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PBDEs and PCBs in sediments of the Thi Nai Lagoon (Central Vietnam) and soils from its mainland

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HIGHLIGHTS

- ▶ Levels and patterns of PCBs, PCB 11, and PBDEs in surface sediments and soils.
- ▶ Main natural and anthropogenic processes in tropical areas are changing rapidly.
- ▶ Key processes are identified by salinity, porosity and grain size patterns.
- ▶ PCBs, PCB 11 and PBDEs levels are similar to those found far from direct sources.
- ▶ Efficacy of degradation processes are confirmed by congener patterns and statistics.

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ABSTRACT

Concentration and distribution of PCBs, PCB 11, and PBDEs in both surficial sediment and soil samples, taken from a zone subject to recent accelerated development, were investigated to assess the environmental quality and understand both natural and anthropogenic processes that influence contaminant behaviors. Values of PCB and PBDE are in the lower range of those reported in literature, typical of low impacted coastal zones. This could be due to efficient processes of resuspension and removal. Contaminants in the lagoon showed higher concentrations in sediments from sites close to the city and the outfalls of the industrial area, while soils showed maximum values in the northern samples. In addition, congener patterns and statistical analyses suggest the presence of effective degradation processes, especially for PBDEs, with the exception of the most concentrated samples that may indicate a direct input. PCB 11 is a significant component (up to 18%) in most lagoon sediments. Its presence is strongly associated with fine particles, thus the distribution seems to be driven mainly by the system hydrodynamic and does not trace the sources. Due to evaporation, only flooded agricultural soils show a similar relative abundance of this congener.

1. Introduction

Halogenated organic chemicals have been widely used for a variety of purposes since the beginning of the 20th century, and their industrial production has been widespread for commercial purposes (Alaee et al., 2003). PCBs and PBDEs are two groups of organic chemical substances, both forming a family of 209 congeners.

PCBs, commercially produced mainly as Aroclors, had a myriad of applications (Hu and Hornbuckle, 2010). Their toxicity was confirmed in the 1970s, and therefore their use in open systems has been forbidden ever since. However, they remain a current concern because they are still present in closed systems or stored in landfills, and can be reintroduced in the environment by evaporation and leakage (Bhavsar et al., 2004). Moreover, second-hand items (goods produced before the ban as coolants and lubricants in transformers and capacitors, hydraulic and heat exchange fluids, and so on) are widespread through the black market in Asian

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regions (Wong et al., 2007). The congener PCB 11 (3,3′-dichlorobiphenyl) is absent or present at very low concentration in original commercial Aroclor mixtures (Hu and Hornbuckle, 2010; Rodenburg et al., 2010), and its production from degradation is not likely (Rhee et al., 1993). However, PCB 11 has been shown to be a global contaminant (Rodenburg et al., 2010) and is measured in consumer goods mainly containing azo- and phthalocyanine pigments, including newspapers, packaging, plastic bags, and so on (Rodenburg et al., 2010).

The commercial production of PBDEs began in 1970s, as flame retardants in a variety of industrial and consumer applications (Alaee et al., 2003). The commercial products principally contain penta-, octa-, or deca-BDE mixtures (Alaee et al., 2003). Their toxicity and increasing levels in marine mammals, sediments, bird eggs and human tissues make them of environmental concern (De Wit, 2002). Such as PCBs, PBDEs are bioaccumulative, resistant to degradation, and subject to long-range transport (Wang et al., 2005). Currently, the production of penta- and octa-BDEs has been banned in the European Union (EU) and North America. Deca-BDE has also been banned from some of these countries but no restriction on PBDEs exists in Asia (Yan-Ping et al., 2010).

The information about PCB and/or PBDE sources and concentrations in Vietnam is limited to the most industrialized metropolitan areas (e.g., Ramu et al., 2007; Nguyen et al., 2010; Tuan et al., 2010) and some data are available for PCBs in coastal lagoons (Frignani et al., 2007; Giuliani et al., 2011). However, Vietnam has undergone a wide process of economic reform in 1986, which laid the foundations for a market economy, and since then, the country has experienced a high economic growth together with a boom in household food and no-food consumption (Figuié and Moustier, 2009). Then, it is likely that environmental levels of anthropogenic contaminants have increased in response to the recent rapid industrialization/economic development.

The aim of this study was to investigate PCBs, PCB 11, and PBDE concentrations and distributions in surface sediments of the Thi Nai Lagoon and in the mainland soils, improving the knowledge of main natural and anthropogenic processes active in the Lagoon, and some of its environmental characteristics.

2. Study area

Recently, the Thi Nai Lagoon (Fig. 1) has acquired a particular economic importance, because it is one of the key areas designed to drive the socioeconomic development in Central Vietnam, which completion is scheduled for 2020. The Thi Nai bridge, whose construction was completed in 2006, represents the access way to the new economic zone in the Phuong Mai peninsula. This will include tourist sites, together with industrial and residential zones and the enlargement of the commercial port with the building of new facilities. The port of Quy Nhon is one of the most important gates of Vietnam, which is part of the East-West corridor of the Greater Mekong Subregion (NEZA), and can handle ships up to 30 000 dwt. To allow the cargo entrance, the area is often dredged (Quy Nhon port website, 2011; VPA, 2011). Presently, the most important economic activities in the lagoon are aquaculture and fisheries.

