treatment

The monitoring space for this study was designed along that

utilized by Jaward et al., 2005. Fifty-five sites in Japan (37 rural, 4

sub-urban and 14 urban), 20 in China (3 rural and 17 urban), 30 in

Korea (12 rural, 2 sub-urban and 16 urban) and 1 in Taiwan were

simultaneously monitored (Table A.1), applying the flying saucer shaped PUF disk PAS described in detailed elsewhere (Shoeb and Harner, 2002; Jaward et al., 2004). The samplers were deployed for 8 weeks, from 21st March to 16th May, 2008. Deployment points extended between latitude 18–45°N and longitude 102–145°E. The PUF disks were supplied by Klaus Ziemer GmbH, Germany, and have the following parameters: diameter – 14 cm; thickness – 1.35 cm; surface area – 365 cm²; mass – 4.40 g; volume – 207 cm³; and density – 0.0213 g cm⁻³. Prior to assembling of samplers for subsequent deployment, PUF disks were pre-extracted; first by washing in water and then soxhlet extracted with acetone for 12 h. The PUF disks were then dried under vacuum, sealed in poly-bags, wrapped in aluminum foil and stored in the dark at room temperature until required for deployment. The samplers were assembled at the National Institute for Agro-Environmental Sciences (NIAES), Tsukuba, Japan, sealed in fairly large poly-bags and dispatched in sealed brown boxes to volunteers at the various sampling points for simultaneous deployment. At the end of the deployment period, PUF disks were harvested and returned to NIAES for chemical analysis.

2.2. Chemical analysis

Harvested PUF disks were soxhlet extracted with acetone for approximately 12 h and concentrated to 50 mL. in supporting document. In summary, the clean-up process consisted of three steps. Step 1 – elution with hexane through the combined silica gel and activated carbon columns (captured non-planar PCBs). Step 2 – the activated carbon column was detached and subjected to elution with 25% dichloromethane (DCM) in hex-

ane (captured mono dioxin-like PCBs). Step 3 – further elution through the activated carbon column with toluene (captured PCNs and non-ortho dioxin-like PCBs). The hexane fractions were combined and concentrated (using rotary evaporator) to about 1 mL. The toluene fraction was similarly concentrated. Five hundred (500) pg of injection spikes – 12C12-PCB (MBP-153, Wellington Laboratories Inc.) and 12C12-PCN (ECN-5260, Cambridge Isotope Laboratories Inc.) – in decane solution were respectively added to the hexane and toluene fractions. Each fraction was reduced to a final volume of 50 µL under a gentle stream of nitrogen. In the process, the respective solvents were each exchanged to 50 µL of decane containing the injection spike as internal standard. PCBs and PCNs in samples were quantified congener specifically using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) (Micromass AutoSpec-Ultima). DB-5 MS (J&W Sci-

2.3. Statistics

2.3.1. k-Means clustering

k-Means clustering is a type of cluster analysis with the goal of partitioning n observations into k clusters (k ≤ n). In this study, k-means clustering was executed with Statistica 7 software. The k-means algorithm ensures that each observation is placed in a cluster with the nearest mean, such that within-cluster variance is minimized and between cluster–cluster variance maximized (Statsoft Inc, 2011). The objective of applying k-means clustering in the present study was to create distinctive clusters of sites based on the levels of emissions emanating from these sites. The essence was to find out whether sites in each cluster shared characteristics that might account for the common extent of emissions associated with that cluster.

2.3.2. Principal component analysis (PCA)

PCA is a multivariate exploratory technique applied to reduce the number of variables and detect structure in a large dataset based on correlation or co-variance matrix. Simply, in a dataset, variables that are highly correlated converge into a single latent factor or principal component (PC). To this extent, the PCs so extracted often do not correlate with each other and each portrays
an independent factor. Typically, the first extracted PC accounts for majority of the variance in a dataset, with subsequent components accounting for progressively less. Hence, the first few PCs, together, contribute the greatest percentage of total variance and constitute the major PCs. The major PCs when plotted on a scatter plot, often upon appropriate rotation, allow visualization of the structure underlying a particular dataset. Such plots, known as factor loadings plots, project the relationship between the major PCs and variables. In chemical contamination studies, the point of interest in source characterization when performing a PCA is, first, to identify the cluster of chemical species correlating with a particular PC. Then, to find out what this group of species might inform about a source based on identifiable reference marker species. In this study, PCA was conducted with Statistica 7 software (Statsoft Inc, 2011).

