

DISTRIBUTION OF ORGANOHALOGENATED CONTAMINANTS IN SEDIMENTS AND BIVALVES FROM THE COAST OF KUWAIT

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Introduction:

Organohalogenated contaminants (OHCs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated biphenyls (PBDEs) are physico-chemically very stable, and less degradable in the environment^{1,2,3}. Due to high lipophilicity, they accumulate in the tissue of organisms and biomagnify through the food chain and consequently affect organisms in higher trophic level^{1,2,3}. Occurrence of these OHCs has been reported in various compartments of the environment^{1,2,3}. As a result many of these OHCs are classified as persistent organic pollutants (POPs) under Stockholm Convention⁴. A handful studies have reported OHCs in the environment of Kuwait but few focused on the coastal environment⁵. Sediment profiles are a good tool to estimate the historical deposition of OHCs in the coast by local and regional sources. OHCs in sediments may become bio-available to the aquatic organisms, hence becomes an important step in mapping possible exposure pathways to aquatic web. The objective of this study was to understand the environmental levels of selected OHCs in sediments and bivalves collected from the coast of Kuwait. Status of OHCs contamination in the study area was compared with those of other previous studies in Kuwait and other countries. Spatial distribution patterns and characteristics of POPs were discussed.

Material and methods:

Sampling and sample preparation Sediments (N=30) and bivalves (N=16) were collected from different sites along the coast of Kuwait. The samples were kept in a freezer until further analysis. The procedure for extraction and clean-up of selected contaminants from sediments is described elsewhere⁶. Briefly, the sediment sample (~2 g) and bivalve (~1 g) was placed into a hexane pre-washed extraction thimble. A triple amount of copper powder (b63 Am, Merck) was added and mixed with the sediment, followed by the addition of internal standards. Samples were extracted using a Soxhlet extractor B-811 (BÜchi, Switzerland) operated in hot extraction mode. Solvent mixtures (hexane/acetone (3:1, v/v) 80 ml) were used for extraction for 2 hr. After that the extract was concentrated and transferred onto a solid-phase extraction (SPE) cartridge filled (from the bottom) with ~8 g acidified silica (44% concentrated sulphuric acid, w/w), 0.5 g anhydrous sodium sulphate and 1 g copper powder. The elution of PCBs, OCPs and PBDEs was done with 15 ml hexane followed by 10 ml DCM. The elute was concentrated to near dryness by a rotary evaporator and further by a gentle nitrogen stream. The final extract was re-solubilized in 80 µl of iso-octane for instrument analysis.

Instrumentation Analysis of PCBs, OCPs and PBDEs was performed using 6890 Agilent (Palo Alto, CA, USA) gas chromatography (GC) coupled to a 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI). A DB-5 column (30 m × 0.25 mm × 0.10 µm) was used for separation and the MS was deployed in selected ion monitoring (SIM) mode. The ion source, quadrupole and interface temperatures were set at 200, 150 and 300 °C, respectively. Additionally, the analysis of PCBs and OCPs was performed by GC-MS in electron ionization (EI) mode. A HT-8 column (25 m × 0.22 mm × 0.25 µm) was used and the MS was operated in SIM mode with two characteristic ions acquired for each compound. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300°C, respectively.

QA/QC The analytes identification was based on relative retention times and ion chromatograms to the standards. A deviation of the ion intensity ratios within 20% of the mean values of the calibration standards was considered acceptable. Quality for OHCs analysis was assured through procedural blanks and blind duplicate samples. Procedural blank levels were consistent (RSD<25%) and therefore the median blank value was used for subtraction. To avoid possible photo-degradation of analytes, extraction and clean up steps were performed using amber glass under fume hood without light.

Results and discussion:

Concentration of OHCs in sediments and bivalves: The OHCs concentrations detected in bivalves and sediments collected from the coast of Kuwait are summarized in Table 1. Different OHCs were detected at varies detection frequencies (DF), with more frequently in bivalves samples compare to sediments. PCBs followed by OCPs and PBDEs were the order of OHCs importance for both bivalves and sediments. \sum PCB levels in surface sediments range from <LOQ to 150 ng/g dw. The available data for PCBs in sediments from Arabian Gulf region is scarce. Similar levels of \sum PCB contamination (range 0.4 to 82 ng/g dw) was earlier reported from the Kuwait sediments⁵. The dominant PCBs congeners were 101, 118, 138, 153, and 180, although there were detected in <40% of the sediment and >75% of the bivalve samples. The most abundant PCB congener detected in the investigated sediment (<LOQ-18ng/g dw) and bivalve (<LOQ-105 ng/g lw) samples was PCB 153. DDTs was the major OCP in both sediments (range <LOQ-6 ng/g dw) and bivalves (range <LOQ-190 ng/g lw) samples. Other OCPs such as hexachlorocyclohexane (HCHs), chlordanes and hexachlorobenzene etc were generally low, some below and others just above the detection limit. In >90% of the sediments and bivalve samples The ratio p,p' -DDT/ \sum DDTs was <0.1 suggests past exposure to DDTs, this indicates that fresh DDT exposure may have ceased now. For all samples, \sum PBDEs ranged from <LOQ to 6 ng/g dw in sediment, and from <LOQ to 365 ng/g lw in bivalves. The value of \sum PBDEs refers to the sum of BDE 28, 47, 100, 99, 154, 153, and 183. BDE-47 is predominant in both sediment and bivalves, which is in agreement with other studies^{7,8}. PBDEs were detected in <20% of the total sediment samples with no specific congener detected in more than 10 % of the samples.