3. Materials and methods

Sampling locations are shown in Fig. 1a. Sediments (TN) and soils (TS) were collected in June 2010. Soils were collected at selected sites around the border of the Lagoon, each representing an area of particular interest (Fig. 1a): a flooded rice field (TS02); a dry soil from a rice field (TS04); a cultivated field, quite close to a small village (TS05); a flooded rice field by the lagoon border, where several aquaculture ponds are located (TS06); a domestic garden, quite close to the industrial area of the Nhon Hoi Economic Zone (TS09); a sediment from the Truong Uc River bank in Phuong Dong Da, the residential area of Qui Nhon (TS11), and an urban grassy soil collected from Nguyen Tat Thanh Park close to the main urban road (TS13).

PCBs and PBDEs were determined on soils and surficial sediment samples by High Resolution Gas Chromatography-Low Resolution Mass Spectrometry (HRGC-LRMS) after extraction and clean-up. 76 chromatographic peaks, representing 92 PCBs congeners (12 as double and 2 as triple peaks), were detected among the total 127 congeners searched (IUPAC names of homologues are given in the Supplementary material, Table S1): 1DiCB (11), 16 TriCBs (19, 18, 17, 24 + 27, 16 + 32, 34, 29, 26, 25, 31, 28, 20 + 33 and 22), 20 TeCBs (45, 46, 52, 49, 47 + 48, 44, 42 + 59, 41 + 64 + 71, 40, 67, 63, 74, 70, 66, 56 + 60), 19 PeCBs (104, 93 + 95, 91, 92, 84 + 90 + 101, 99, 97, 87 + 115, 85, 110, 82, 107, 123, 118 and 105), 18 HxCBs (136, 151, 135 + 144, 147, 149, 146, 153, 132, 141, 138 + 164, 158, 128 + 167, 156, 157 and 169), 13 HpCBs (179, 176, 178, 187, 183, 174, 177, 171, 172, 180, 193 and 170 + 190), 4 OcCBs (199, 196 + 203 and 194), 1 NoCB (208) and PCB 209 (the sole DeCB). 9 PBDEs were detected (17, 28, 47, 66, 100, 99, 85, 153, 183) on a total of 14 searched.

All reported concentrations are relative to dry weight. Detailed information on extractions, analyses, analytical quality, gridding interpolation methods and statistic are reported in the Supplementary material.

4. Results

4.1. Sediment features

Fig. 1a shows the areal distribution of sediment porosity. Values generally increase along a N–S gradient, being lower at the western edge of the lagoon, close to artificial fish farms, and maximum in proximity of the lagoon inlet and the industrial port of Quy Nhon City. In particular the central area, north of the Thi Nai bridge, shows a patchwork distribution with zones characterized either by lower (~0.55) or higher (~0.65) porosities. The content of fines reflects the porosity distribution (Table 1): sediments of the southern area of the lagoon and the bay are almost exclusively composed by fine particles, whereas the central zone and the eastern edge present intermediate values (about 60% of fines), and the coarsest samples belong to the north-western part with about 14% of fines or less. Soil sample grain sizes show a great variability, the fine content ranging between 0.20 and 72.1% (Table 1).

The areal distribution of salinity (Fig. 1b) divides the lagoon into two main sub-bodies: the lagoon northern of the bridge, with lower salinity (6–19‰) and the southern one, with higher values (15–25‰). Open sea salinity, just in front of the lagoon inlet, is 30‰. In general, salinity increases with the distance from the Cai and Con river mouths, along a NW–SE gradient.

OC contents are relatively low, ranging from 0.33 to 1.95% (Table 1). Soil samples TS02 and TS13 are the richest, with values of 3.78 and 3.86%, respectively. The C/N molar ratios are close to 9.60 or higher than 10 (10.0–14.9) in lagoon samples. Soils, except for TS05 and TS11, show values above 15 (Fig. 1c). Moreover, $\delta^{13}C$ values range within −28.3 to −17.3‰ in surficial sediments and from −25.7 to −22.9 ‰ in soils (Fig. 1c).

4.2. PCB and PBDE concentration and compositional patterns

Table 1 summarises total concentrations of PCBs (including PCB 11 concentrations), PBDEs, PCB 11 and its relative abundance on total PCBs.