3. Results and discussion

3.1. Spatial distribution of PCBs and PCNs

Out of 202 PCB and 63 PCN congeners screened, 142 PCBs and all of the 63 PCNs were routinely detected and quantified across the various jurisdictions (co-eluents were counted as multiple congeners). The range of total ambient air PCBs and PCNs concentrations were as follows: \( \sum_{202} \text{PCBs (Cl}_{2-8}\text{)} \text{(pg m}^{-3}\text{)} \) – Japan = 40–760 with a major outlier at 7300; China = 300–2500 with a major outlier at 7700; Taiwan = 317; Korea = 36–600; and \( \sum_{63} \text{PCNs (Cl}_{1-4}\text{)} \text{(pg m}^{-3}\text{)} \) – Japan = 2–77 with a major outlier at 160; China = 23–110; Taiwan = 22; Korea = 3 to 59 (Fig. 1; Tables A.3 and A.4). Excluding the major outliers, averagely, \( \sum_{202} \text{PCBs (pg m}^{-3}\text{)} \) (mean ± standard error) in Japan, China and Korea were respectively 184 ± 24, 1100 ± 118, and 156 ± 20; while \( \sum_{63} \text{PCNs (pg m}^{-3}\text{)} \) were respectively 9.5 ± 1.5, 61 ± 6, and 16 ± 2.4. Thus, on the average, air PCBs concentration in Japan and Korea was comparable, while that of China was much higher. Air PCNs concentrations were least in Japan and highest in China. The PCBs were generally one to two orders of magnitude greater than the PCNs.

Very high PCBs concentrations were recorded at sites 25 (Kushimoto in Wakayama, Japan) and 101 (Tianjin in China), 7200 and 7700 pg m\(^{-3}\) respectively (Fig. 1). PCNs concentration was also very high at Kushimoto (site 25) (Fig. 1). Being predominantly rural, the relatively high concentrations of PCBs and PCNs at Kushimoto seem quite unusual, but potentially suggestive of emissions from technical formulation related sources. Considering that at this site samplers were placed at the rooftop of an old local building, we presume possibility of an impact from the indoor environment of this structure; window and door sealants and old electrical cables are among some of the factors imagined culpable

In the case of Tianjin, PCBs concentration was above the Chinese average not only in this present survey but also in a similar one conducted earlier in 2004 (Jaward et al., 2005). In both studies, the Tianjin site emerged with the highest PCBs contamination. Tianjin lies in the northeastern part of China, an enclave that once served as an industrial base of China. Hence, the relatively high PCBs at this site is thought to reflect a legacy of contamination from past industrial activities (Zhang et al., 2008b).

3.2. Comparison with other studies in Asia

Compared with earlier studies from Japan, Korea and China, total PCBs concentrations derived in the present study are quite elevated, and expectedly so, in view of the higher number of congeners evaluated (\( \sum_{202} \text{PCBs} \) (Table A.5). Thus, the likelihood is that ambient \( \sum_{202} \text{PCBs} \) and \( \sum_{63} \text{PCNs} \) might be understated when smaller numbers of congeners are evaluated. For a more useful comparison, PCB congener common among three East Asian studies – the present (samples collected in 2008), Jaward et al. (2005) (samples collected in 2004) and Zhang et al. (2008b) (samples collected in 2005) – were extracted, expressing all concentrations in pg m\(^{-3}\) (Table A.6). Average concentrations of common \( \sum_{27} \text{PCB} \) congeners with respect to Japan and Korea yielded 82.55 and 73.07 pg m\(^{-3}\) in 2008 (present study), compared to estimated averages in 2004 deduced from Jaward et al. (2005) as 63.82 and 39.61 pg m\(^{-3}\), respectively (Tables A.6a and A.6b). The increases in concentration realized in the present study over that of 2004 were marginal for Japan and doubled for Korea. As the respective increases were within the same order of magnitude, they perhaps might not constitute a major change in air concentrations (Fig. 2). In the case of China, the necessary comparison was drawn considering average concentrations of \( \sum_{18} \text{PCB} \) congeners found common to the studies in 2008, 2005 and 2004, respectively 458.12, 82.21 and 65.84 pg m\(^{-3}\) (Table A.6c). Clearly, PCBs concentration in air
over China has increased by one order of magnitude, between 2004 and 2008 (Fig. 2).

