Determination of Dioxins, dioxin-like PCBs and Flame Retardants (PBDEs) in Sediments Collected in Pakistan

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Introduction

Pakistan, is a large (about 800 000 km^2) country located in the western reaches of the Indo-Gangetic plain in the north-west of the Indian subcontinent. The River Indus enters in the north and flows south from the Himalayas in the northern part of Pakistanis to Karachi the key metropolitan area (> 8 Mio inhabitants) located on the Arabian Sea coast. Much of the about 140 Mio inhabitants of Pakistan live in the vast, fertile plain that is formed by the Indus River. The coastline of Pakistan is 1046 km long some part of it being formed by the Indus River delta, the 12th largest delta in the world (i.e. about 30,000 km^2).

Dioxin-like chemicals are predominantly generated as unintended by-products of combustion processes and are usually emitted into the atmosphere however the aquatic environment is an important sink for these chemicals and consumption of seafood is an important exposure pathway for humans. Environmental monitoring of persistent organic pollutants (POPs) such as PCDD/PCDF and the dioxin-like PCBs is quite expensive and requires specialized laboratory facilities ideally equipped with High Resolution Mass Spectrometry (HRMS) instrumentation. Hence, by far the majority of work on PCDD/PCDF and dioxin-like PCB has been carried out in industrialized countries in Europe, North America and Japan. In contrast there is very little – or no information available on the levels of these chemicals in the environment of developing nations and to our knowledge no data are available on the levels of these chemicals in the aquatic environment in Pakistan. The aim of this study was thus to evaluate dioxin-like chemicals in sediments collected along a transect in the Indus River to the Arabian Sea as well as in sediments from the most urbanised and industrialised area south of Karachi to obtain a first in-sight on the levels of dioxin-like chemicals in Pakistan.

Methods and Materials

For the purpose of this study sediment samples were collected from 9 locations following a transect of the Indus River (5 Locations) and in the vicinity of the industrial areas of Karachi Harbor and Gizri Creek, a key industrialized area on the major urbanized area of Pakistan's coastline.

Figure 1: Map of Pakistan showing the Indus River and Karachi

Table 1: Sampling sites for the sediments in Pakistan

Code	Station	Salinity	Pool (No of samples)	Description
PK 1	Indus River	Fresh water	Samples from Indus River up stream	Collected at different barrages at Indus River
PK 2	Indus River	Fresh water	Dto	dto
PK 3	Indus River	Fresh water	Dto	dto
PK 4	Indus River	Fresh water	Dto	dto
PK 5	Indus River	Fresh water	Dto	dto
PK 6	Indus River, down stream	Oceanic	Indus River down stream, entrance of the sea (pool of 2 samples)	
PK 7	Korangi Creek area	Estuarine	Pool of 4 samples	Including steel mill area and Port Qasim Area.
PK 8	Gizri Creek	Estuarine	Pool of 2 samples	During low tide receiving untreated Industrial and Domestic waste in area
PK 9	Karachi Harbour	Oceanic	Pool of 4 samples	About 15 km area within Karachi harbour

Analytical Methods

For analysis freeze-dried, homogenized samples were send to the ERGO Laboratory in Hamburg. All analyses were performed following the isotope dilution method. Samples were analysed for 2,3,7,8-substituted PCDD/PCDF and dioxin-like PCB. In brief, the freeze-dried, homogenised samples were soxhlet extracted for 20 hours using toluene. A blank was included. Prior to extraction samples were spiked with a ^{13}C-labelled PCDD/PCDF, PCB and PBDE standards of known quantity. The extracts were concentrated and subject to clean up using acid-base (H_2SO_4/CsSiO) and alumina (Alox B-super, ICN) columns in series. Samples were further purified on activated carbon and an acid-base (H_2SO_4/CsSiO) cleanup, if required. Samples were concentrated to near dryness and transferred into vials with a known quantity of 1,2,3,4-TCDD, used as recovery standard. Analysis was performed on a GC (DB-5 fused silica column, 60 m, 0.25 mm i.d., 0.1 µm film thickness) interfaced to a VG Autospec mass spectrometer operating on a resolution of approximately 10 000. Identification of 2,3,7,8-substituted PCDD/Fs was performed using retention times of the ^{13}C-labelled standard and isotope ratios M^+ and M^{2+}.Several criteria had to be fulfilled for quality control: a) the retention times (RT) of the analyte in a sample had to be within 2 s of the RT of the internal standards b) isotope ratios for each congener of the M^+ and $M+2^+$ ions had to be within 20% of the respective individual value c) the limit of quantification was defined by a signal to noise ratio greater than 3 times the average baseline variation and a substance quantity in the sample greater than 3 times the quantity in the respective blank (2 times for PBDEs). It should be noted that reduction of solvents and control of blank data is an important step in quality control for all chemicals but particularly when analyzing PBDEs at ultra trace levels. Solvents and reagents were tested before the laboratory procedures. All glassware was rinsed by solvents prior to use. Silica gel and sodium sulfate were pre-washed. To reduce the risk of contamination, rotary evaporators or any plastic equipment was avoided. For quality control reasons a laboratory blank and a QC pool was run with the batch of nine samples.