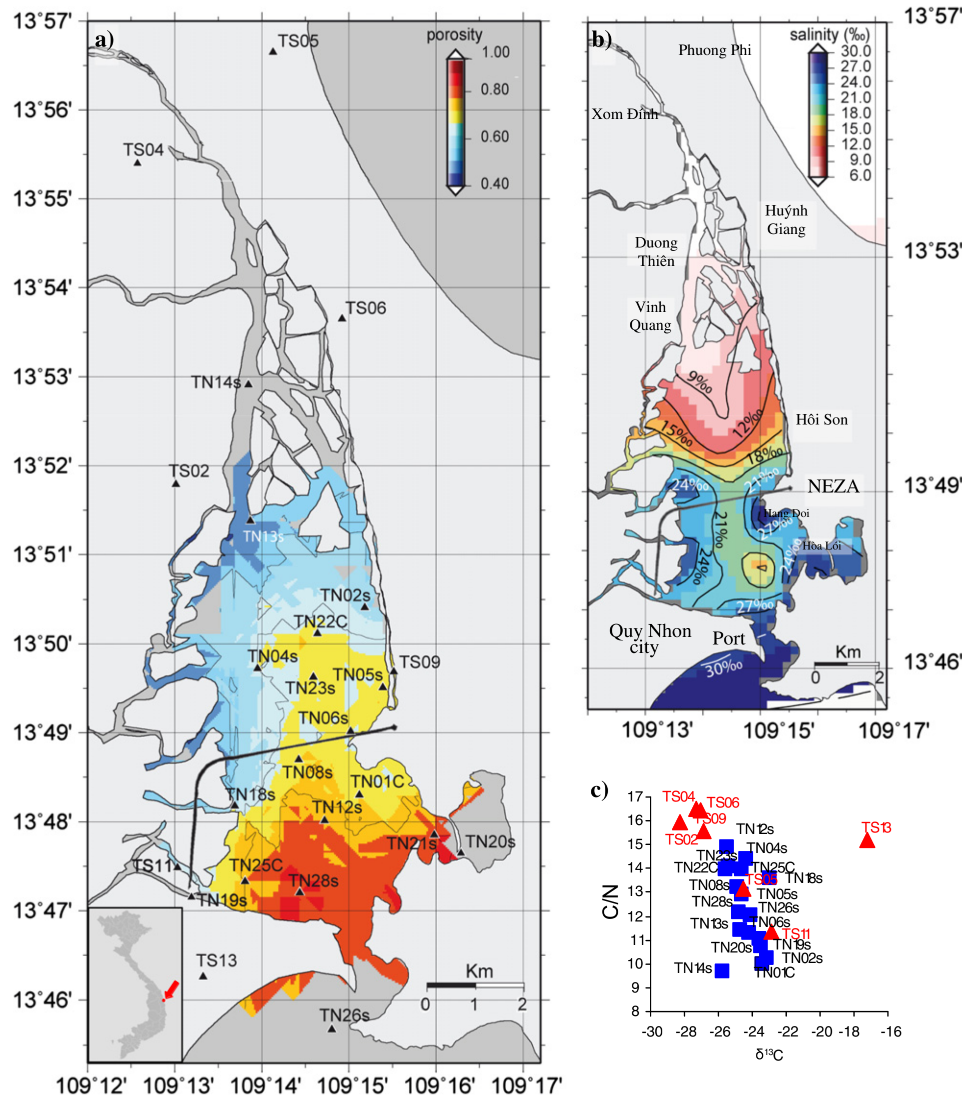

Fig. 1. (a) Map of the Thi Nai Lagoon and the surrounding mainland with sediment and soil sampling locations. Lower script letters identify core (C) or surficial (s) lagoon samples. Distribution of sediment porosities is also shown; (b) map of salinity gradients within the lagoon and indication of toponyms (river names, city, villages, industrial area, port); (c) plot of C/N ratio vs. δ^{13}C.

Soil samples TS05, TS06 and TS04 present by far the highest PCB concentrations: 18.6, 15.3 and 13.5 μg kg^{-1}, respectively. Within the lagoon, the highest values are found at TN25C and TN19s (6.40 and 5.19 μg kg^{-1}, respectively), followed by sites TN20s and TN22C (~4 μg kg^{-1}). The remaining sample concentrations are around 2 μg kg^{-1}, while lower values (below 1 μg kg^{-1}) are recorded at TN02s; TN13s; TN14s and TN18s along the northern and western borders of the lagoon.

PBDEs in lagoon samples show the highest values at TN19s and TN22C (9.62 and 8.93 μg kg^{-1}, respectively), while the other samples have concentrations below 1 μg kg^{-1}, with the exception of TN01C and TN28s (1.04 and 1.65 μg kg^{-1}, respectively). Among soils, maximum values are found at TS05 and TS04 (4.02 and 3.27 μg kg^{-1}, respectively), whereas the others show concentrations comparable with the majority of lagoon samples.

PCB and PBDE congener distributions are shown in Fig. 2. PCBs in lagoon samples are generally dominated by low chlorinated congeners, in particular TeCBs, followed mainly by TriCBs. HpCBs and OcCBs are generally low. Samples TN08s and TN12s are characterized by the presence of NoCBs, and traces of DeCBs are found at sites TN19s, TN25C, TN26s and TN28s. Soils contain a wider spectrum of congeners, with the exclusion of MoCBs. There, TeCBs are dominant, followed by TriCBs- and PeCBs. Samples with the highest total concentrations (TS05 and TS06) are an exception, because they show the predominance of intermediate chlorination classes: HxCBs, followed by HpCBs- and PeCBs.

Interestingly, the global contaminant PCB 11 is present in most samples (being below detection limits only at sites TN14s and TS11) at concentrations up to 1.31 μg kg^{-1} (Table 1). This means that, when present, PCB 11 accounts for 7.3–18.0% and 0.8–15.0% of total PCBs in sediments and soils, respectively.

Surficial sediments and soils are characterized by similar PBDE congener patterns (Fig. 2) with the prevalence of low brominated congeners and the predominance of PBDE 47, 99 and 100. PBDE 153 is present at sites TS04, TS05, TS06, TS13, TN19s, TN22C, TN25C, TN26s and TN28s. Of these, TN22C composition looks peculiar, because it shows a pattern of brominate congeners shifted to higher classes with the prevalence of PBDE 99.

Table 1
Analytical results for sediments and soils from the Thi Nai Lagoon and its mainland. PCB and PBDE concentrations, contents of sand, fine particles (silt plus clay), organic carbon and organic nitrogen are reported. Contents of PCB 11 and its percent contribution to the total PCBs are also shown.

