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Levels and Distribution of Organochlorine Pesticides and Polychlorinated Biphenyls in Water and Sediment from the International Anzali Wetland, North of Iran

Islam Javedankherad · Abbas Esmaili-Sari · Nader Bahramifar

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Abstract Organochlorine pesticides (OCPs) and PCBs were determined in water and sediment from the Anzali Wetland, north of Iran. The total concentrations of OCPs were 71.75–315.16 ng/l, 1.8–12.68 ng/g dry wt in water and sediments respectively, and those of polychlorinated biphenyls (PCBs) in the two phases were: nd–141.09 ng/l and 0.39–2.64 ng/g dw, respectively. Also, the results indicated that β-HCH, DDE were the most common organochlorine pesticides contaminants. In this study, the ∑PCB/∑DDT reflect the relative importance of agricultural than industrial sources in this area. a significant difference was observed between the stations. Station number 3 showed the highest range of the pollutants studied.

Keywords Anzali Wetland · Water · Sediment · Organochlorine · PCBs

Organochlorines (OCs), such as polychlorinated biphenyls (PCBs) and chlorinated pesticides, represent an important group of POPs which have caused worldwide concerns as toxic environmental contaminants (Law et al. 2003). There are several input mechanisms that lead to the deposition of OCs in the environment. These include urban run off, municipal sewage, industrial waste, outflow from agricultural areas, chemical spills, and atmospheric deposition (Vallack et al. 1998). Organochlorine pesticides (OCPs) have been extensively used to increase the production of agriculture crops by preventing losses due to pest. In January 2000, over 27,000 tons of pesticides were used in Iran, Although this huge amount of pesticides is distributed all over the country, 60 % of all pesticides are applied in three Northern Provinces (i.e. Gilan, Mazandaran and Golestan), close to the Caspian Sea, while rice production alone accounts for a quarter of the national pesticides usage (Behrooz et al. 2009). Organic pollutants released into water system via various mechanisms readily are adsorbed to particles, and then incorporated into sediments. Thus the concentrations of OCs in surface sediments provide information on recent contamination (Hong et al. 2003). The Anzali Wetland is one of the most important water bodies in the province of Gilan and Southern coast of the Caspian Sea in Iran. Its open water surface area is more than 58 km^2. There are recreational facilities for boating on the wetland.The Anzali Wetland with its fascinating landscapes attracts many visitors and represents an internationally important wildlife which is listed under Ramsar Covention (Pourang 1995). During the last recent decades, the wetland has been threatened and destroyed by environmental pollution from seven identified sources of rivers, municipal, industrial sources, commercial sources, mines, agricultural sources, and hospitals. Discharge of used oil from ships, illegal construction, discharge of all kinds of wastewater from fish farms, and solid waste disposal are the major sources which have negatively affected this wetland environment which was registered on the Montreux Record in 1993 (Jafari 2009). The objectives of this study were to investigate the levels of OCPs and PCBs in water and sediments in the Anzali Wetland of Iran and to

I. Javedankherad (✉) · A. Esmaili-Sari
Department of Environmental Sciences, Faculty of Natural Resources and MarineScience, Tarbiat Modares University, P.O. Box 46414-356, Noor, Mazandaran, Iran
e-mail: Ijavedan@gmail.com

N. Bahramifar
Department of chemistry, Payame Noor University (PNU), Sari, Iran

compare these values with guidelines and to collect baseline data as a first step in compiling a databank to be used later to detect changes in environmental levels of these pollutants.

Materials and Methods

Sampling was carried out from January to February 2009. Water (n = 45) and sediment (n = 45) samples were also collected at 9 stations (Fig. 1). All top sediment (0–5 cm) and subsurface water (0.5 m) samples were collected in each site, using a stainless steel grab and precleaned glass bottles, respectively. All the water samples were filtered through 0.45 µm fiber glass filters to remove sand and debris. Then they were returned to the laboratory and stored at temperature between 0°C and 4°C prior to extraction. Also, all sediment samples were immediately transported to the laboratory and stored in the laboratory at −20°C. All the equipment used for sample collection, transportation, and preparation were free of organochlorine contamination.