Results and Discussion

Dioxin-like chemicals were detectable in all sediment samples collected from Pakistan. If the concentrations are expressed on a toxicity equivalency basis, the concentrations range from 0.63 to 4.8 pg TEQ g^{-1} dwt. The sum of the detectable 2,3,7,8-PCDD/PCDF ranged from 3.3 pg ΣPCDD/PCDF g^{-1} dwt in the sample collected from the most upstream site in the Indus River to about 300 pg PCDD/PCDF g^{-1} dwt in the sample from Karachi Harbour. 2,3,7,8-TCDD was detectable in 5 of the 9 samples. Overall PCDD contributed to about 50 % of the TEQ in the samples with concentrations above 2 pg TEQ g^{-1} dwt and TCDD together with 1,2,3,7,8-PeCDD and 3,3',4,4',5-Penta-CB were the key contributors to the TEQ.

PBDE concentrations (Σ10 PBDEs) ranged from <LOD to 7.1 ng g^{-1} dwt. The PBDE concentrations are overall relatively low in the Indus River and followed a similar trend to those of the dioxin-like chemicals with highest concentrations in the sediments from the Karachi Harbour, Gizri Ck and Site 4 in the Indus River.

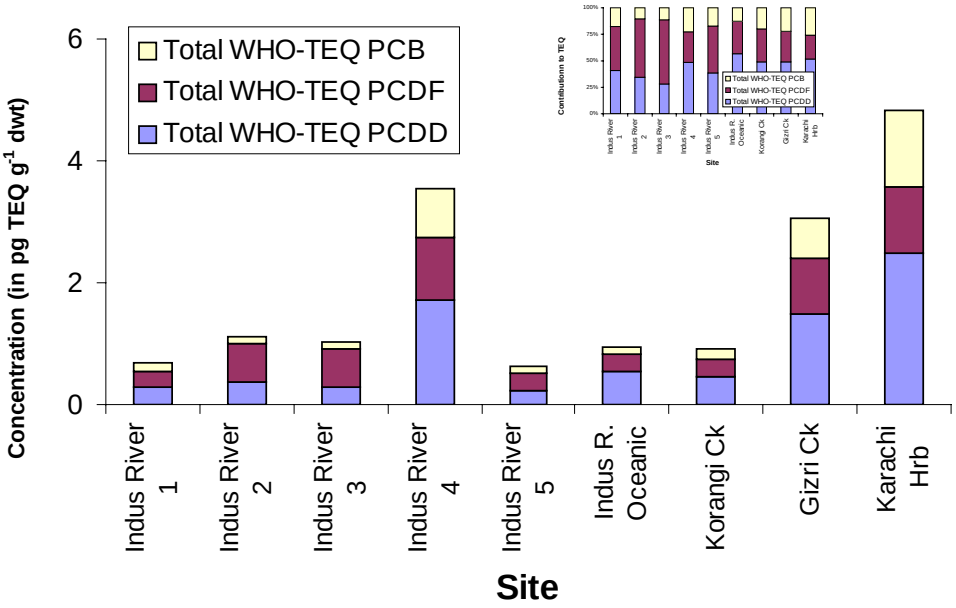

Figure 2: Concentration of dioxin-like chemicals in sediments from the Indus River and Karachi coastal areas expressed as pg TEQ g^{-1} dwt.