Sample	Total PCBs (μg kg^{-1})	PCB 11 (μg kg^{-1})	PCB 11 (%)	PBDEs (μg kg^{-1})	Sand (%)	Fines (%)	OC (%)	ON (%)
Sediments								
TN01C	2.67	0.25	9.4	1.04	66.9	33.1	0.52	0.061
TN02	0.71	0.08	10.8	l.d.l.	92.2	8.8	0.33	0.037
TN04	1.83	0.18	9.9	0.04	30.3	69.7	1.23	0.100
TN05	1.92	0.32	16.6	l.d.l	44.2	55.8	1.31	0.119
TN06	1.21	0.10	8.5	0.06	69.1	30.9	0.79	0.081
TN08	2.51	0.25	9.9	0.13	11.4	88.6	1.63	0.144
TN12	1.94	0.29	15.2	0.44	21.3	78.7	1.72	0.134
TN13	0.47	0.04	7.3	0.07	85.6	14.4	0.51	0.052
TN14	0.71	l.d.l.	–	0.06	88.4	11.6	0.68	0.083
TN18	0.62	0.05	8.3	0.12	84.1	15.9	0.57	0.049
TN19	5.19	0.55	10.6	9.62	82.2	17.8	0.93	0.101
TN20	4.24	0.33	7.7	0.55	1.0	99.0	1.78	0.189
TN21	2.36	0.36	15.4	0.10	16.2	83.8	1.51	0.145
TN22C	4.13	0.34	8.3	8.93	40.1	59.9	1.26	0.105
TN23	1.15	0.09	7.6	l.d.l	62.2	37.8	0.92	0.076
TN25C	6.40	0.61	9.5	0.03	2.59	97.4	1.95	0.163
TN26	2.10	0.21	18.0	0.10	21.3	78.7	1.33	0.128
TN28	2.97	0.48	16.1	1.65	1.4	98.6	1.70	0.165
Soils								
TS02	3.31	0.50	15.0	0.62	39.2	60.8	3.78	0.276
TS04	13.5	1.31	9.68	3.27	63.7	36.3	1.56	0.11
TS05	18.6	0.30	1.6	4.02	68.8	31.2	1.15	0.102
TS06	15.3	0.12	0.8	0.59	99.8	0.2	0.44	0.032
TS09	0.96	0.09	9.3	0.29	96.3	3.7	0.49	0.037
TS11	0.67	l.d.l.	–	0.21	97.3	2.7	0.14	0.014
TS13	2.68	0.36	13.4	0.82	27.9	72.1	3.86	0.297

l.d.l. = lower than detection limits.

5. Discussion

5.1. Depositional patterns and particle origin in the Thi Nai Lagoon and surrounding soils

Porosity is defined by the complex interaction of many factors (Athy, 1930), however, the highly significant correlation (Pearson correlation coefficient) observed between fine particles' content and porosity ($r = 0.98$, $p < 0.01$; see Tables S2 and S3 in the Supplementary material) allows to identify some key processes that influence its areal distribution. Indeed, the lagoon's depositional pattern is dominated by the joint flow of the rivers Cai and Con, along a NW-SE gradient, the area close to the lagoon inlet acting as a fine sediment trap (Fig. 1a). North of the bridge, porosity distribution seems to explain how inputs from the Nhon Hoi Economic Zone (in front of samples TN05s and TN06s) were redistributed by currents, thus producing a complex pattern where sample TN22C records a punctual accumulation of fine sediments.

The location of the saltwater/freshwater interface (Fig. 1b), defined by the balanced interaction between river flows and tidal forcing (Conrads and Roehl, 2006), supports our considerations on sediment dynamic in the area. In particular, it suggests that Cai and Con rivers in the North are the dominant fluvial forcings, with higher flows, whereas the Ha Thanh River and its branches (that receive the sewage from Quy Nhon City in the South) probably is affected by a partial saline ingression during high tides. Per se, saline ingression could act as a stopper for the transport of particles (and particle-reactive chemicals) from the river catchment toward the lagoon (e.g., Oguchi et al. 2000), thus creating storage areas at the river mouths that are successively dismantled by a sudden increase of river flow (e.g., flash floodings, quite common in the area). The coarse grain size at TN19s, in the proximity of the inlet, suggests the occurrence of processes of fine particles removal.

The provenance of organic matter is environment-dependent, and the main sources distinctly present different $\delta^{13}C$ and C/N values (Fry and Sherr, 1989). The plot in Fig. 1c suggests that all surficial samples (also TN26s, taken from the marine area in front of the lagoon inlet), fall within a range of values that defines the mixed influence of marine ($\delta^{13}C > -25‰$ and C/N > 10) and freshwater derived organic matter ($\delta^{13}C < -25‰$ and C/N > 10; Lamb et al., 2006), with a general predominance of terrestrial sources. Indeed, rice cultivation and mangroves, that are abundant along the edges of the lagoon, may partially overcome the marine sources. As expected, $\delta^{13}C$ and C/N in soils account for different situations: TS02, TS04 and TS06 are characterized by higher C/N and lower $\delta^{13}C$, typical of C3 plants (as paddy rice cultivations), whereas the urban soil (TS13) falls within the C4 plant range ($\delta^{13}C > -18$ and C/N > 15), and only TS05 and TS11 show values similar to the lagoon sediments. This is explained by the sampling location for TS11 (not properly a soil because collected in Truong Uc River banks) whereas TS05 is probably influenced by local conditions and anthropogenic inputs. Indeed, TS05 (North-East from the lagoon and very close to the South China Sea coastline) is peculiar with respect to the other soils because it is located in a horticultural area, not in a rice field, and is quite close to residential houses. Therefore, its chemical–physical parameters can have been altered by wastewaters and the use of fertilizers, as generally observed in farmlands (Scott et al., 2004; Wang et al., 2010).

5.2. Comparison with worldwide concentrations in sediments and soils

According to the literature, PCB concentrations in Vietnamese sediments and soils range from 0.61 to 320 μg kg^{-1}, with the highest values usually measured in the suburbs of large cities (Thao et al., 1993; Tuan et al., 2010). In this study, total PCB concentrations in sediments are generally low and similar to those of other low impacted coastal zones (Jiang et al., 2011; Giuliani et al., 2011 and references therein). Furthermore, PCB values are lower than those reported by Giuliani et al. (2011) for samples collected in 2005 and 2008 at site TN01C, and of the same order of magnitude of those measured by the same authors in other Central Vietnam coastal lagoons.

