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ENVIRONMENTAL LEVELS - POSTERS

INSTRUMENTAL ANALYSIS OF DIOXIN-LIKE COMPOUNDS IN ENVIRONMENTAL SAMPLES FROM ULSAN BAY, KOREA

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Introduction

Ulsan Bay, located on the east coast of Korea, is highly industrialized and encompasses Korea's largest commercial harbor (Figure 1). Rapid industrialization of this area has been accompanied by environmental deterioration which has led to social and environmental health problems[1]. Despite this, little is known regarding contamination by persistent, toxic, organic contaminants. This study represents a first effort to examine the concentrations, fate, distribution, and biological potency of organic contaminants in environmental samples collected from Ulsan Bay and its vicinity. Sediment, pore water, and water samples were collected from Ulsan Bay and its adjacent coast. (Figure 1). Due to the complex nature of contaminants in environmental matrices, samples were fractionated based on polarity to help isolate and identify contaminants. Instrumental analyses and *in vitro* bioassays were used to quantify target contaminants and to evaluate dioxin-like and estrogenic potencies of each fraction. This article presents the results of instrumental analysis on the distribution of nonylphenol (NP), octylphenol (OP), bisphenol A (BPA), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine (OC) pesticides. The results of *in vitro* bioassays and mass balance analyses are presented elsewhere.

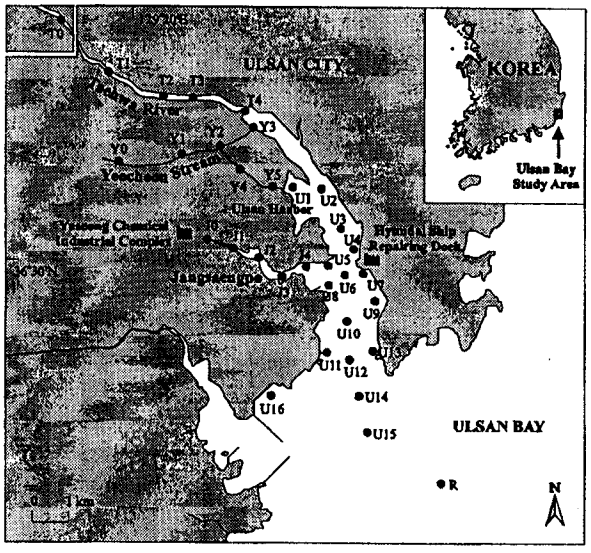

Figure 1.

Map of the Ulsan Bay study area in Korea. Sediment and water samples were collected at Taehwa River (T locations), Yeocheon Stream (Y locations), Jangsaengpo (J locations), and Ulsan Bay (U locations and Reference site) in May, 1999.

Methods and Materials

The area adjacent to Ulsan Bay, Korea, is one of the most highly industrialized regions in Korea. The Ulsan petrochemical industrial complex, composed of over 100 plants, discharges up to 200,000 t of effluent per day to Ulsan Bay, via the Woihwang and Taehwa rivers. Sediment and water samples were collected from 32 locations on Ulsan Bay and its influent rivers and/or streams in May 1999. Sediment samples were collected using a Van Veen grab sampler and pore water (PW) samples were obtained from sediment samples using a compression method. Water samples were separated into particulate matter (PM) and dissolved fractions (DF) using GF/F filtration. Total organic carbon (TOC) was analyzed for the sediment samples, allowing organic chemical concentrations to be normalized to TOC. Sediments and PM samples were Soxhlet extracted using 400 mL dichloromethane. PW and DF samples were extracted by the Empore disk extraction methods. Extracts were passed through 10 g of activated Florisil packed in a glass column (10 mm i.d.) for fractionation. Three fractions (F1, F2, and F3) were collected by the polarity using solvents appropriate for both instrumental analyses and in vitro bioassay. Reverse phase high performance liquid chromatography (HPLC) with fluorescence detection was used to quantify NP, OP, and BPA. PAHs were quantified using a Hewlett Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometer detector. OC pesticides and PCBs were quantified using a gas chromatograph (Perkin Elmer series 600) equipped with ^{63}Ni electron capture detector (GC-ECD). Further details of the fractionation procedure and instrumental analysis procedures are presented elsewhere[3,4,5].