3.3. Site characteristics

K-Means clustering was applied to the \( \Sigma \text{PCBs} \) and \( \Sigma \text{PCNs} \) to generate three site clusters each, corresponding to sites with relatively low, medium and high pollutant concentration brackets in each country (Fig. 3). Sites with outlying concentrations – sites 25, 76 and 101 (for PCBs) and 14 and 25 (for PCNs) – were omitted in this cluster analysis.

**PCBs:** Clusters 1, 2 and 3 in Japan respectively consisted of 41, 4 and 8 sites. Predominantly, rural sites grouped into Cluster 1 and urban sites into Cluster 3. Sub-urban sites were distributed among Clusters 1 to 3. Sites with highest PCBs concentrations grouped into Cluster 2, which consisted of two rural sites (Kitakami, Iwate and Setoda, Hiroshima), a sub-urban site (Nagakute, Aichi) and an urban site (Hongo, Bunkyo Ward, Tokyo). It is interesting that rural sites dominated in this group, which perhaps suggests that past use or disposal of PCBs was prominent in some rural places in Japan. With particular reference to Setoda in Hiroshima, this sampling site was located near a huge shipbuilding yard, which probably influenced the levels of PCBs measured, especially as large quantity of paint and lubricating and flushing oil were previously applied under open conditions at this yard. It appeared that the sites in China clustered along a south-north gradient rather than based on rural–urban factors. Sites in the northern parts of China mostly grouped into Cluster 3, the highest concentration bracket, while those in the southern parts predominantly grouped into Clusters 1 and 2. For Korea, Clusters 1 and 3 each contained a mix of rural and urban sites, but those sites noted for heavy industrial activities such as Yeosu, Pohang, Ulsan and Gwangyang were contained in Cluster 1. The few Korean sites that grouped into Cluster 2 (the high concentration bracket) were mostly urban.

**PCNs:** Approximately 62%, 22% and 14% of the rural sites in Japan were captured in Clusters 1, 2 and 3 respectively, while the urban sites were nearly equally distributed among these Clusters, at about 30%, 40% and 30% respectively. Thus, most rural sites in Japan recorded lower air PCNs concentrations. The sub-urban sites were distributed among the lower concentration bracket in Clusters 1 and 2. Sites that grouped in the high concentration bracket of Cluster 3 include Nasushiobara, Tochigi; Suzaka, Nagano; Setoda, Hiroshima; and Yukuhashi and Ookimachi in

![Fig. 2. Changes in air PCBs concentrations in Japan, Korea and China between 2004 and 2008 (only common congeners were compared between studies conducted in each country).](image)

![Fig. 3. Box-whiskers plots of site clusters derived by k-means clustering of aerial \( \Sigma \text{PCBs} \) and \( \Sigma \text{PCNs} \) concentrations (\( \square \) = mean ± SE; \( \bigtriangleup \) = mean ± SD).](image)
Population density can be regarded as a good indicator of human activity. Thus, it was used as a measure to assess the impact of local activities on emissions of ambient POPs. With availability of GIS based population density data of Japan, 10 km population density buffers were estimated for each sampling site in Japan using ArcGIS and correlated with PCBs and PCNs concentrations (Fig. 5). The two pollutants, excluding outlying concentrations, correlated quite significantly with population density (Fig. 5). The presumption is that congener profiles might relate more robustly as chemical signatures to characterize POPs sources than homologue profiles. This stems from the fact that source congener ratios are not easily distorted. For example, when congener react to temperature effect, response to volatilization is expected to be even across congeners of same homologue. On the contrary, different homologues do vary in the extent of their response to temperature, in which case homologue ratios at source might differ from the ratios in air. Presented in Figs. A.2 and A.3 are congener profiles of tri-CBs and tri-CNs, both dominant homologues in air. The tri-CBs congener profiles were very consistent among sites across the various jurisdictions and dominated by the co-eluted congeners PCB-31/28 (Fig. A.2). The profiles generally compared favorably with profiles in PCB formulation, but more especially to the lowly chlorinated. The air tri-CBs congener profiles also matched corresponding profiles in some flue gas samples. Thus, air PCBs across East Asia probably were technical formulation and combustion related. It appeared though that as ambient air PCB homologues approached very low concentrations, as evidenced with the octa-CBs, their congener profiles no longer matched source profiles, while consistency among profiles from the various sites greatly reduced (Fig. A.4).