Organochlorine pesticides including HCHs (α-HCH,β-HCH, γ-HCH), hexachlorobenzene (HCB), p,ṕ-DDT, o,ṕ-DDT, o,ṕ-DDE, p,ṕ-DDE, p,ṕ-DDD, and target congeners of PCB (IUPAC Nos. PCB 28, 52, 101, 118, 138, 153 and 180) were analyzed. Standards were obtained from Ehrenstorfer Inc. (Augsburg, Germany) and chemicals were purchased from Merck Inc. (Darmastadt, Germany).

Sediments sample treatment and analysis followed the method described by Covaci et al. (2006) with slight modifications. The sediment sample was first freeze-dried and then (around 5 g) was placed into a hexane pre-washed extraction thimble. A triple amount of copper powder (<63 Am, Merck) was added and mixed with the sediment. Samples were spiked with internal standards (ε-HCH and PCB 143) and were extracted for 4 h by Soxhlet apparatus with 100 ml hexane/acetone (3/1, v/v), respectively. Then the solvents

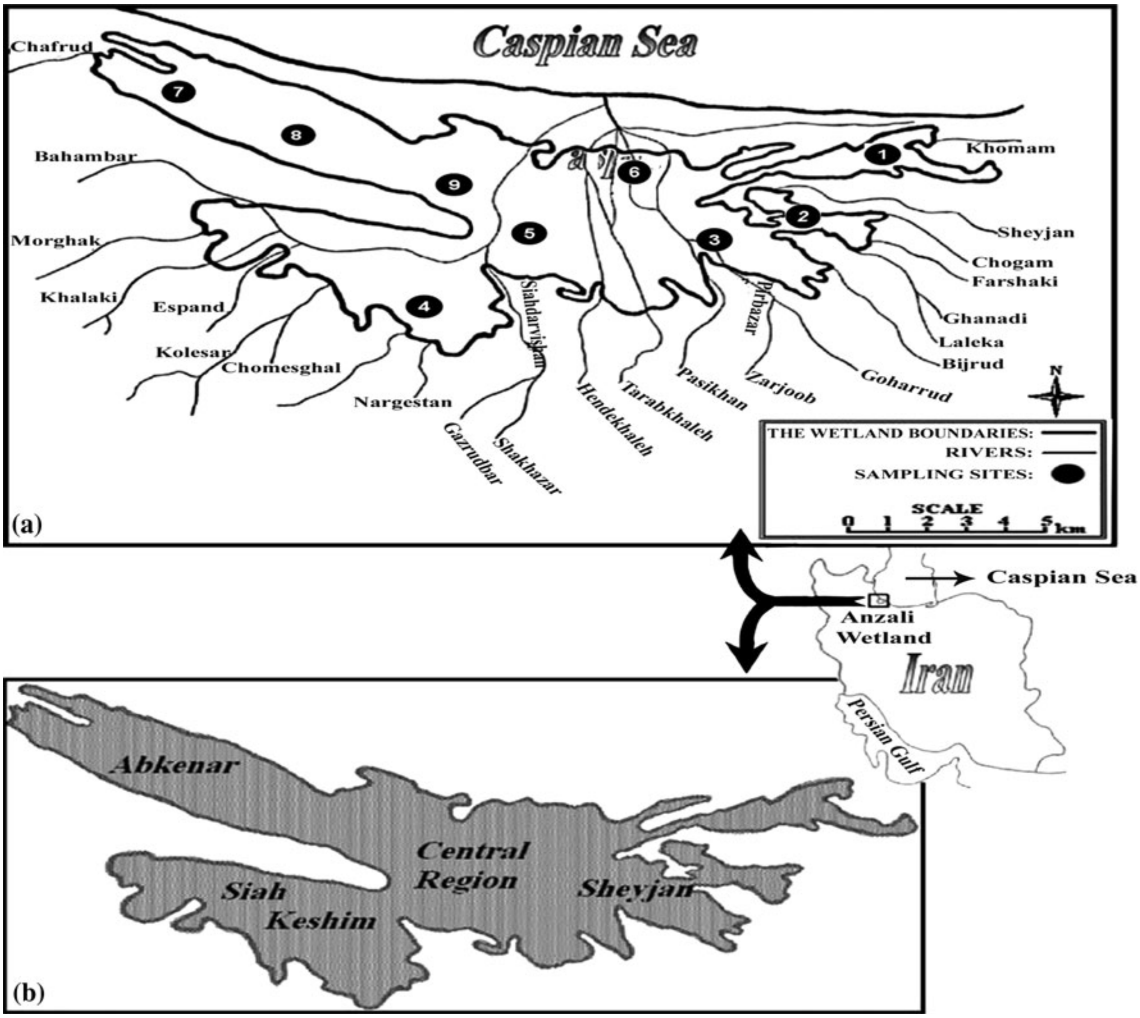


Fig. 1 Map of the Anzali Wetland showing the location of the sampling sites (**a**) and differentiations of the wetland (**b**)

