

Persistent organic pollutants and sedimentary organic matter properties: A case study in the Kishon River, Israel

Adi Oren^a, Zeev Aizenshtat^b, Benny Chefetz^{a,*}

^a Department of Soil and Water Sciences, Faculty of Agricultural, Food and Environmental Quality Sciences,
The Hebrew University of Jerusalem, P.O. Box 12, Rehovot 76100, Israel

^b Casali Institute of Applied Chemistry and Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Petrogenic-derived xenobiotics affect the properties of sedimentary organic matter and its sorption capabilities.

Abstract

The Kishon River, the second largest coastal river in Israel, has been severely polluted for several decades. Sediments from upstream and downstream sites of the river were analyzed, lipid-extracted and evaluated for phenanthrene uptake. Total polycyclic aromatic hydrocarbon (PAH) concentration in downstream sediments was $299 \mu\text{g kg}^{-1}$, consisting mostly of petrogenic-derived PAHs. Downstream sedimentary lipids were found to be dominated by fresh and decomposed petroleum-derived *n*-alkanes. The total PAH concentration in upstream sediments was $173 \mu\text{g kg}^{-1}$, consisting mostly of pyrogenic-derived PAHs, whereas lipids from these sediments were mostly vegetation-derived. Spectroscopic data suggested an exceptionally high aromatic content in downstream humic acid, which originated from PAHs attached to its structure. Sorption data suggested that upstream sedimentary cuticle-derived lipids function as a sorption domain, while downstream sedimentary lipids, consisting of shorter-chain-length petroleum-derived alkanes, compete with phenanthrene for sorption sites.

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1. Introduction

Persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), make up a class of compounds that are highly stable in the environment, bioaccumulate through the food chain and carry the risk of having adverse effects on human health and environmental niches. PAHs can be introduced into the environment by various processes: (i) incomplete combustion of organic material (i.e., pyrogenic origin), (ii) discharge of petroleum and its products (i.e., petrogenic origin), and (iii) post-depositional transformation of biogenic precursors (i.e., diagenetic origin)

(Tolosa et al., 2004). Pyrogenic sources of PAHs include vehicular and other exhaust emissions, wood burning, asphalt, coal tar and used crankcase oil. These PAHs are introduced into streams and rivers through runoff, overflow from wastewater-treatment facilities and atmospheric deposition (Lake et al., 1979; Latimer and Quinn, 1996). The influx of PAHs from petrogenic origin into aquatic environments has been reported to come from shipping activities, overflow from wastewater-treatment facilities and effluents of petroleum refineries (Readman et al., 2002; Zakaria et al., 2002). Each PAH source produces a characteristic PAH distribution pattern which is influenced by various chemical and physical processes that occur from the time of their formation to their final deposition (Benlahcen et al., 1997; Colombo et al., 1989). Therefore, clues to the source of PAHs can be obtained by molecular indices based on ratios of individual PAH concentrations in the

* Corresponding author. Tel.: +972 8 948 9384; fax: +972 8 947 5181.

E-mail address: chefetz@agri.huji.ac.il (B. Chefetz).

sediments (Baumard et al., 1998; Benlahcen et al., 1997; Budzinsky et al., 1997). Similarly, distribution patterns and molecular indices of aliphatic hydrocarbons in sediments can provide information about their sources (e.g., terrestrial vegetation, marine algae or petroleum) (Aboul-Kassim and Simoneit, 1995; Colombo et al., 1989; Jacquot et al., 1999; Le Dreau et al., 1997). Some aliphatic petroleum constituents can serve as geochemical biomarkers, hence their analysis can be used to fingerprint spilled petroleum and elucidate the extent of degradation of the petroleum spill (Aboul-Kassim and Simoneit, 1995; Colombo et al., 1989; Jacquot et al., 1999; Le Dreau et al., 1997; Volkman et al., 1992).

Ascertaining the sources and loadings of POPs carried by rivers to sea is fundamental to understanding the risks posed by human activities to riverine and marine ecologies. Due to their low aqueous solubility and highly hydrophobic nature, POPs tend to associate with particulate matter and to accumulate in the sediments. Thus, riverine and estuarine sediments that contain large pools of organic matter can constitute a significant repository for POPs (Tolosa et al., 2004). Moreover, sediments containing significant concentrations of POPs may serve as a preferred sorbent for additional POPs (De Jonge et al., 1997; Jonker et al., 2003; Sun and Boyd, 1991). In the same vein, the reversibility of POP sorption may be influenced by pre-existing POPs in the sediments (Rutherford et al., 1997). A low level of sorption reversibility might situate the sediments as a long-term source of pollutant release, which could impede remedial attempts (Fattore et al., 2002; Simpson et al., 2005).