Table 1 Levels of OHCs in sediment (ng/g of dry weight) and bivalves (ng/g of lipid weight) samples from Kuwait.

Analytes	Sediments (N=30)			Bivalves (N=16)		
	DF	Mean±StDev	Median; (Range)	DF	Mean±StDev	Median; (Range)
CB 153	40	0.6±2.7	0.05; (<LOQ-18)	88	20±25	11; (<LOQ-105)
CB 138	38	0.6±3	0.05; (<LOQ-20)	88	14±15	7; (<LOQ-550)
\sum PCBs	47	4.0±22	0.1; (<LOQ-150)	94	90±90	65; (<LOQ-340)
p,p' -DDE	29	0.3±0.6	0.1; (<LOQ-4)	88	20±17	10; (<LOQ-60)
p,p' -DDT	13	0.3±0.8	0.1; (<LOQ-5)	25	17±45	3; (<LOQ-180)
\sum DDTs	29	0.5±1	0.1; (<LOQ-6)	88	35±45	20; (<LOQ-190)
\sum HCHs	4	0.06±0.05	0.05; (<LOQ-0.3)	44	3±2.5	1.5; (<LOQ-11)
\sum OCPs	31	0.5±1	0.1; (<LOQ-6)	94	40±45	30 (<LOQ-195)
BDE 47	9	0.1±0.2	0.05; (<LOQ-1.5)	69	13±17	8; (<LOQ-70)
\sum PBDEs	18	0.3±1	0.05; (<LOQ-6)	75	72±115	18; (<LOQ-365)

Congener patterns in sediment and bivalves: The most abundant PCBs congeners, OCPs and PBDEs congener (BDE 47) was selected to compare the profile of OHCs in both sediments and bivalves. Contributions of PCBs congeners to the total OHCs was (mean) 46% in bivalves and 68% in sediment (Figure 1). PCB 153 and 138 were the major contributor followed by DDTs congeners. The OHCs specific patterns in sediment and bivalves were different. The higher contribution of DDT congeners (~40%) and BDE47 (~15%) in bivalves compare to sediments indicate varied bioaccumulation potential and ability to metabolize these chemicals.

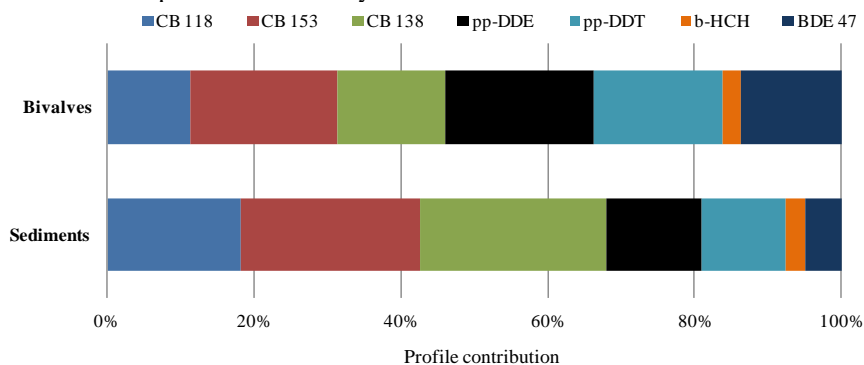


Figure 1 Composition of OHCs in sediments and bivalves collected from the coast of Kuwait.

Comparison with other studies: OHCs pollution of sediments and bivalves resulting from different human activities has been well documented around the world, therefore selected OHCs levels in present study were compared with levels reported from several other countries (Figure 2). The concentrations of PBDEs in present study are multifold less than those reported from Hong Kong⁹. This is understandable since Kuwait coastal area is less densely populated and unlike Hong Kong neither shipping nor electronic industries are the major potential sources. Levels of PCBs in both sediments and bivalves were in similar range to earlier studies except from Japan¹⁰ and Belgium⁶. Although, the use of PCBs was prohibited in Belgium and Japan long ago but extensive use in past and recycling of the PCBs material resulted high levels of PCBs in Belgian and Japanese environment^{10,11}. Kuwait is not an agricultural country therefore low level of DDTs and other OCPs are not surprising. Levels of DDTs were multifold lower than those reported from India, China and Korea. Large amounts of technical DDT have been used in China and India in recent past, which might have resulted high DDTs in the environment^{12,13}. Monirith et al.,¹⁰ reported that the compositions and residue levels of DDTs in mussels in Asian developing countries (China, India, Hong Kong, Vietnam) indicate current usage of DDT for agriculture and public health purposes. Overall, the OHCs concentrations, in sediments and bivalves measured in our study were on the lower side than those in literature^{5,9-25}.