were evaporated, using a rotary evaporator (Heidolph WB 2000, Kelheim, Germany), and further clean up was accomplished on a column filled with 8 g acidified silicagel and anhydrous sodium sulfate (and 1 g copper powder). The column was eluted with 15 ml hexane and 10 ml dichloromethane. The eluate was concentrated to 100 μl under a gentle nitrogen stream. One μl of extract was injected into a gas chromatographic (GC) system.

Water samples were extracted, using a solid- phase extraction (SPE) system from Supelco following established procedures Zhang (2001) with minor modifications. The Supelco SPE cartridges were first conditioned with 2 × 5 ml of methanol followed by 2 × 5 ml of deionized water. Water sample (1,000 ml) was spiked with internal standards (ε-HCH and PCB 143) and was passed through the cartridges at a flow rate of 6 ml min^{-1} under vacuum. Following extraction, the cartridges were eluted with15 ml of dichloro-methane. After water was removed from the extracts by anhydrous Na_2SO_4, the extracts were reduced in volume by putting them under a gentle nitrogen stream.

Analysis was performed using a Dani 1000 gas chromatograph (Monza, Italy) equipped with ^{63}Ni electron capture detector and a DB-5 capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness, Macherey–Nagel). Helium was used as the carrier gas at a flow rate of 2 ml/min. The operating conditions were split (1:1) injection mode. Temperature program was as follows: 100°C (1 min), 10°C/min to 240°C (1 min), 3°C/min to 260°C (1 min), 20°C/min to 300°C (10 min). The injection port temperature and detector temperature were 250 and 300 C, respectively. Multiple-level calibration curves were created for the quantification. Good linearity ($r^2 > 0.998$) was achieved for tested intervals that included the whole concentration range found in the samples. Each analyte was identified by a comparison of its relative retention time to the peaks form the calibration standards.

Recoveries of PCBs and OCPs into samples which passed through the analytical procedure were between 85 and 111 %., and RSD for the recoveries of OCPs and PCBs were below 15 % (OCPs 6–14 % and 5.5–11.8 % for the water, sediments, respectively). Limit of quantification

Table 1 Concentrations of organochlorines in water (ng/l) and sediment (ng/g dry wt.) from the Anzali Wetland

Compounds	Water	Sediment				
	Range	Mean	SD	Range	Mean	SD
α -HCH	nd-27.21	11.07	5.25	0.08–0.49	0.19	0.4
β -HCH	7.73–45.06	26.25	12.24	0.13–1.92	0.88	0.61
γ -HCH	8.54–34.04	20.41	9.83	0.13–1.05	0.51	0.22
HCB	nd[d]- 28.04	14.03	8.87	0.06–0.35	0.15	0.6
o,p′-DDT	4.49–14.02	7.46	3.05	0.07–0.46	0.21	0.8
o,p′-DDE	5.73–18.04	11.28	5.59	0.08–0.79	0.36	0.14
p,p′-DDT	4.08–22.07	12.97	7.09	0.09–1.5	0.58	0.37
p,p′-DDD	8.87–52.61	22.96	15.04	0.23–1.79	0.78	0.39
p,p′-DDE	33.59–73.37	54.13	30.19	0.93–4.24	2.23	1.12
PCB 28	nd -33.05	16.94	6.62	nd-0.17	0.05	0.02
PCB 52	nd -29.77	12.11	4.76	nd-0.22	0.1	0.06
PCB 101	nd-18.04	6.09	3.51	0.15–0.81	0.42	0.24
PCB 118	nd-17.02	3.07	1.5	0.05–0.4	0.18	0.07
PCB 138	nd-15.21	4.01	2.65	0.12–0.46	0.21	0.12
PCB 153	nd-15.77	5.50	2.99	0.45–0.31	0.14	0.06
PCB 180	nd-12.23	3.25	1.76	0.04–0.27	0.13	0.08
∑PCBs	nd-141.09	50.99[a]	26.26	0.39–2.64	1.27[a]	0.07
∑HCH	16.27–106.31	57.73[c]	28.41	0.34–3.46	1.59[c]	0.95
∑DDT	55.48- 180.81	108.83[b]	49.63	1.42–8.87	4.19[b]	1.98
∑OCPs	71.75–315.16	180.6	96.28	1.8–12.68	5.94	2.84
p,ṕ-DDTs	47.26–129.37	90.08	–	1.25–7.53	3.61	1.98
p,ṕ-DDE/p,ṕ-DDTs	0.38–0.71	0.49	–	0.56–0.74	0.61	–

