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Study and Measurement of Some Persistent Organochlorine Residues in Sediments from the Two Great Rivers (Tajan and Neka) of Mazandaran Province (Iran)

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Abstract: The extent of contamination of two great rivers (Tajan and Neka) of Mazandaran province in Iran by selected organochlorine compounds has been assessed through the analysis of surficial sediments taken from four sites of each river by using GC (Hewlett Packard HP5880) equipped with an electron capture detector and split/splitless injector. Concentrations of HCHs at sites influenced by the agricultural regions in Mazandarn province are among the highest recorded on a global basis (up to 30 ng g^{-1} dry wt.). The ratio between the a-and β-isomers was relatively low indicating contamination through the use of lindane. Concentrations of DDTs (73-91 ng g^{-1} dry wt. in Tajan and 49-81 in Neka) and PCBs (8-26 ng g^{-1} dry wt. in Tajan and 9-15 in Neka river) were not especially high in comparison to levels reported from throughout the world.

Key words: Organochlorine, PCBs, DDTs, HCHs, HCB, sediment, river, Iran

INTRODUCTION

Synthetic organochlorines such as DDTs, PCBs (polychlorinated biphenyls), HCHs (hexachlorocyclo-hexanes), CHLs (chlordane), cyclodienes and HCB (hexachlorobenzene) are highly resistant to degradation by biological, photochemical or chemical means. They are also liable to bioaccumulation, are toxic and probably hazardous to human and/or environmental health. Most are prone to long-range transport (Aibulatov, 1987; Benezet and Matsumara, 1973). These compounds are also typically characterised as having low water solubility and highly-pid solubility. The organochlorines have been associated with significant environmental impact in a wide range of species and at virtually all tropic levels. Many organochlorines have been implicated in a broad range of adverse human health and environmental effects, including impaired reproduction, endocrine disruption, immunosuppression and cancer (Benezet and Matsumara, 1973). Exposure to organochlorines has been correlated with population decline in a number of marine mammals (Aibulatov, 1987).

The primary transport routes into marine and River environments include atmospheric deposition and surface run-off, the former being by far the greatest albeit dispersed over large areas. Because many organochlorines are relatively volatile, their re-mobilization and long-distance redistribution through atmospheric pathways often complicates the identification of specific sources. Nevertheless, those (the majority) used in agriculture are also washed off the land into rivers, thence to the sea or directly into the sea via outfalls or run-off. Many organohalogens follow quite complex biogeochemical pathways (Burt and Ebell, 1995). Whilst there is substantial information concerning contamination of many industrialised countries and a number of studies have been conducted regarding organochlorine contamination in the Eastern Europe and Asia (Dannenberger, 1996; European Environment Agency, 1995; Galindo *et al*., 1996; Harrison *et al*., 1996; Hong *et al*., 1995).

Concentrations of DDTs, HCHs and PCBs in Mazandaran rivers and Caspian Sea fish and mammals are high by comparison with those reported for other regional seas. Due to the toxic effects of organochlorines in humans and aquatic organisms, the use and/or sale of most organochlorine pesticides has been banned or restricted in many Asian countries since the mid-1980s, although DDT is still used to control mosquito vectors of malaria in numerous countries of the world. In most countries of the Caspian Sea, however, the use of these pesticides has also been restricted or banned (Harrison *et al*., 1996; Hong *et al*., 1995).

For elucidating the present status of chemical contamination, this study focuses on organochlorine residues in sediments from several areas along two great rivers (Tajan and Neka) of Mazandaran province in Iran.

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MATERIALS AND METHODS

Location and geology: The location of the study area is on the four sites in Tajan (T_1-T_4) and four in Neka (N1-N4) river of Mazandaran province in the north of Iran.

Neka River Originates from Shah-Koh Mountain and enters the sea through Neka city. After flowing through the pass of Shamshir Bor, it flows into the Caspian Sea in the vicinity of Nowzar Abad. At first the course that this river flows is a mountainous one, with beautiful valleys covered with forests. On the condition that access is gained to the fringes of this river, recreational grounds or areas near Yanehsar can be accounted as attractive regions. It is one of the important and nourishing rivers. Its length is about 180 km with a basin area of about 3000 km^2. It is a permanent river with an annual average flow of 148. 2 million m^3.

Tajan River Originates from Tizabad Mountain and after receiving many other small rivers (e.g., Lajim, Garmab-rood, Farim River,) passes through the city of Sari (the center of the province) and then enters the sea through Farahabad city. It is about 170 km long and is one of the most important rivers of Mazandaran province. Its catchment area is about 4, 000 km^2 with an annual average water flow of 207. 4 km^2.

