OCCURRENCE, SPATIAL DISTRIBUTION AND COMPOSITION OF PCBs AND OCPs IN THE SURFACE SEDIMENTS OF HARAZ RIVER, IRAN

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Introduction

Persistent Organic Pollutants (POPs) includes polychlorinated biphenyls (PCBs) and several organo chlorine pesticides (OCPs) including 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (DDT), hexachlorocyclohexanes (HCHs). Environmental monitoring involves several persistent PCBs congeners; either a simple set of seven[1-2] or several tens of congeners[3]. Some studies have covered the entire 209 congeners[4]. Environmental analysis of DDT includes the degradation products such as *ortho* and *para* isomers of DDD [2,2-bis(2-chlorophenyl,4′-chlorophenyl)1,1-dichloroethane] and DDE [2,2-bis(2-chlorophenyl1,4′-chlorophenyl)1,1-dichloroethylene]. Synthesized raw HCH contains a total of eight stereoisomers which are termed α- to θ-HCH depending on the spatial arrangements of the chlorine atoms. Among these, only the α, β, γ, δ, and ε isomers are stable and are formed in the following percentages in reaction mixtures: α, 55–80%; β, 5–14%; γ, 8–15%; δ, 2–16%, and ε, 3–5%. The remaining three isomers are formed in trace amounts[5]. The water and sediment quality of the River Haraz in Iran have been significantly changed from industrial discharges, agricultural activities, and urban wastes[4]. The present study investigates the extent of pollution in the surface sediment of Haraz River in Iran.

Materials and methods

Haraz River is the second largest river in the southern Caspian Sea basin, which originates from the central Alborz Mountains, and empties into the Caspian Sea[4]. The water quality parameters such as DO, BOD, COD, NH_3, EC and Turbidity in River Haraz were not meeting the regulatory standards[6] mainly from waste discharges from the nearby city Amol and fish farming activities on the river. Agricultural, orchard farming and cattle grazing are major activities in the upstream part of the river that adds target pollutants to the river. The downstream area near Caspian Sea sees agricultural activities with rice paddy

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Surface sediments (approximately 0–5 cm) were collected from both upstream and downstream locations at fifteen places in Haraz River during December 2012. Sample preparation, extraction, and clean-up steps are after Covaci et al., [7]. Sensitive and selective gas chromatograph equipped with electron capture detector (GC-ECD) was the choice of quantitation method. The QA/QC procedures included spiked internal standards, analysis of duplicate, and filed blanks. Internal standards were used at the start of the procedure, extraction, and cleanup steps to specify recovery. The recovery from blank spike and matrix spike was appropriate with an average of 85% and 97%, respectively, and the RSD for the recoveries was less than 15%.

Results and discussion

7 PCB congeners (28, 52, 101, 118, 153, 138, 180), o,p´-DDT, p,p´-DDT and their degradation products o.p´-DDD, p,p´-DDD, o,p´-DDE, p,p´-DDE; α,β,γ, and δ-HCH were determined in surface sediments from the selected sites. The results are represented in Figs. 1 - 3. It was obvious from Fig 1 and 2 that the level of contamination near the industrial and urban areas was higher than those from remote regions. High concentration of PCBs (>89.34 ng/g) and DDTs (>39.22 ng/g) were identified in locations with intense agricultural (especially rice paddy), industrial activities; locations with urban and rural land use (e.g., stations S12, S13, S14, S15). However this trend is not noticable in Fig.3 for HCHs isomers.