[a] ∑PCBs = sum of seven target congener of PCB(28,52,101,118,138,153,180)

[b] ∑DDT = p,ṕ-DDE + o,p′-DDE + p, p′-DDD + o, p′-DDT + p,ṕ-DDT

[c] ∑HCH = α-HCH + β-HCH + γ–HCH

[d] Non-detected

(LOQ) for OCPs ranged between 0.7 and 1 ng/l, 0.05–0.1 ng/g dry wt and LOQ for PCBs ranged between 0.5–1 ng/l and 0.03–0.09 ng/g dry wt for the water, sediments, respectively.

The data were tested for normality using a Kolmogorov–Smirnov test. Differences in concentration of OCPs and total PCB between stations were evaluated by one-way analysis of variance (ANOVA). When significant differences were observed among the stations, the Tukey multiple-comparison test was applied to the ANOVA to determine which means were significantly different. Compounds in which over 50 % of the measurements were below the LOQ were excluded from our statistical analysis to ensure accuracy. SPSS Software (Version 11.5) was utilized for Statistical analysis and $p < 0.05$ was set to indicate significance.

Results and Discussion

Concentration data for the level of organochlorine pesticides and PCBs in water and sediment are showed in Table 1.

The OCPs concentrations ranged from 71.75 to 315.16 ng/l, with a mean concentration of 180.60 ng/l for the water sample). In comparison, the levels of total organochlorine pesticides in The Anzali Wetland water are higher than those in South China Sea (1.27–121.8 ng/l, with a mean of 16.49 ng/l; Zhang. 2001), Qiantng River (7.68–269.4 ng/l, with a mean of 61.54 ng/l; Zhou et al. 2006). When comparing individual components, it was found that, for HCHs and DDTs, the concentrations in wetland water are higher than that in Humber catchments (Meharg et al. 1998), and in the coast of Alicante, Spain (Prats et al. 1992). The results indicated that water in Anzali wetland is moderately polluted by organochlorine pesticides.The total organochlorine pesticides concentration in sediment varied from 1.8 to 12.68 ng/g dry weight with a mean concentration of 5.94 ng/g dry weight (Table 1). In addition, regarding total DDT concentration in the sediments, the situation is comparable with Black Sea, Turkey and Russian coast (Fillmann et al. 2002), Caspian Sea, Azerbaijan (De Mora et al. 2004). In terms of individual component distributions, as shown in Fig. 2, it was again found that β-HCH and DDE of total HCHs, DDTs, respectively were predominant in water and sediment samples. On average, β-HCH collectively accounted for 46 % of total HCHs in water and 56 % in sediment, and DDE accounted for about 50 % of total DDTs concentration in water and 53 % in sediment. It indicated that β-HCH is more stable than other isomers of HCHs. DDE, being metabolites of DDTs, difficult to degrade (Zhang et al. 2003). This observation may suggest the lack of new input of the HCHs into the wetland (Nakata et al. 2005). Of course, β-HCH is a known metabolite product of the biodegradation of γ-HCH and α-HCH in sediments (Wu et al. 1997). Also, the high concentration of p,ṕ- DDE in sediments may be attributed to the presence of various species of riparian benthic organisms which can accelerate the biodegradation process (Pandit et al. 2001). The concentrations of HCB in water and sediments are in the range of nd–28.04 ng/l and 0.06–0.35 ng/g, respectively. It could be argued that it came from atmospheric deposition and other emission sources.

Total PCB levels in water varied from nd to 141.09 ng/l (Table 1), probably due to inputs of PCBs from atmosphere and other sources. Such levels are higher than the levels in New York Harbor waters (Totten et al. 2001), Sao Paulo, Brazil (Rissato et al. 2006), Lake Michigan, USA (Pearson et al. 1996). Therefore, the Water in the Anzali Wetland is polluted by PCBs. Such levels may be partly due to the wet season when the samples were taken. PCBs in sediments varied from 0.39 to 2.64 ng/g dry wt. with mean concentration of 1/27 ng/g dry wt. (Table 1), such levels were higher than those detected in the Caspian Sea, Iran and Kazakhstan (De Mora et al. 2004).