Tri-CNs congener profiles of air samples were similarly examined across the three jurisdictions, making comparisons with reported profiles in PCN (Halowax) and PCB formulations (Fig. A.3). The PCN profiles in Halowax and PCB technical mixtures were adapted from Falandysz et al. (2006) and Yamashita et al. (2000), respectively. The tri-CN congener profiles in air sampled from most sites in Japan were dominated by PCN-14/21/24 (~30%), followed by approximately comparable amounts of PCN-22/23 (~23%) and PCN-17/25/26 (~22%) (Fig. A.3). This is quite different from the profiles in most Halowaxes overwhelmingly dominated by PCN-14/21/24 (~67%), and followed by PCN-22/23 (~20%) and very little PCN-17/25/26 (~2%). Similarly, tri-CN congener profiles in air sampled in Korea and China did not match profiles in the PCN formulations (Fig. A.3). Some tri-CN profiles in air in Japan rather appeared comparable to profiles in the PCB technical mixture, Kanchelor 300. Importantly noted also is an unusual tri-CN congener profile in air in Taiwan, dominated by PCN-15, completely different from observations in China, Japan and Korea (Fig. A.3).

3.5. Principal component analysis (PCA)

As a source apportionment tool, PCA has provided a useful approach to elucidating probable source factors of air POPs (Kim et al., 2004, 2007; Kim and Masunaga, 2005; Mari et al., 2008a; Li et al., 2011). In the present analysis, the datasets of PCB and PCN congeners were each normalized to their percentage compositions and then subjected to PCA in normalized varimax rotation mode using Statistica 7 software. Only major principal components (PCs) were extracted, with significant clusters defined by factor loading coefficients >0.7.
3.5.1. PCA of PCB congeners

Four major principal components – PC1, PC2, PC3 and PC4 – were extracted as affecting PCBs emissions in each of the jurisdictions. For Japan, these constituted approximately 49%, 22%, 8% and 6%; China – 43%, 25%, 11% and 7%; and Korea – 33%, 15%, 9% and 7% of total variance, respectively (Fig. 6).

Japan: PC1 correlated highly with the Group 1 cluster of PCB congeners, which are generally highly chlorinated (Fig. 6a). This cluster to an extent might denote local impacts, given that heavier congeners travel relatively poorly in air. Identified in this cluster also are some characteristic congeners of KC500 and 600 and combustion (Kim et al., 2004), suggesting that either of these sources might be important in local emissions of PCBs in Japan. The Group 2 set of congeners, which correlated highly with PC2, contains some of the congeners reportedly enrich in both lowly and highly chlorinated Kanechlor (Kim et al., 2004). The range of congeners identified as enrich in KC300 and 400 stretches from those that correlated highly with PC2 (in Group 2) to those that correlated negatively with both PC2 and PC1 (in Group 3). Congeners in the Group 3 cluster are very lowly chlorinated with high susceptibility.
to re-emissions via volatilization. The Group 4 cluster of congeners bears important sources markers of combustion such as PCB-81, -126, and -169 (Alcock et al., 1998; Kim et al., 2004).

China: Among the four clusters identified on the factor loadings plot, combustion markers of PCBs cut across three of the groups – i.e. groups 1, 2 and 4 (Fig. 6c). This might point to quite widespread combustion sources of PCBs in China. Group 2 set of congeners is however more related to sources of highly chlorinated PCBs formulations, while Group 3 related to lowly chlorinated PCBs formulations. So, to an extent, PCBs formulations were still relevant to contemporary air PCBs contamination in China.

Korea: Group 1 (highly correlated with PC1) could be associated with some characteristic congeners of both combustion and highly chlorinated PCBs formulations, while group 2 (highly correlated with PC2) bears markers of both the lowly and highly chlorinated PCBs formulations. Very lowly chlorinated PCB congeners quite enrich in lighter PCB formulations and very susceptible to volatilization clustered into Group 3. Group 4 set of congeners bears some of the notable markers of combustion.