PBDE concentrations in worldwide coastal areas range from below detection limit to 1270 μg kg^{-1}, with maxima generally between 0.55 and 22 μg kg^{-1} (Moon et al., 2007; Jiang et al., 2011; and references therein). The data found in this study are comparable to those reported for coastal and open sea sediments in areas not influenced by the presence of highly urbanised zones or flame retardant manufactory plants (Jiang et al., 2011).

5.3. Sediment areal distribution and patterns

PCBs can enter the lagoon basin either dissolved in the water or by solid load adhering to fine-grained and OC rich sediments, the primary carriers of lipophilic contaminants in aqueous systems (Olsen et al., 1982). A linear significant correlation ($p < 0.05$) exists between total PCB concentrations with both fine sediment fractions and OC contents in sediments (see Table S2 in the Supplementary material). This emphasizes the role of particle size, and hydrophobic proprieties, in driving PCB distribution. The subsequent fate of sediments (i.e. their sedimentation, hydrodynamic dispersion and erosion behavior) will determine the fate of the contaminant. Therefore, samples show a general higher concentration in those lagoon areas with accumulation of fine-grained sediments. A contribution from the long-range atmospheric transport is likely but the airborne PCBs, once fallen out, interact with particles and follow the lagoon current pathways.

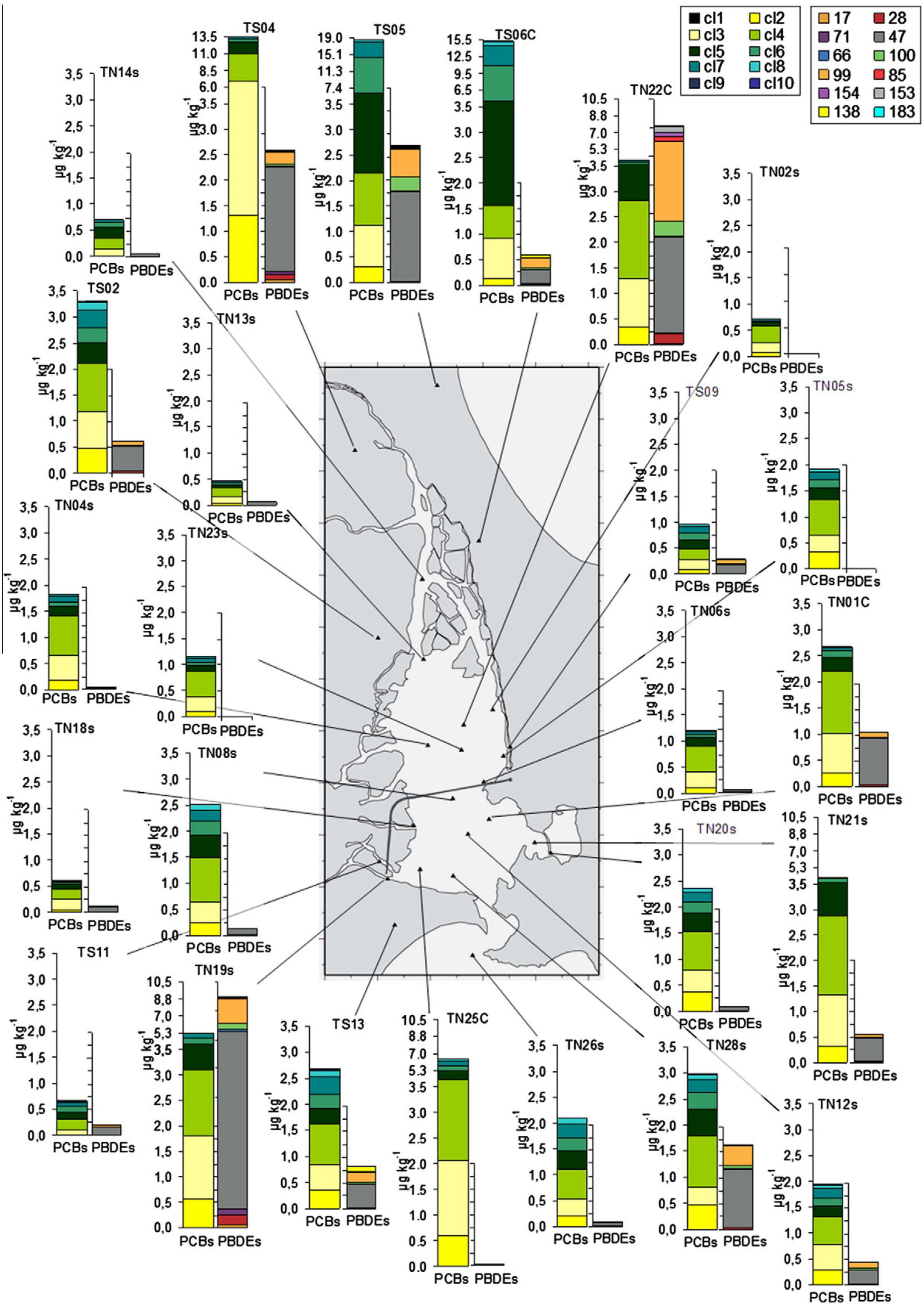

Fig. 2. Map distribution of both PCB homologue and PBDE congener compositions in sediment and soil samples of Thi Nai Lagoon.