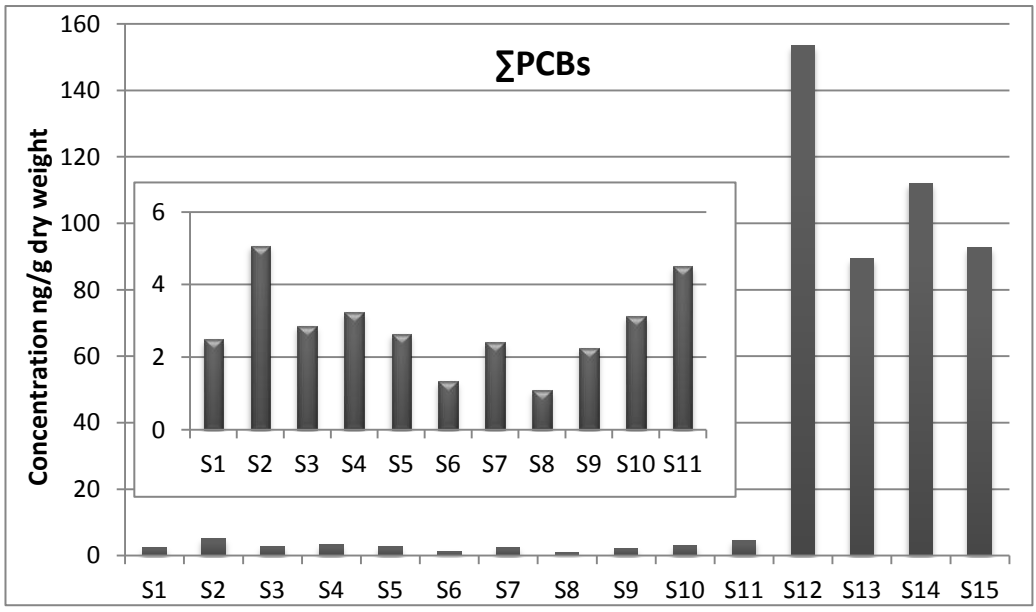

Fig. 1 Concentration (ng/g DW) of total PCBs (sum of 7 congeners) in 15 stations in River Haraz (insert shows the low concentration area enlarged)

Total PCB concentrations in surface sediment varied from 1.09 to 153.41ng/g. The PCBs distribution among the 15 locations points out clearly those stations influenced by urban municipal waste and industrial discharges (Fig.2). Thus, station S12 at the downstream of Haraz River near Amol city had the highest PCB concentration (153.41 ng/g). The lowest PCB concentration was recorded at station S8. Similarly, all the upstream locations recorded low levels compared to urban locations. The second highest PCB levels were found at stations

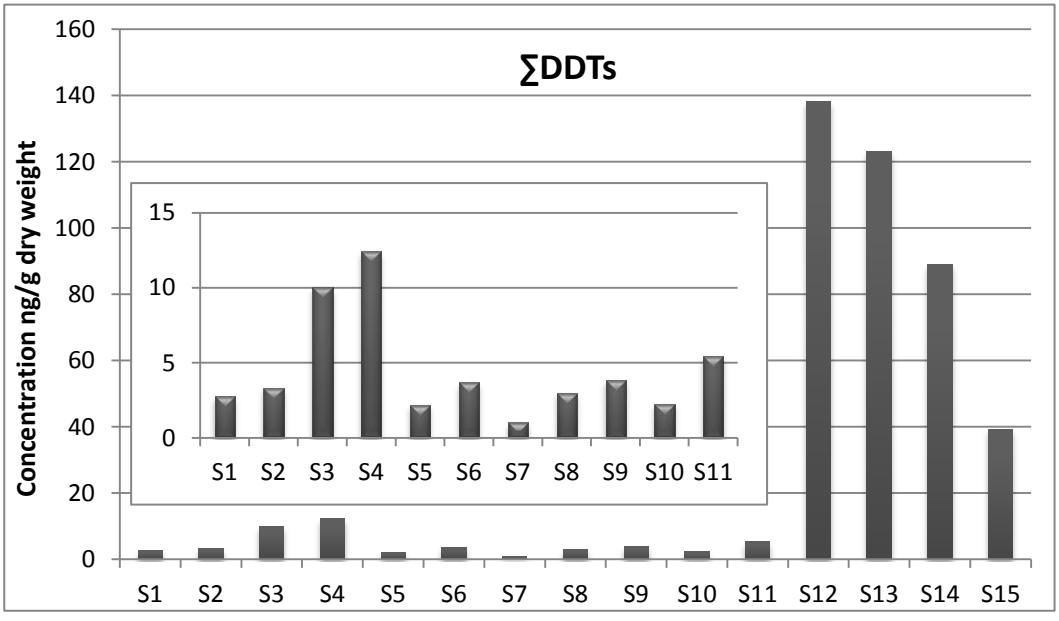

Fig. 2 Concentration (ng/g DW) of total DDTs (sum of *p,p', o,p* isomers of DDT, DDD and DDE) in 15 stations in River Haraz (insert shows the low concentration area enlarged)