In terms of individual PCB congener distributions, as shown in Table 1 and Fig. 3, almost all congeners were present in the sediments. The predominance of highly chlorinated congeners (CBs 101 and 138) and low chlorinated congeners (28 and 52) in sediments and water samples were clearly observed.

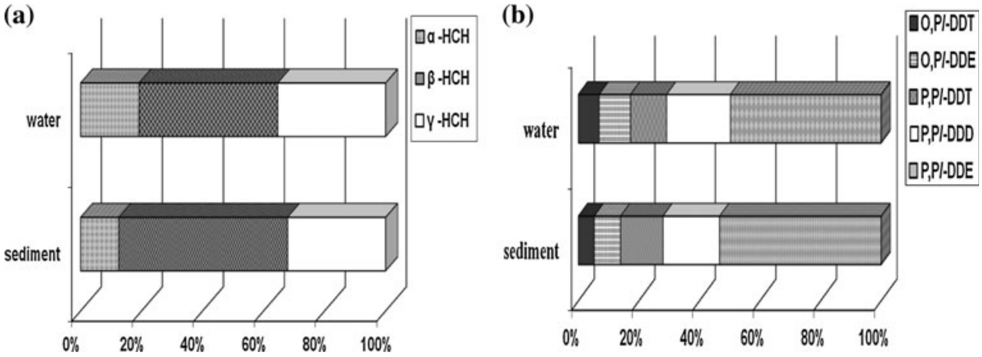
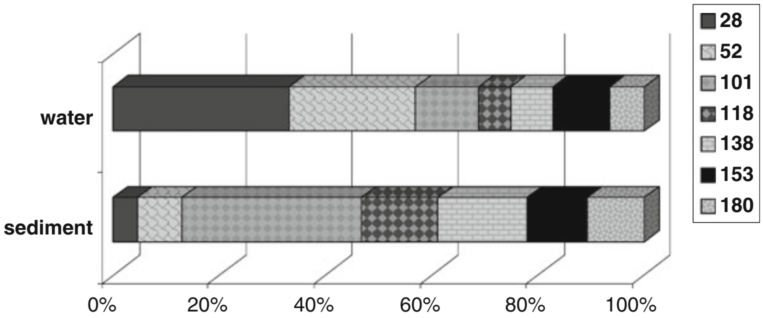


Fig. 2 Composition of HCH (**a**) and DDT (**b**) isomers in water and sediment from the Anzali Wetland, Gilan, Iran

Fig. 3 Composition of PCB congeners in water and sediment from the Anzali Wetland, Gilan, Iran



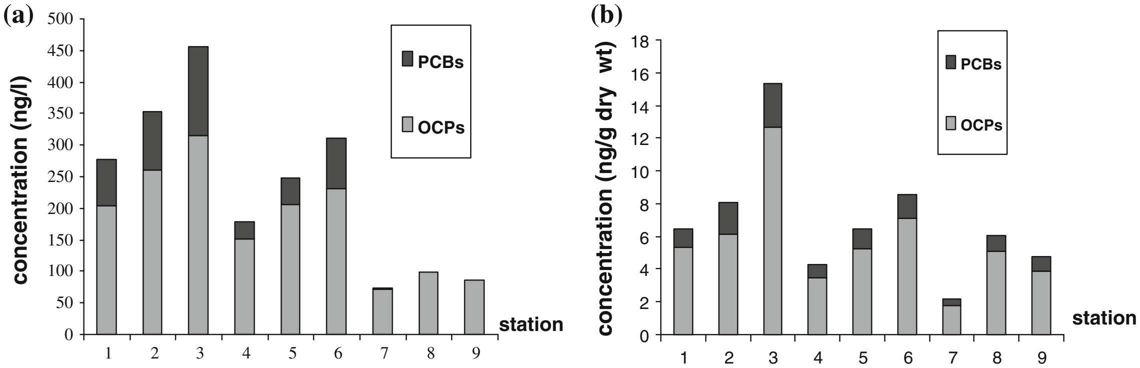


Fig. 4 The OCP and PCBs concentrations in water (**a**) and sediment (**b**) from a sampling sites of the Anzali Wetland of Iran