Chemical extraction methods: All procedures were done in central laboratort of Mazandaran medical university of Sari -Iran at September 2004 according to Burt and Ebell (1995). Surface sediment (0-2 cm) samples were collected from the studied locations using a stainless-steel grab. Individual sediment samples were well mixed and stored frozen (-20°C) in pre-cleaned glass jars until analysis. Samples were collected in September 2004 by the research group of Islamic Azad university of Sari and Payam-e-Nour University. The sediments were freeze-dried, dry/wet weight ratios determined and then sieved (250 μm stainless steel).

Each sediment sample (10-20 g) was spiked with internal standards: 2, 4, 5-trichlorobiphenyl and cHCH. These standards were used to quantify the overall recovery of the procedures. The samples were Soxhlet extracted for 8 h into 250 mL of hexane followed by re-extraction into 250 mL of dichloromethane for 8 h. The dichloromethane and the hexane were then combined and concentrated down to a few milliliters using rotary evaporation followed by gentle nitrogen "blow down". Sulphur was removed by shaking the extracts with mercury. Extractable Organic Matter (EOM) was then determined by evaporating a small measured volume of the extract on the pan of an electrobalance. The clean-up and fractionation was performed by passing the extract through a Florisil (17 g) column which had been activated at 130°C for 12 h and partially deactivated with 0.5% water. From this column, three fractions were collected: the first fraction with 70 mL of hexane; the second fraction with 50 mL of hexane/dichloromethane (70:30) and then a third fraction with 40 mL of dichloromethane. Each fraction was concentrated and injected into a GC (Hewlett Packard HP5880) equipped with an electron capture detector and split/splitless injector. The capillary column used was an SE54 fused silica (HP-Ultra 2 crosslinked 5% Ph Me Silicone, 25 m length, 0. 2 mm i.d., 0.33 μm film thicknesses). The oven temperature was programmed from an initial temperature of 70°C (2 min hold) to 260°C at a rate of 3 "Grain"1 and was then maintained at 260°C for 20 min. Injector and detector temperatures were maintained at 250 and 300°C, respectively. Helium was used as the carrier (1.5 mL min^{-1}) and nitrogen as the make-up (60 mL min^{-1}) gas. Concentrations of individual organochlorines were quantified relative to the peak area of the respective external standards following calibration with authentic standards. Confirmation of peak identify was obtained for selected extracts using GC with mass spectrometry (GC-MS) (Hewlett-Packard 5889B MS "Engine"). Appropriate blanks were analysed and, in addition, reference material IAEA-357 was analysed simultaneously.

RESULTS

On the basis of these data (Table 1 and 2), the ranking of concentrations of the various compounds in

Table 1: The concentration of some chlorinated hydrocarbons (on a dry weight basis) in Tajan river sediments in each sample

Sample codes (pg g^{-1})	T_1	T_2	T_3	T_4
HCB	7	10	7	6
α-HCH	16	28	25	32
β-HCH	20	23	30	27
P, P'-DDD	73	88	93	91
P, P'-DDT	<10	<10	<10	<10
Heptachlor	<5	<5	<5	<5
Aldrin	<7	<7	<7	<7
Dieldrin	11	17	17	13
PCB 44	26	8	9	11
PCB 49	16	<4	<4	<4

Table 2: The concentration of some chlorinated hydrocarbons (on a dry weight basis) in Neka rivers sediments in each sample

Sample codes (pg g^{-1})	N1	N2	N3	N4
HCB	<1	<1	<1	<1
α-HCH	11	12	14	16
β-HCH	15	17	22	29
P, P'-DDD	49	78	73	81
P, P'-DDT	<5	<5	<5	<5
Heptachlor	<7	<5	<5	<5
Aldrin	<7	<7	<7	<7
Dieldrin	<5	<5	<5	<5
PCB 44	15	8	9	9
PCB 49	9	<4	<4	<4

Table 3: Worldwide concentrations of organochlorines in sediments (ng g^{-1} dry wt.)

Area	PCB	DDTs	HCHs	References
Pearl River Delta, China	11.5-485	NA	NA	(Iwata *et al*., 1993; Iwata *et al*., 1994)
North Coast Vietnan	0.5-28.1	6.2-10.4	1.2-33.7	(Iwata *et al*., 1993; Iwata *et al*., 1994)
South-Western Coast, Baltic Sea	0.1-11	0.04-88	<0.04-1.2	(Iwata *et al*., 1993; Iwata *et al*., 1994)
Vanuatu and Tonga, South Pacific Islands	NA	<0.1-1027	0.1-0.3	(Iwata *et al*., 1993; Iwata *et al*., 1994)
San Francisco Estuary, USA	<0.1-8. 1	0.1-9	NA	(Iwata *et al*., 1993; Iwata *et al*., 1994; Karakaya and Ozlap, 1987; Malaiyandi and Shah, 1984)
Cities, India	4.8-1000	8-450	0.6-38	(Maldonado *et al*., 1999)
Cities, Thailand	11-520	4.8-170	0.5-3.1	(Nhan *et al*., 1999)
Cities, Japan	63-240	2.5-12	4.5-6.2	(Nhan *et al*., 1999)
Cities, Taiwan	2.3-230	0.4-11	0.3-0.8	(Maldonado *et al*., 1999; Nhan *et al*., 1999)
Cities, Australia	0.5-790	0.08-1700	0.02-17	(Nhan *et al*., 1999)
Danube River	0.02-85	0.04-41	0.03-6.4	(Malaiyandi and Shah, 1984)