Results and Discussion

Several sediment and water samples contained NP, OP, BPA, OC pesticides (hexachlorobenzene [HCB], hexachlorocyclohexanes [HCHs], chlordanes [CHLs], and DDTs), PCBs, and PAHs (Table 1). The relative abundance of target organic contaminants measured in sediment from Ulsan Bay was, PAHs>NP>OP>PCBs>OC pesticides>BPA (Table 1). PAHs were detected in nearly all sediment and water extracts from Ulsan Bay and its inland areas (Table 1). The detectable sedimentary PAH concentrations ranged from 17.0 to 3100 (mean 405) ng/g dry weight basis (dry wt). PAHs were predominated by 2 and 3 ring aromatic hydrocarbons in river and/or stream, and 4 to 6 ring aromatic hydrocarbons in Ulsan Bay sediment. Concentrations of PAHs in pore water samples were generally 2 or 3 order magnitude less than those of corresponding sediment samples. Generally, water-borne PAH concentrations were less than 0.5 and 1.0 ng/L for dissolved fraction (DF) and particulate matter (PM) samples respectively Maximum concentrations of NP, OP, and BPA in sediments were 1040, 120, and 53.5 ng/g dry wt, respectively. Concentrations of OP and BPA were, on average, 5- to 13-fold less than those of NP. PCB concentrations in sediment ranged from 1.29 to 64.6 ng/g, dry wt, which were predominated by relatively lower chlorinated congeners such as di- through tetra-chlorinated biphenyls (Table 1). Among different OC pesticides analyzed, concentrations of DDTs were the greatest, ranging from 0.02 to 41.9 ng/g, dry wt (Table 1). Generally there were poor relationships between sediment characteristics such as TOC content and mean grain size and concentrations of target organic compounds examined in this study (Table 2). NP concentrations were greater at inner locations proximal to wastewater discharges into rivers and/or stream, whereas the concentrations of PCBs and PAHs were greater near the sites of high industrial activities (Table1, Figure 1). Although the mean concentrations of PCBs and PAHs in Ulsan Bay sediments were less than the suggested consensus sediment quality guidelines (SQGs), their concentrations in some locations were close to or above the SQGs for toxic effects in benthic organisms.

Table 1. Total Organic Carbon (TOC) Content (%) and Concentrations (ng/g, Dry Wt) of Nonylphenol (NP), Octylphenol (OP), Bisphenol A (BPA), PAHs, PCBs and OC pesticides (HCB, HCHs, CHLs, DDTs) in sediment from Ulsan Bay, Korea.