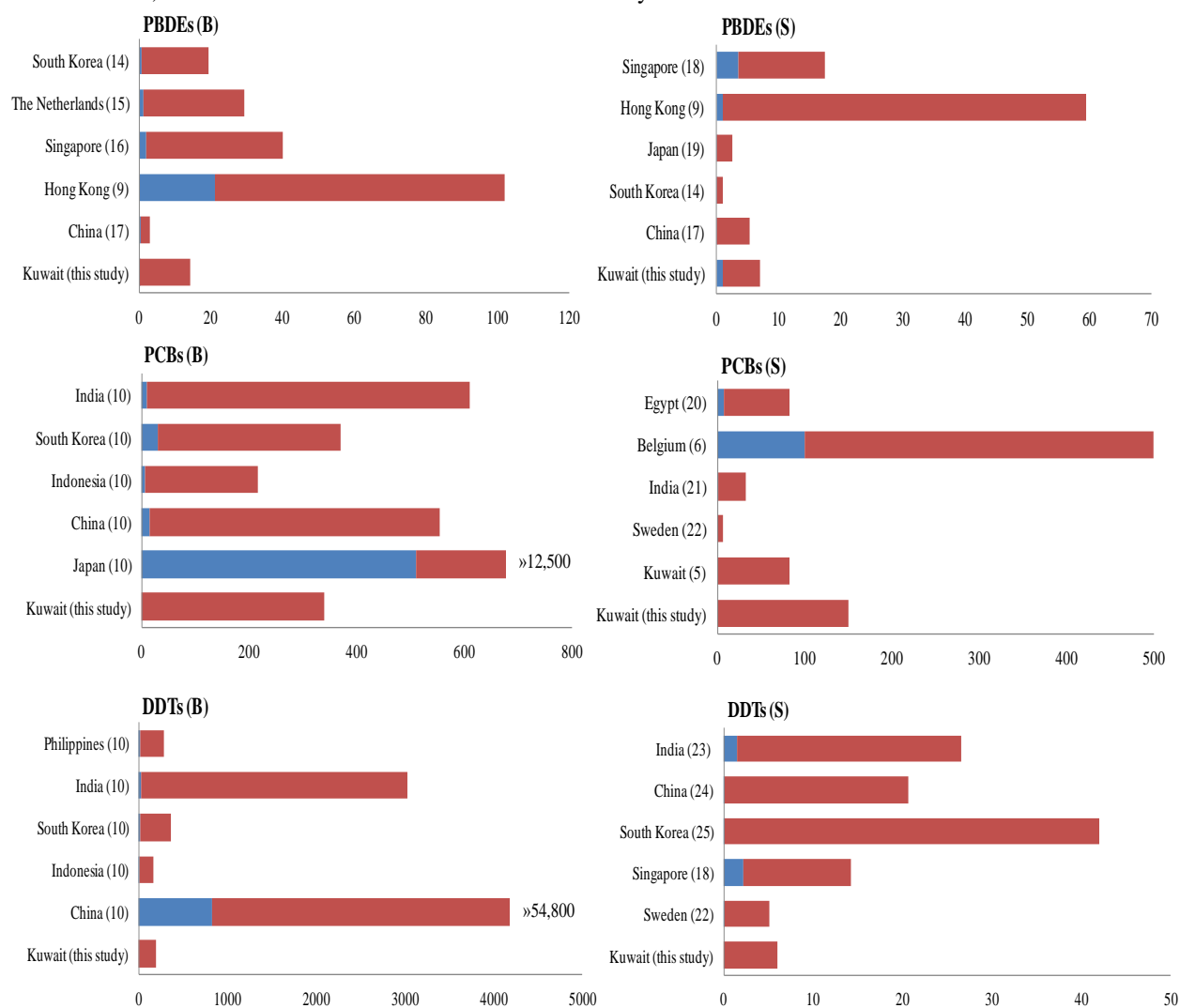


Figure 2 Comparison of important OHCs levels (range ng/g dw (Mini Max)) with other studies from different regions. Levels of PCBs and DDTs in bivalves are in ng/g lw. B – bivalves, S – sediments.

Atmospheric deposition is known to play a very significant role in delivering POPs to water bodies in Europe and North America. Due to extremely high temperatures coupled with low annual precipitation in the Arabian Gulf, the phenomenon of atmospheric deposition is not significant in this region. In Kuwait average annual temperatures are about 35°C (range 10–50 °C) and average annual rainfall ranges between 78 and 152 mm. At this high temperature many of these POPs almost entirely exist in the gas phase for the better part of the year. The significant difference in the POPs concentration of the studied samples indicates point source input as the primary delivery mechanism of POPs to the sediments and bivalves. The most likely source is wastewater discharged from the various discharge points along the shoreline. In conclusion, the observed distribution pattern suggests that the principal delivery mechanism for OHCs to coastal samples in this study is from point source inputs.

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