The Kishon River, which is the second largest coastal river in Israel, is considered to be highly polluted due to its long history of contamination. This river drains an area of about 1100 km² in the northern part of the country and is perennial for most of its course (70 km) until it flows into the Mediterranean Sea in Haifa Bay. Upstream, the water in the river and its tributaries is relatively clean and its quality is affected only by semi-treated municipal wastewater overflow and agricultural runoff. However, the last 7 km downstream have been heavily contaminated for dozens of years by wastewater drainage from nearby industries, including oil refineries, fertilizer and chemical factories, and by poorly treated municipal wastewater. For many years, the downstream section of the river has been the recipient of uncontrolled industrial effluents containing high loads of organic matter, heavy metals and nutrients (Kishon River Authority, 1999). In recent years, a significant reduction in the pollution level of this part of the river has been recorded due to the enforcement of new environmental regulations (Kishon River Authority, 2003).

Although data is available on the Kishon River's water quality, data concerning pollution of the river sediments by POPs is scarce. Therefore, the objectives of this study were to evaluate the origin of important groups of POPs in sediments from upstream and downstream sites of the river and to characterize the sedimentary organic matter (SOM). In addition, we studied the sorption capabilities of sediments from these sites to evaluate the influence of contamination and SOM characteristics on the sorption and desorption potential of phenanthrene. Understanding the physico-chemical nature of

the SOM is essential for assessing the behavior of POPs in the sediments and can help reveal their fate during water-remediation processes.

2. Materials and methods

2.1. Sampling sites

Sediments were sampled from upstream and downstream sites along the Kishon River. Upstream, sediments were sampled in two locations near Kfar Yehoshua (designated KY1 and KY2). Downstream, sediments were sampled about 4 km before the river estuary in the Haifa industrial zone (HIZ). This sampling site is located about 25 km downstream from KY and samples from this site were designated HIZ1 and HIZ2. Sediment samples were collected from the surface of the sediments (0–20 cm) at least 1 m away from the riverbank, except for HIZ2 which was sampled from the riverbank. A composite 10-kg sample was prepared at each sampling site by mixing several samples collected from five nearby spots. Upon reaching the laboratory, samples were immediately frozen until analysis. General sediment characteristics are presented elsewhere (Chefet et al., 2004).

2.2. Lipid extraction

The sediment samples (400 g) were Soxhlet-extracted with dichloromethane for 16 h. The extracts were concentrated to about 20 mL by room-temperature volatilization. The concentrated extracts were then desulfurized with activated copper and loaded onto a microcolumn containing alumina and silica (1:2). The column was eluted with 16 mL hexane and then by a similar volume of toluene. The hexane elution was concentrated and analyzed by gas chromatograph/mass spectrometer (GC/MS). The GC (HP-5890 series II, splitless mode) was equipped with a 30-m long capillary column (SIL 24 CB) with internal diameter of 0.25 mm. The GC was coupled to a HP-G-1800B quadrupole MS running in electron impact mode with an electron energy of 70 eV. The source temperature was 200 °C, the tested mass range was 45–450 Da and the scan time period was 1 s, with helium as the carrier gas. The oven-temperature gradient was 4 °C/min from 50 to 300 °C with an initial temperature constant for 5 min and a maximal temperature constant for 20 min.

2.3. Extraction of persistent organic pollutants from the sediments

POP analysis of the sediments was performed by accelerated solvent extraction (ASE) following the protocol reported by Hubert et al. (2000). These authors describe ASE as a highly efficient extraction technique in comparison to Soxhlet, with differences of an order of magnitude in the concentrations of extracted POPs. Briefly, 10 g of fresh sediment sample were extracted three times with 33 mL toluene in a Dionex ASE 200 (Dionex Corp., Sunnyvale, CA). Extraction cycles (10 min each) were performed under a constant pressure (15 MPa) at two temperatures (80 and 140 °C). The extract was concentrated to 2 mL and further cleaned up using a Florisil column for the separation of lipophilic compounds. Then, the extract was injected into an HP-5890 GC coupled with an HP-5971 MS (SIM mode) for semi-quantitative analysis.

2.4. Humic acid extraction, isolation and characterization

Humic acids (HAs) were isolated from the sediment samples according to the protocol outlined by Swift (1996). Briefly, the sediments were extracted three times with 0.1 M NaOH for 24 h. The alkaline supernatant was decanted and then acidified to pH 2 with 6 M HCl to obtain the HA fraction. The HA was then purified with a 0.3 N HF/0.1 N HCl mixture for a week and then rinsed several times with deionized water, centrifuged and freeze-dried.

¹³C nuclear magnetic resonance (NMR) spectra of the HAs were acquired on a Bruker DSX-300 spectrometer, using cross-polarization magic-angle spinning with total sideband suppression. The spectra were integrated into the following chemical-shift regions: paraffinic carbon (0–50 ppm); methoxy

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