Location	TOC	NP	OP	BPA	PAHs	PCBs	HCB	HCHs	CHLs	DDTs
T0	NA[a]	2.58	<1.00	<1.00	NA	<1.00	<0.01	0.04	<0.01	0.02
T1	0.41	11.3	1.25	17.6	<10.0	NA	NA	0.05	<0.01	<0.01
T2	0.21	12.4	4.25	1.60	<10.0	<1.00	<0.01	0.08	<0.01	0.02
T3	0.10	<1.00	2.94	<1.00	<10.0	<1.00	<0.01	0.03	<0.01	0.02
T4	0.10	<1.00	2.94	<1.00	<10.0	NA	<0.01	0.03	<0.01	0.02
Y0	1.64	<1.00	<1.00	<1.00	<10.0	1.44	0.04	0.19	3.96	0.12
Y1	6.92	1040	120	<1.00	54.5	11.9	0.11	0.03	0.16	0.30
Y2	4.94	335	56.3	<1.00	86.8	<1.00	0.11	0.02	0.20	0.29
Y3	1.46	2.83	2.19	<1.00	<10.0	2.23	0.02	0.03	<0.01	0.03
Y4	6.37	57.3	1.49	<1.00	1370	4.27	3.23	4.55	0.07	1.16
Y5	4.00	248	11.0	<1.00	951	NA	NA	1.34	0.33	0.88
J0	0.65	1.49	<1.00	<1.00	53.8	1.56	<0.01	0.03	<0.01	0.90
J1	2.58	666	8.78	53.5	601	15.0	1.56	0.30	<0.01	0.80
J2	2.38	12.2	<1.00	<1.00	97.7	2.82	<0.01	0.05	<0.01	0.03
J3	1.96	7.25	<1.00	1.09	184	11.0	<0.01	0.35	<0.01	0.58
J4	1.59	2.98	<1.00	2.33	214	1.93	<0.01	0.24	<0.01	0.58
U1	2.97	19.9	<1.00	1.23	174	<1.00	0.39	4.12	0.10	1.99
U2	1.53	2.07	<1.00	<1.00	20.8	<1.00	<0.01	0.05	<0.01	3.94
U3	1.30	1.05	<1.00	<1.00	29.2	<1.00	0.03	0.11	<0.01	0.14
U4	0.76	1.18	<1.00	<1.00	93.8	<1.00	<0.01	2.41	0.24	1.65
U5	1.33	1.82	<1.00	<1.00	79.7	<1.00	0.13	0.03	<0.01	2.78
U6	1.32	1.95	2.91	10.4	870	11.7	0.48	0.46	0.10	1.00
U7	1.49	6.37	1.22	13.1	1310	64.6	<0.01	2.26	0.16	21.1
U8	1.69	3.76	<1.00	1.42	83.9	<1.00	0.17	0.50	0.79	41.9
U9	1.30	2.45	1.17	6.76	445	3.11	<0.01	0.15	1.08	3.22
U10	1.30	NA	NA	NA	33.0	13.3	0.11	0.13	0.13	12.6
U11	1.18	1.05	<1.00	<1.00	54.7	6.75	0.10	0.29	<0.01	0.54
U12	1.16	<1.00	<1.00	<1.00	40.0	5.06	0.09	0.31	0.04	0.45
U13	1.32	2.04	<1.00	<1.00	112	1.29	<0.01	0.17	0.05	0.33
U14	1.31	<1.00	<1.00	<1.00	17.0	2.46	0.02	0.03	0.08	2.39
U15	1.39	<1.00	<1.00	<1.00	57.5	2.01	0.03	0.03	<0.01	0.21
U16	NA	3.75	<1.00	<1.00	3100	<1.00	<0.01	0.03	<0.01	0.71
R[b]	1.44	1.48	<1.00	<1.00	39.0	<1.00	<0.01	0.74	<0.01	0.37

T: Taehwa River, Y: Yeocheon Stream, J: Jangsaengpo, U: Ulsan Bay.
[a] NA: not analyzed.
[b] R: Reference site, See the study map for the location.

Table 2. Relationship (R^2) between sediment characteristics (TOC content and Mz) and concentrations of target compounds (PAHs, alkylphenols, bisphenol A, PCBs, organochlorine pesticides) in Ulsan Bay sediments, Korea.

	TOC[a]	Mz[b]	PAHs[c]	APs[d]	OCs[e]
TOC	-	0.006	0.156	0.466	0.001
Mz	-	-	(-)	(-)	0.013
PAHs	-	-	-	(-)	0.075
APs	-	-	-	-	0.070
OCs	-	-	-	-	-

[a] TOC: total organic carbon content (%).
[b] Mz: sediment mean grain size (ϕ).
[c] PAHs: sum of 16 priority PAHs compounds (EPA method 8310).
[d] APs: sum of nonylphenol, octylphenol, and bisphenol A.
[e] OCs: sum of total PCBs, and OC pesticides (HCB, HCHs, CHLs, and DDTs).

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