To our knowledge this has been the first study on dioxin-like chemicals in environmental samples from Pakistan. A comparison of the results obtained in Pakistan shows that the concentrations found in Pakistan are relatively low compared to many other countries in Asia as well as results from Europe and North America and are similar to results from estuaries in New Zealand and Australia (Table 2).

Table 2: Concentration of dioxin-like chemicals in sediment from different regions/countries

Area	Environment	n	Concentration in pg TEQ g^{-1} dwt Mean (Min – Max)	Author
Pakistan	Fresh – Marine	9	1.9 (0.63 – 4.8)	This study
Hong Kong Harbour	Marine & Estuarine	8	12 (4 – 33)	1
Japan	Marine	205	6.8 (nd – 260)	2
Korea	Marine	19	(0.01 – 5.5)	3
Russia, Caspian Sea	Marine	17	(0.7 – 28)	4
Australia	Estuarine + Marine	8	3.0 (0.05 – 9.9)	5
New Zealand	Estuarine	26	0.53 (0.08 – 2.7)	6
North America	Marine (Florida) Fresh. (Ran. Riv)	32 45	0.5 – 77.8 0.3 – 34	7, 8
EU, estuaries	Background	22	<1 – 19 but up to > 200	9

Acknowledgments

We would like to thank our colleges at the NIO in Pakistan, at EnTox in Australia and at the analytical laboratory in Hamburg for their fast and skilful work to analyze the samples: i.e. Holger Jürgensen, Bernd Schilling, Peter Ebsen, Klaus Scheunert and Dr Tamara Istanova. EnTox is cofunded by Queensland Health.

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Table 3: Concentrations of 2,3,7,8-chlorine substituted PCDD/PCDF and non-ortho and mono-ortho PCBs in sediments from Pakistan.