The behavior of PCBs in water is entirely different from that of sediment in the wetland. In water, the results of low chlorinated biphenyls (tri and tetra) were 33.22 % and 23.75 % in the wetland, respectively, while the results for high chlorinated biphenyls (penta and hexa) were 48.29 % and 27.99 % in the sediment samples, respectively (Fig. 3). Low chlorinated biphenyls are more water-soluble than high chlorinated biphenyls, which might account for the elevated levels of tri- tetrachloro biphenyls, in relation to penta- to heptachloro biphenyls, in water (Rissato et al. 2006). Difference in congener composition in the aquatic systems may also be attributed to the proportion of less chlorinated PCBs that are more susceptible to losses through volatilization, sedimentation, and possibly microbial degradation (Maskaoui et al. 2005). Moderately and highly chlorinated PCBs may, therefore, remain persistent in the aquatic environment because they are less volatile and more soluble in lipids, adsorb more readily to sediments, and are more resistant to microbial degradation (Tyler and Millward. 1996).

Existing sediment quality guidelines (CCME 1999), ecotoxicological assessment criteria (OSPAR Commission 2000) and Water Quality Criteria (Lee et al. 2001) were used for the assessment of the relative sediment/water quality and potential risk to the aquatic species in the Anzali Wetlad. None of the sediment samples (Table 1) exceeded the Canadian sediment quality PEL (probable effect level, i.e. the level above which adverse effects on aquatic biota are expected to occur frequently) guideline values (total PCB 277; p,ṕ-DDT 4.77; p,ṕ-DDE 6.75 and p,p;-DDD 8.51 ng/g dry wt.) for the protection of aquatic biota for total PCBs and DDTs. In the case of water of the wetland (ng/l), concentrations of γ -HCH (lindane) were greater than the ecotoxicological assessment criteria (EAC) range of 0.5–5.0 ng/l, suggested by OSPAR Commission (2000). The total PCBs concentrations from the water of Anzali Wetland were higher than the Water Quality Criteria (WQC) (Lee et al. 2001) of 0.03 μg/l. From these assessments, it can be concluded that the levels of the xenobiotic compounds in Iranian marine environment are alarming and may cause toxicological effects on the marine species inhabiting the Anzali Wetland.

Figure 4 demonstrates the total concentration profiles of PCBs and OCPs from 9 sampling stations in the Anzali Wetland. There is a significant difference between the investigated stations regarding the pollutants studied ($p < 0/0$ 5), and Stations number 2 and 3, located in the eastern part of the wetland, showed the highest range of the studied pollutants while Station number 7, located in the western part of wetland, showed the lowest amount of the studied pollutants. The higher concentration of these pollutants in the east of the wetland may be associated with high agricultural activities (such as, cotton, rice, etc.), human population, intense shipping and related activities (dry-docking, repairing and painting.), soil erosion due to deforestation and industrial activities (leather, paper, electronics, fabrics, plastic, etc.) around the eastern region of the wetland. Moreover, the entrance of the pollutants residues from Station number 3 (Pir-Bazar) is the main cause of the high rate of the pollutants in the eastern part and Station number 3.

The ratio of $\sum$PCB to $\sum$DDT provides a means to assess the relative importance of industrial and agricultural sources of chlorinated compounds in the environment.A small value indicates that the organochlorinated substances are predominantly derived from agricultural sources rather than industrial ones (De Mora et al. 2004). In this study, the $\sum$PCBs/$\sum$DDTs ratio in the water and sediments samples is 0.41 and 0.32, respectively. These quite low values reflect the relative importance of agricultural sources in this area and highlight the overall importance of agrochemical DDTs. Also, in general, high OCP concentrations in these locations may be due to their intensive usage in agricultural activities such as the cultivation of cotton, sugarcane and rice.