ND, Not Detected; NA, Not Analysed

two rivers are as follows: DDTs >HCHs>PCBs>HCB> cyclodienes in both rivers. A similar ranking has also been observed in organisms from Black Sea (Hong *et al*., 1995).

The concentrations of PCBs (sum of 8 Stations) in sediments from two great rivers (Tajan and Neka) are low in comparison with those reported for other locations (Table 3). The highest concentration of PCBs in sediments 26 and 15 ng g^{-1} dry wt.) was found in a sample taken from the Tajan and Neka river respectively. Substantial levels of PCBs have been previously recorded in porpoise samples from the Black Sea indicating inputs of contaminants from the surrounding countries (Malaiyandi and Shah, 1984; Maldonado *et al*., 1999). Some of the Eastern European countries, such as the former USSR produced PCBs (Sovol) for use as a dielectric fluid in power capacitors and transformers (Malaiyandi and Shah, 1984; Pereira *et al*., 1994; Ramesh *et al*., 1989). A recent study showed that the composition of PCBs in Sovol was similar to that in Aroclor 1254, which contains mainly tetra-to hexa-chlorinated congeners (Safe, 1990). Although comparatively low concentrations of PCBs were found in this survey, Significant concentrations in air, water, sediments, soil, fish and seals have been reported for other regions in the Russian Federation e.g. Lake Baikal (Sherblom *et al*., 1995; Suntio *et al*., 1988; Tanabe *et al*., 1994; Thompson *et al*., 1996).

Among the 209 PCB congeners, some attain coplanarity and elicit highly toxic biological effects that can approach that of 2, 3, 7, 8-TCDD (Tuncer *et al*., 1998). Results from our sediment analyses confirm the presence of co-planar congeners, especially IUPAC No. 138 and 153 (di-ortho) and 118 (mono-ortho) which dominate (Tables 1 and 2). Concentrations of DDT and its related compounds in sediments from Two rivers are shown to be generally lower than those reported for the Baltic Sea and most Asian sites. They are comparable, or slightly higher, than those reported for other regions of Russian Federation (Table 3). Highest concentrations of DDTs in the case of the Tajan river Samples is associated with lipid rich sediments in this region (93 ng g^{-1} dry in T_3) and 81 in N4 station of Neka River. Similar variations have also been observed in other studies (Tuncer *et al*., 1998; Tyler and Millward, 1996). HCH concentrations were found to be in the range of 16-32 ng g^{-1} dry wt. in Tajan and 11-22 in Neka River.

CONCLUSIONS

The ranking of concentrations of the various organochlorine compounds in sediments from two great rivers in Mazandaran province (Tajan and Neka) are as follows: DDTs > HCHs > PCBs > HCB > cyclodienes.

Concentrations of PCBs in sediments of Tajan and Neka rivers are relatively low in comparison with those reported for other regions of the world. Highest concentrations of PCBs are recorded for the Tajan (26 ng g^{-1} dry wt. for T_1 station). Concentrations of DDT related compounds in sediments from these two rivers are shown to be generally lower than those reported for the Baltic Sea and most Asian sites. They are comparable (or slightly higher) than those reported for other regions of the world. Highest concentrations of DDTs in these rivers are associated with lipid rich sediments in the Mazandaran province. Elevated concentrations are also reported for indicate current usage of DDT around the Tajan and Neka rivers. Concentrations of lindane and the other HCH isomers are low in samples from these rivers. These levels are comparable to the low to medium range of values for estuarine sediments from eastern and southern Asia and Oceania. However, they are much lower than values reported for areas that are subjected to intensive sources of HCH contamination, e.g., India and Vietnam(Tyler and Millward, 1996; Van Bavel *et al*., 1995; Wakeham and Beier, 1991). The composition of the HCH isomers in the sediments showed a high percentage of the β-isomer at the highly contaminated locations along the Tajan and Neka rivers. HCB and cyclodienes were also found in sediments from the Tajan and Neka rivers, albeit at much lower concentrations than those recorded for the

other compounds (Van Bavel *et al*., 1995; Wakeham and Beier, 1991).

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