To reduce the effect of grain size pattern and OC content on PCB distribution and attempt a source identification, we normalized the PCB concentrations to the contents of both fine particles and OC (see Figs. S1 and S2 in the Supplementary material). PCB total concentrations of some sediments significantly increase (i.e., at TN01C, TN02s and TN14s), whereas TN22C and TN25C, TN20s and TN21s are not significantly affected because of the finer bottom composition at these locations. In turn, the value at site TN19s is greatly increased, due to the already high concentration and the mainly sandy composition. The PCB areal distribution pattern is not biased by normalization, hence inputs can be better identified. In particular, sewage outputs from Nhon Hoi Economic Zone seem to affect sites TN05s and TN06s and a northward redistribution process of particles is evidenced by the accumulation at TN22C. Other inputs appear to be the lagoon embayment South-East from the bridge (TN20s and TN21s), together with Quy Nhon City and its port (TN19s, TN28s).

PBDEs, as hydrophobic chemicals, are expected to be associated both with fine particles and organic matter (Bailey et al., 2002), but no such correlations are evidenced by our results (see Table S3 in the Supplementary material). This situation usually occurs when the factor driving the contaminant distribution is the proximity of the inputs. However, the lagoon is characterized by low concentrations, with no clear evidence of significant sources. The PBDE areal distribution almost parallels that of PCBs because maximum concentrations are found in correspondence of Quy Nhon sewages and industrial discharges (TN19s and TN22C: 9.62, 8.93, $\mu g\ kg^{-1}$, respectively). Low correlation between PBDE congeners and OC has been reported by other authors, and attributed to the combined effect of local inputs, transport, mixing, and deposition (Moon et al., 2007; Jiang et al., 2011).

5.4. Sediment homologue/congener patterns and potential sources

In most samples, the concentration of each class of PCB homologues (Fig. 2) is generally below 2.16 $\mu g\ kg^{-1}$ (e.g., TeCBs, TN25C) for sediments and 5.62 $\mu g\ kg^{-1}$ (e.g., TriCBs, TS04) for soils, and a significant ($p < 0.05$) or highly significant ($p < 0.01$) correlation with fines is observed (Table S2 in the Supplementary material). The general predominance of light congeners may account for selective long range atmospheric transport (Iwata et al., 1994) and/or degradation processes such as photolysis of highly chlorinated PCBs (Bailey et al., 2002). Contrarily, the higher contributions of heavier congeners at TS05 and TS06, coupled to the fact that they present the highest total PCB concentrations (as for TS04), suggest the occurrence of a close direct input. These sites are located in the proximity of small rural settlements, far from Quy Nhon city (Fig. 1), and common practices there are both the use of untreated wastewater or water from contaminated rivers for farmland irrigation (Tuan et al., 2010), and the disposal of wastes close to households. All these factors can enhance the presence of halogenated contaminants in soils. Moreover, the construction of wastewater treatment facilities in these areas has not followed the pace of urbanization (IWMI – International Water Management Institute, 2001) and, when present, the plants are hardly functioning or have a very low coverage.

The relevant presence of PCB 11 in most samples (at least 7% of total PCBs, Table 1) accounts for specific sources. The release of PCB 11 must be associated with human activities utilizing pigments or dyes (Hu and Hornbuckle, 2010) and thus linked to the increasing use of new consumer goods. These products are likely to enter wastewaters and combined sewer overflows, therefore PCB 11 can be a tracer of emissions from industrial syntheses of paint pigments (Hu and Hornbuckle, 2010). Indeed, its relative abundance is higher than 15% at TN05s (in front of the NEZA sewage outputs), and in the proximity of Quy Nhon port (TN26 and TN28), but its highest percentages are to be found near the lagoon inlet, where fine sediments accumulate. Clearer conclusions are weakened by the fact that DiCBs (composed exclusively by PCB 11 in this study) show highly significant correlation with fines ($r = 0.61$, $p < 0.01$, Table S2 in the Supplementary material), which influence DiCBs' distribution and pattern. In addition, volatilization processes occurring in dry agricultural soils, urban parks and river banks cannot be excluded.

Many PBDE congeners are significantly correlated among themselves, while no relationships are found between these chemicals and OC contents, fine fractions, and porosity (see Table S3 in the Supplementary material). Several studies have reported that high molecular weight congeners can be metabolized to less brominated compounds including tri- to hexa-BDEs, e.g. PBDE 47, 99 and 100 (Moon et al., 2002, 2007; Soderstrom et al., 2004). Therefore, debromination may be their principal source in the area.