PCDD/F congeners	Indus 1	Indus 2	Indus 3	Indus 4	Indus 5	Indus Oc	Korangi	Gizri Ck	Kara. H.
2,3,7,8-Tetra-CDD	n.d.(0.1)	n.d.(0.1)	n.d.(0.1)	0.74	n.d.(0.1)	0.24	0.25	0.48	1.2
1,2,3,7,8-Penta-CDD	n.d.(0.1)	n.d.(0.2)	n.d.(0.1)	0.61	n.d.(0.1)	n.d.(0.2)	n.d.(0.1)	0.46	0.71
1,2,3,4,7,8-Hexa-CDD	n.d.(0.3)	n.d.(0.3)	n.d.(0.3)	0.39	n.d.(0.1)	n.d.(0.3)	n.d.(0.2)	1.1	0.72
1,2,3,6,7,8-Hexa-CDD	n.d.(0.2)	n.d.(0.2)	n.d.(0.2)	1.1	n.d.(0.1)	n.d.(0.3)	0.25	1.5	1.8
1,2,3,7,8,9-Hexa-CDD	n.d.(0.2)	n.d.(0.2)	n.d.(0.2)	0.75[a]	n.d.(0.1)	n.d.(0.2)	n.d.(0.2)	0.99	0.87
1,2,3,4,6,7,8-Hepta-CDD	n.d.(0.2)	n.d.(0.7)	1.8	12	1.2	2.0	2.8	19	21
OCDD	2.9	7.1	6.2	116	5.4	8.0	18	144	222
2,3,7,8-Tetra-CDF	0.43[a]	n.d.(0.5)	0.72[a]	3.3[a]	0.33[a]	0.30[a]	0.52[a]	0.69	0.76
1,2,3,7,8-Penta-CDF	n.d.(0.1)	n.d.(0.4)	0.36	0.92	n.d.(0.2)	n.d.(0.2)	0.32	0.60	0.70
2,3,4,7,8-Penta-CDF	n.d.(0.2)	n.d.(0.5)	0.39[a]	0.55[a]	n.d.(0.2)	n.d.(0.2)	0.14[a]	0.70	0.65
1,2,3,4,7,8-Hexa-CDF	n.d.(0.3)	n.d.(0.9)	1.3[a]	1.3[a]	0.56[a]	0.47[a]	0.49[a]	1.1	2.1
1,2,3,6,7,8-Hexa-CDF	n.d.(0.2)	n.d.(0.4)	0.30	0.49	n.d.(0.2)	0.16	0.14	0.90	1.2
1,2,3,7,8,9-Hexa-CDF	n.d.(0.4)	n.d.(0.7)	n.d.(0.9)	n.d.(0.3)	n.d.(0.2)	n.d.(0.4)	n.d.(0.3)	0.39	n.d.(0.5)
2,3,4,6,7,8-Hexa-CDF	n.d.(0.2)	n.d.(0.7)	0.52	0.98	n.d.(0.3)	n.d.(0.3)	n.d.(0.3)	1.5	1.8
1,2,3,4,6,7,8-Hepta-CDF	n.d.(0.6)	n.d.(0.6)	0.86	4.7	0.23	0.79	1.9	4.3	9.7
1,2,3,4,7,8,9-Hepta-CDF	n.d.(1)	n.d.(1)	n.d.(2)	n.d.(2)	n.d.(0.6)	n.d.(0.8)	n.d.(0.7)	n.d.(0.8)	n.d.(0.7)
OCDF	n.d.(0.6)	n.d.(1)	n.d.(2)	13	n.d.(0.6)	n.d.(3)	8.0	14	36
3,3',4,4'-Tetra-CB 77	n.d.(4)	n.d.(4)	n.d.(4)	42	n.d.(4)	n.d.(4)	8.1	41	82
3,4,4',5-Tetra-CB 81	n.d.(0.4)	n.d.(0.4)	n.d.(0.4)	1.4	n.d.(0.4)	n.d.(0.4)	n.d.(0.4)	1.8	3.1
3,3',4,4',5-Penta-CB 126	n.d.(0.7)	n.d.(0.7)	n.d.(0.7)	7.0	n.d.(0.7)	n.d.(0.7)	1.3	5.6	9.7
3,3',4,4',5,5'-Hexa-CB 169	n.d.(0.3)	n.d.(0.3)	n.d.(0.3)	1.0	n.d.(0.3)	n.d.(0.3)	n.d.(0.3)	1.1	1.6
2,3,3',4,4'-Penta-CB 105	n.d.(34)	n.d.(27)	n.d.(32)	143	n.d.(17)	n.d.(47)	n.d.(54)	129	335
2,3,4,4',5-Penta-CB 114	n.d.(15)	n.d.(16)	n.d.(14)	19	n.d.(15)	n.d.(14)	n.d.(17)	29	34
2,3',4,4',5-Penta-CB 118	n.d.(148)	n.d.(85)	n.d.(86)	218	n.d.(66)	n.d.(134)	n.d.(162)	320	878
2',3,4,4',5-Penta-CB 123	n.d.(22)	n.d.(21)	n.d.(20)	n.d.(20)	n.d.(21)	n.d.(19)	n.d.(20)	n.d.(22)	n.d.(24)
2,3,3',4,4',5,-Hexa-CB 156	n.d.(16)	n.d.(18)	n.d.(16)	60	n.d.(16)	n.d.(15)	n.d.(22)	53	164
2,3,3',4,4',5'-Hexa-CB 157	n.d.(15)	n.d.(16)	n.d.(14)	n.d.(13)	n.d.(15)	n.d.(14)	n.d.(15)	n.d.(17)	31
2,3',4,4',5,5'-Hexa-CB 167	n.d.(16)	n.d.(16)	n.d.(16)	27	n.d.(15)	n.d.(15)	n.d.(15)	34	59
2,3,3',4,4',5,5'-Hepta-CB 189	n.d.(18)	n.d.(19)	n.d.(17)	n.d.(16)	n.d.(18)	n.d.(17)	n.d.(18)	n.d.(22)	n.d.(21)
Total WHO-TEQ (PCDD/F/PCB)	**0.67**	**1.1**	**1.0**	**3.5**	**0.63**	**0.95**	**0.92**	**3.1**	**4.8**

[a] potential contribution from a coeluting non-2,3,7,8-isomere.