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References

Behrooz RD, Esmaili Sari A, Bahramifar N, Ghasempouri SM (2009) Organochlorine pesticide and polychlorinated biphenyl residues in human milk from the Southern Coast of Caspian Sea, Iran. Chemosphere 74:931–937

CCME (1999) (Canadian Council of Ministers of the Environment). Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. Canadian environmental quality guidelines, Winni- peg, Manitoba

Covaci A, Gheorghe A, Hulea O, Schepens P (2006) Level and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediment and biota from the Danube Delta, Romania. Environ Pollut 140:136–149

De Mora S, Villeneuve JP, Sheikholeslami MH, Cattini C, Tolosa I (2004) Organochlorinated compounds in Caspian Sea sediments. Mar Pollut Bull 48:30–43

Fillmann G, Readman JW, Tolosa I, Bartocci J, Villeneuve JP, Cattini C, Mee LD (2002) Persistent organochlorine residues in sediments from the Black Sea. Mar Pollut Bull 44:122–133

Hong SH, Yim UH, Shim WJ, Oh JR, Lee IS (2003) Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. Mar Pollut Bull 46:244–253

Jafari N (2009) Ecological integrity of wetland, their functions and sustainable use. J Eco Natur Environ 1(3):045–054

Law RJ, Alaee M, Allchin CR, Boon JP, Lebeuf M, Lepom P (2003) Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. Environ Int 29:757–770

Lee KT, Tanabe S, Koh CH (2001) Contamination of polychlorinated biphenyls (PCBs) in sediments from Kyeonggi Bay and nearby areas. Korean Mar Pollut Bull 42:273–279

Maskaoui K, Zhou JL, Zheng TL, Hong H, Yu Z (2005) Organochlorine micropollutants in the Jiulong River Estuary and Western Xiamen Sea China. Mar Pollut Bull 51:950–959

Meharg AA, Wright J, Osborn D (1998) The frequency of environmental quality standard (EQS) exceedance for chlorinated organic pollutants in rivers of the Humber catchments. Sci Total Environ 210(211):219–228

Nakata H, Hirakawa Y, Kawazoe M, Nakabo T, Arizono K, Abe SI, Kitano T, Shimada H, Watanabe I, Li W, Ding X (2005) Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. Environ Pollut 133:415–429

OSPAR Commission (2000) Quality status report. London7 OSPAR Commission

Pandit GG, Mohan Rao AM, Jha SK, Krishnamoorthy TM, Kale SP, Raghu K, Murthy NBK (2001) Monitoring of OCP residues in the Indian marine environment. Chemosphere 44:301–305

Pearson RF, Hornbuckle KC, Eisenreich SJ, Swackhamer DL (1996) PCBs in Lake Michigan water revisited. Environ Sci Technol 30:1429–1436

Pourang N (1995) Heavy metal bioaccumulation in different tissues of two fish species with regards to their feeding habits and trophic levels. Environ Monit Assess 35:207–219

Prats D, Ruiz F, Zarzo D (1992) Polychlorinated biphenyls and organochlorine pesticides in marine sediments and seawater along the coast of Alicante, Spain. Mar Pollut Bullet 24(9): 441–446

Rissato SR, Galhiane MS, Ximenes VF, de Andrade RMB, Talamoni JLB, Libanio M, de Almedia MV, Apon BM, Cavalari AA (2006) Organochlorine pesticides and polychlorinated biphenyls in soil and water samples in the Northeastern part of Sa˜ o Paulo State, Brazil. Chemosphere 65:1949–1958

Totten LA, Brunciak PA, Gigliotti CL, Dachs J, Glenn TR, Nelson ED, Eisenreich SJ (2001) Dynamic air–water exchange of polychlorinated biphenyls in the New York–New Jersey Harbor Estuary. Environ Sci Technol 35:3834–3840

Tyler AO, Millward GE (1996) Distribution and partition of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls in the humber estuary. Mar Pollut Bull 32:397–403

Vallack HW, Bakker DJ, Brandt I, Brostrom-Lunden E, Brouwer A, Bull KR (1998) Controlling persistent organic pollutants–What next? Environ Toxicol Phamacol 6:143–175

Wu WZ, Xu Y, Schramm KW, Kettrup A (1997) Study of sorption, biodegradation and isomerization of HCH in stimulated sediment/water system. Chemosphere 35:1887–1894

Zhang ZL (2001) Environmental behavior and primary assessment of organic pesticides in the estuarine agricultural watershed, Ph.D Thesis, Xiamen University, China

Zhang ZL, Hong HS, Zhou JL, Huang J, Yu G (2003) Fate and assessment persistent organic pollutants in water and sediment from Minjiang River Estuary. Chemosphere 52:1423–1430

Zhou R, Zhu L, Yang K, Chen Y (2006) Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. J Hazard Mater 137:68–75