Fig. 7. Factor loadings and corresponding factor scores plots for PCN congeners. Numbers on factor loadings plots indicate congener numbers while those on the factor scores plots indicate site numbers. Marker congeners were obtained from the following references: ○ (Falandysz, 1998; Meijer et al., 2001; Noma et al., 2006; Lee et al., 2007); ▲ (Falandysz, 1998; Falandysz et al., 2006); ▼ (Falandysz, 1998; Falandysz et al., 2006).
The PCB congeners most susceptible to volatilization (Group 3 in each of the factor loadings plot) correlated negatively with the other extracted factors. To this extent, we visualized that re-emissions driven by volatilization might increase as some of the known traditional source factors of PCBs decrease. Corresponding factor scores plots reveal useful information on how sites in the various jurisdictions were affected by the principal components. Most of the Japanese sites clustered apparently in relation to Groups 4 and 3 (on the corresponding factor loadings plot), making combustion and re-emissions probably the most important source factors of PCBs emissions in Japan (Fig. 6b). Similarly, these source factors emerged the most important among the factors that impacted majority of sites in China and Korea, considering sites’ behaviors on their respective factor scores plots (Figs. 6d and f). Thus, although signals of PCB formulations were picked up as possible source factors, in reality, the most important contributions related to these formulations might be coming from re-emissions.

3.5.2. PCA of PCN congeners

Three principal components – PC1, PC2 and PC3 – were generally extracted for PCNs emissions in each country. Respectively, these components accounted for the following percentages of total variance: Japan – 22%, 18% and 10%; China – 31%, 27% and 10%; and Korea – 24%, 19% and 12% (Fig. 7).

Japan: Considering the three important clusters derived on the factor loadings plot, combustion markers of PCNs were prominent in Group 1 (PCN-50, -66/67 and -73) and Group 3 (PCN-39, -41, -42, -44, -45/36, and -54) (Falandysz, 1998; Falandysz et al., 2006). Comparing the factor loadings and scores plots, it is apparent that most Japanese sites related to Group 3, a combustion factor. So we can assume that specific combustion processes (reflected in Group 3) were most culpable in PCNs emissions in Japan. The three major principal components accounted for only 50% of total variance, in which case we thought there were substantial residual factors presently unexplained by this analysis.

China: Just as in the case of Japan, two of the clusters – Groups 1 and 3 – appeared combustion related, given identifiable PCN congener markers of combustion (Fig. 7c). Group 1 correlated strongly, and Group 2 moderately, with PC1. Group 2 bore congener signatures of Halowax or its equivalent mixtures. On the factor scores plot, sites were generally scattered with less defined clustering (Fig. 7d). But relatively, the combustion factors (Groups 1 and 3) impacted a greater number of sites (e.g. sites 101, 109, 110, 112, 116, 118 and 120) compared to Group 2 (which appeared significant for only two sites – 102 and 111) (Fig. 7d). Yet, about 50% of sites seemed unaccounted for by these three major components. This leaves a gap of unexplained factors, perhaps, inherent as residual factors. Most of the unaccounted sites were somewhat individually inclined towards lowly chlorinated congeners (comparing Fig. 7c and d). To this extent, we presumed volatilization might constitute a significant part of the residuals impacting these remaining sites.

Korea: Some of the PCN congeners enrich in Halowax or their equivalents correlated strongly with PC1 and PC2, while some notable PCB congener markers of combustion correlated negatively with PC1 and PC2 (Fig. 7e). This presupposes that the contemporary relevance of combustion and PCNs technical mixtures as source factors of air PCNs were sharply opposed. Meiher et al. (2001) had argued regarding studies conducted in the UK that with the decline of PCNs application, contributions from combustion sources have become relatively larger. Among the PCN congeners that correlated neither with PC1 nor PC2 were PCN-66/67 and -73, both markers of combustion. From Fig. 7f, majority of Korean sites seemed impacted by combustion, except for Sites 71, 73, 76, 79, 85, 94, 98, and 100. Since PCNs are also present as trace contaminants in PCB formulation, we are unable to indicate precisely which particular formulation was probably responsible at these sites.

4. Conclusions

The spatial distribution of aerial PCBs indicated existence of a rural–urban gradient of these pollutants in both Japan and Korea, and a south-north gradient along the eastern stretch of China. For aerial PCNs, the spatial trends in Japan and Korea apparently followed similar trends as the PCBs. However in China, the PCNs were somewhat equally distributed across the country. Contemporary source factors of air PCBs across East Asia seemed related mostly to combustion and re-emissions/volatilization (probably from contaminated environmental compartments such as soils). Although PCB formulations were derived among the possible source factors, their real contribution or relevance to contemporary PCBs emissions appeared mostly associated with re-emissions/volatilization tendencies. Regarding the air PCNs, combustion emerged as the major culprit, with less linkage to Halowax or equivalent formulations. Residual factors were substantially inherent in the PCA outcome of PCNs; to this extent, there were probably factors of PCNs emission presently not fully understood.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.10.046.

References