S14 and S15 located near Caspian Sea, which receives run-off from ship repainting, boat maintenance activities and slaughter house effluents. The most predominant PCB congeners in the whole analyses were PCBs -138 and -153 (hexa- chloro biphenyls), comprising of 54.92% of total PCBs. Among the lower chlorinated PCB congeners it was PCB-28 and -52 that contributed about 10.71% (tri, tetra –chlorinated biphenyls respectively).

Concentrations of DDTs include *o,p´*-DDT, *p,p´*-DDT, *o.p´*-DDD, *p,p´*-DDD, *o,p´*-DDE, and *p,p´*-DDE isomers. Like PCBs, locations near Amol city recorded high levels. In general the concentration at upstream locations was much lower than downstream locations. In this study, the high levels were probably due to agriculture activities. For example, rice paddy cultivation is more dominant in the Haraz River basin of the north of Iran. In addition to these sources, the urban sewage waste could also contribute to this contamination.

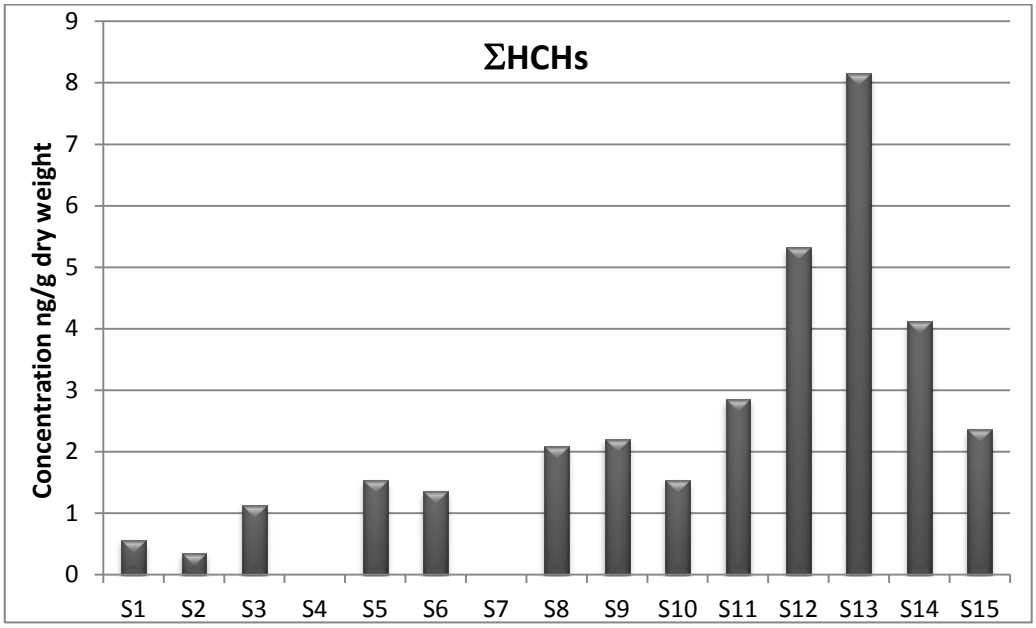

Fig. 3 Concentration (ng/g DW) of total HCHs (sum of α,β,γ, and δ-HCH isomers) in 15 stations in River Haraz (insert shows the low concentration area enlarged)

HCHs showed the lowest concentrations from non-detectable level to 8.15 ng/g in this study. There is no trend in the spatial distribution of HCHs as seen in PCBs and DDTs. The highest levels were detected at stations S13, S12, with 8.15 ng/g and 5.32 ng/g respectively.β-HCH was the dominant isomer among HCH compounds in river sediments. On an average, β-HCH accounted for about 51.64 % of total HCHs level in sediments.

A comparison of contamination levels of Haraz River sediments with similar studies around the world revealed that Haraz River contamination stands in the middle, meaning a moderate contamination.

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