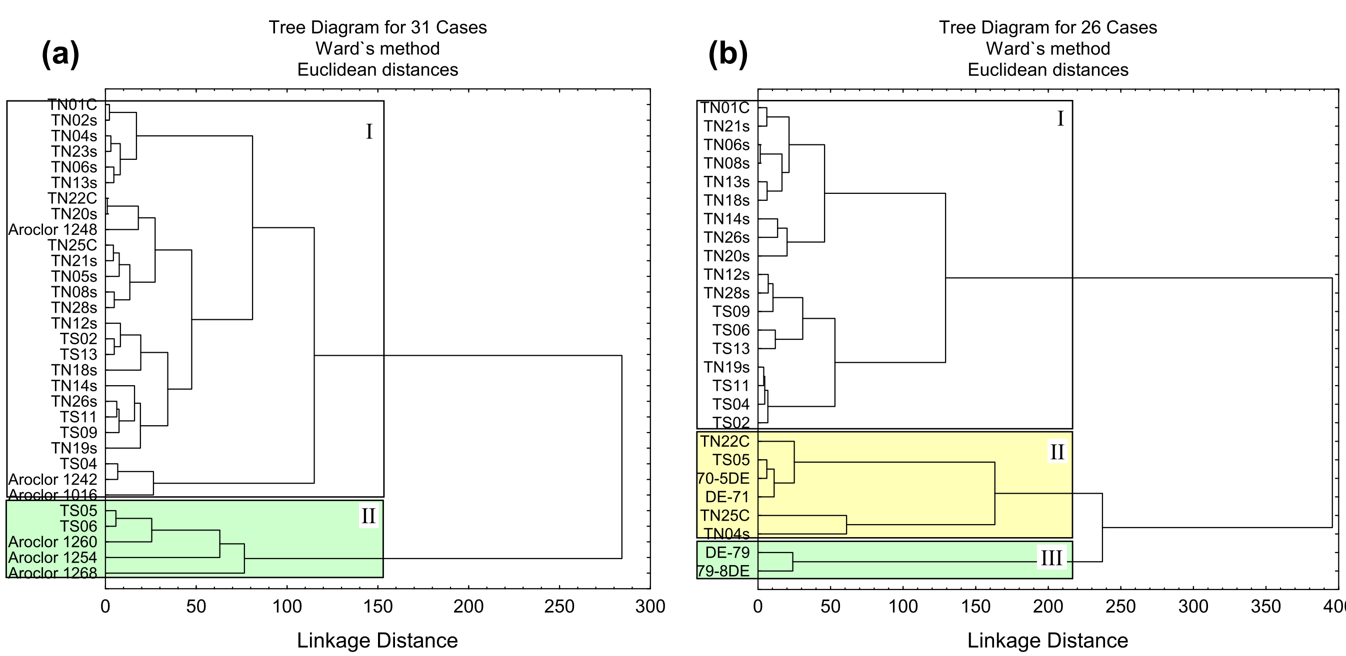

Fig. 3. Cluster analysis (Euclidean distance and Ward's method) for the comparison of sample relative abundances with commercial mixtures for PCBs (a) and PBDEs (b). Color boxes highlight the clusters.

Cluster analyses (using the Euclidean distance and Ward method on relative abundances of congeners/homologues) were performed to compare our samples' fingerprint to main PCB and PBDE commercial mixtures (Fig. 3). As expected, PCB sample compositions show similarities with lighter commercial products (e.g. Aroclor 1248), except for TS05 and TS06. In turn, PBDE commercial mixtures are not grouped with our samples, except for: (1) TN22C and TS05, which show an affinity to major penta-BDE commercial mixtures (70-5DE and DE-74), and (2) TN04s and TN25C that are close to the heavy octa- formulation, due to the absence of PBDE 47 in their pattern. It may be argued that the differences observed in the composition of both PCBs and PBDEs in sediments and soils with commercial products might be due to mixing, selective transport and degradation. The evidences discussed above suggest a significant role of the different stability and resistance to degradation for PCBs and PBDEs. However, at TS04, TS05, TS06, TN19s and TN22C, both PCBs and PBDEs resemble the composition of original mixtures, probably due to recent point inputs. This hypothesis is also confirmed by PCA plots (Figs. S3 and S4, in the Supplementary material) performed on homologues/congeners composition of sediment and soil samples.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.10.067.

References

Alaee, M., Arias, P., Sjödin, A., Bergman, Å., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ. Int. 29, 683–689.

Athy, L.F., 1930. Density, porosity and compactation of sedimentary rocks. Bull. Am. Assoc. Petrol. Geol. 14, 1–24.

Bailey, R.A., Clark, H.M., Ferris, J.P., Krause, S., Strong, R.L., 2002. Haloorganics and pesticides. In: Chemistry of the Environment, second ed. Academic Press, New York, pp. 244–251.

Bhavsar, S.P., Jackson, D.A., Hayton, A., Reiner, Eric J., Chen, Tony, Bodnar, J., 2004. Are PCB levels in fish from the canadian great lakes still declining? J. Great Lakes Res. 33 (3), 592–605.

Conrads, PA., Roehl, Jr Edwin A., 2006. An artificial neural network-based decision support system to evaluate hydropower releases on salinity intrusion. In: 7th International Conference on Hydroinformatics, HIC, Nice, France.

De Wit, C.Y., 2002. An overview of brominated flame retardants in the environment. Chemosphere 46, 583–624.

Figuié, M., Moustier, P., 2009. Market appeal in an emerging economy: supermarkets and poor consumers in Vietnam. Food Policy 34, 210–217.

Frignani, M., Piazza, R., Bellucci, L.G., Cu, N.H., Zangrando, R., Albertazzi, S., Moret, I., Romano, S., Gambaro, A., 2007. Polychlorinated biphenyls in sediments of the Tam Giang-Cau Hai Lagoon, Central Vietnam. Chemosphere 67, 1786–1793.

Fry, B., Sherr, E.B., 1989. δ^{13}C measurements as indicators of carbon flow in marine and freshwater ecosystems. In: Rundel, P.W., Ehleringer, J.R., Nagy, R.A. (Eds.), Stable Isotopes in Ecological Research. Springer-Verlag, New York, pp. 196–229.

Giuliani, S., Piazza, R., Bellucci, L.G., Cu, N.H., Vecchiato, M., Romano, S., Mugnai, C., Nhon, D.H., Frignani, M., 2011. PCBs in Central Vietnam coastal lagoons: levels and trends in dynamic environments. Mar. Pollut. Bull. 62 (5), 1013–1024.

Hu, D., Hornbuckle, K.C., 2010. Inadverted polychlorinated biphenyls in commercial paint pigments. Environ. Sci. Technol. 44, 2822–2827.

IWMI – International Water Management Institute, 2001. Wastewater Reuse in Agriculture in Vietnam:Water Management, environment and human health aspects. In: Proceedings of a Workshop held in Hanoi, Vietnam 14 March 2001. <http://www.iwmi.cgiar.org>.

Iwata, H., Tanabe, S., Sakai, N., Nishimura, A., Tatsukawa, R., 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. Environ. Pollut. 85, 15–33.

Jiang, J-J., Lee, C-L., Fang, M-D., Ko, F-C., Baker, J.E., 2011. Polybrominated diphenyl ethers and polychlorinated biphenyls in sediments of southwest Taiwan: regional characteristics and potential sources. Mar. Pollut. Bull. 62 (4), 815–823.

Lamb, A.L., Wilson, G.P., Leng, M.J., 2006. A review of coastal paleoclimate and relative sea-level reconstructions using δ^{13}C and C/N ratios in organic material. Earth-Sci. Rev. 75, 29–57.

Moon, H.B., Choi, H.G., Kim, S.S., Jeong, S.R., Lee, P.Y., Ok, G., 2002. Contaminations of polybrominated diphenyl ethers in marine sediments from the southeastern coastal areas of Korea. Organo-halogen Compd. 58, 217–220.

Moon, H.B., Kannan, K., Choi, M., Choi, H.G., 2007. Polybrominated diphenyl ethers (PBDEs) in marine sediments from industrialized bays of Korea. Mar. Pollut. Bull. 54, 1402–1412.

Nguyen, M.H., Minh, B.T., Tanabe, S., Isobe, T., 2010. Contamination of polybromodiphenylethers (PBDEs) in sewer system of Hochiminh City and estuary of Saigon-Dongnai River. In: 5th International Symposium on Brominated Flame Retardants (BFR2010). April 7–9, Kyoto, Japan. Abstract Book, ID 90139.

Oguchi, T., Jarvie, H.P., Neal, C., 2000. River water quality in the Humber catchment: an introduction using GIS-based mapping and analysis. Sci. Total Environ. 251,252, 9–26.

Olsen, C.R., Cutshall, N.H., Larsen, I.L., 1982. Pollutant–particle associations and dynamics in coastal marine environments: a review. Mar. Chem. 11, 501–533.

Quy Nhon port website, 2011. <http://www.quinhonport.com.vn/Vi_Tri_E.htm>.

Ramu, K., Kajiwara, N., Sudaryanto, A., Isobe, T., Takahashi, S., Subramanian, A., Ueno, D., Zheng, G.J., Lam, P.K.S., Takada, H., Zakaria, M.P., Viet, P.H., Prudente, M., Tana, T.S., Tanabe, S., 2007. Asian mussel watch program: contamination status of polybrominated diphenyl ethers and organochlorines in coastal waters of Asian countries. Environ. Sci. Technol. 41, 4580–4586.

Rhee, G.Y., Sokol, R.C., Bethoney, C.M., Bush, B., 1993. Dechlorination of polychlorinated-biphenyls by Hudson River sediment organisms – specificity to the chlorination pattern of congeners. Environ. Sci. Technol. 27, 1190–1192.

Rodenburg, L.A., Guo, J., Du, S., Cavallo, G.J., 2010. Evidence for unique and ubiquitous environmental sources of 3,3′-dichlorobiphenyl (PCB 11). Environ. Sci. Technol. 44, 816–2821.

Scott, C.A., Faruqui, N.I., Rashid-Sally, L., 2004. Wastewater use in irrigated agriculture: management challenges in developing countries. Wastewater use in agriculture: coordinating the livelihood and environmental realities. International Development Research Centre.

Soderstrom, G., Sellstrom, U., De Wit, C.A., Tysklind, M., 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environ. Sci. Technol. 38, 127–132.

Thao, V.D., Kawano, M., Tatsukawa, R., 1993. Persistent organochlorine residues in soils from tropical and sub-tropical Asian countries. Environ Pollut. 81, 61–71.

Tuan, N.A., Minh, T.B., Minh, N.H, Hoai, P.M., Viet, P.H., Tuyen, B.C., Son, L.K., Takahashi, S., Tanabe, S., 2010. Brominated flame retardants in Vietnam: a concise review of recent contamination. In: 30th International Symposium on Halogenated Persistent Organic Pollutants (Dioxin, 2010), San Antonio, Texas, USA, September, Abstract Book, ID 1346.

VPA-shipping time trading & transportation review. Binh Dinh to develop port strategy to 2020, 2011. http://www.vpa.org.vn/detail_temp.jsp?id=1988.

Wang, X.M., Ding, X., Mai, B.X., Xie, Z.Q., Xiang, C.H., Sun, L.G., Sheng, G.Y., Fu, J.M., Zeng, E.Y., 2005. Polybrominated diphenyl ethers in airborne particulates collected during a research expedition from the Bohai Sea to the Arctic. Environ. Sci. Technol. 39, 7803–7809.

Wang, T., Wang, Y., Fu, J., Wang, P., Li, Y., Zhang, Q., Jiang, G., 2010. Characteristic accumulation and soil penetration of polychlorinated biphenyls and polybrominated diphenil ethers in wastewater irrigated farmlands. Chemosphere 81, 1045–1051.

Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J., Wong, A.S., 2007. Export of toxic chemicals – A review of the case of uncontrolled electronic-waste recycling. Environ. Pollut. 149, 131–140.

Yan-Ping, D., Xiang-Zhou, M., Chao, Y., Zhao-Yu, P., Ling, C., Ran, Y., Feng-Ting, L., 2010. Polybrominated diphenyl ethers in background surface soils from the Yangtze River Delta (YRD), China: occurrence, sources, and inventory. Environ. Sci. Pollut. Res. 17, 948–956.