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Assessment of marine pollution in Izmir Bay: Nutrient, heavy metal and total hydrocarbon concentrations

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Abstract

Izmir Bay (western Turkey) is one of the great natural bays of the Mediterranean. Izmir is an important industrial and commercial centre and a cultural focal point. The main industries in the region include food processing, oil, soap and paint production, chemical industries, paper and pulp factories, textile industries and metal processing. The mean concentrations showed ranges of 0.01 – 0.19 and 0.01 – 10 μM for phosphate, 0.10 – 1.8 and 0.12 – 27 μM for nitrate + nitrite, and 0.30 – 5.8 and 0.43 – 39 μM for silicate in the outer and middle – inner bays, respectively. The TNO_x/PO_4 ratio is significantly lower than the Redfield's ratio and nitrogen is the limiting element in the middle – inner bays. Diatoms and dinoflagellates were observed all year around in the bay and are normally nitrogen limited.

Metal concentrations ranged between Hg: 0.05 – 1.3, Cd: 0.005 – 0.82, Pb: 14 – 113 and Cr: 29 – 316 $\mu g\ g^{-1}$ in the sediments. The results showed significant enrichments during sampling periods from Inner Bay. Outer and middle bays show low levels of heavy metal enrichments except estuary of Gediz River. The concentrations of Hg, Cd and Pb in the outer bay were generally similar to the background levels from the Mediterranean. The levels gradually decreased over the sampling period. Total hydrocarbons concentrations range from 427 to 7800 $ng\ g^{-1}$ of sediments. The highest total hydrocarbon levels were found in the inner bay due to the anthropogenic activities, mainly combustion processes of traffic and industrial activities.

The concentrations of heavy metals found in fish varied for Hg: 4.5 – 520, Cd: 0.10 – 10 and Pb: 0.10 – 491 $\mu g\ kg^{-1}$ in Izmir Bay. There was no significant seasonal variation in metal concentrations. An increase in Hg concentration with increasing length was noted for *Mullus barbatus*. A person can consume more than 2, 133 and 20 meals per week of fish in human diet would represent the tolerable weekly intake of mercury, cadmium and lead, respectively, in Izmir Bay. Heavy metal levels were lower than the results in fish tissues reported from polluted areas of the Mediterranean Sea.

Keywords: Heavy metals; Nutrients; Total hydrocarbons; Sediment; Fish; Bioaccumulation; Izmir Bay

1. Introduction

Izmir Bay (western Turkey) is one of the great natural bays of the Mediterranean. The main urban conurbation around the bay is the Izmir Metropolitan Municipality, covering 88,000 ha. Izmir is an important industrial and commercial centre and a cultural focal point. The bay has a total surface area of over 500 km^2, water capacity of 11.5 billion m^3, a total length of 64 km and opens in the Aegean Sea. The depth of water in the outer bay is about 70 m and decreases towards to the Inner Bay. The bay has been divided into three sections (outer, middle and inner) according to the physical characteristics of the different water masses. The middle bay is separated from the inner bay by a 13 m deep sill the Yenikale Strait. The Gediz River, which flows to the northern part of the bay, is the second biggest river along the eastern Aegean coast. Gediz River is densely populated and includes extensive agricultural lands and numerous manufacturing, food and chemical industries.

The streams and hundreds of small domestic discharge outlets, flow to the bay. The main industries in the region include food processing, beverage manufacturing and

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bottling, tanneries, oil, soap and paint production, chemical industries, paper and pulp factories, textile industries, metal processing and timber processing.

Nutrient oligotrophic or eutrophic conditions have been characterized as the principal factors affecting the marine ecosystem (Ryther and Dunstan, 1971). Several studies in the past have associated oligotrophy with the absence of measurable concentrations of a nutrient (McCarty and Goldman, 1979; Ignatiades et al., 1992; Kucuksezgin et al., 1995) and have defined eutrophication as a qualitative parameter referring simply to nutrient or organic matter enrichment from external sources and resulting in high biological productivity (Ignatiades et al., 1992). The inner bay is heavily polluted by nutrients and organic material, but metal concentrations were not high enough to indicate heavy metal pollution. Industrial fluxes of Cr, Cd and Hg to the bay are 6700, 20 and 70 kg $year^{-1}$, respectively. Data are not available on fluxes of heavy metal due to domestic discharges. 105,000 m^3 day^{-1} of industrial and 308,000 m^3 day^{-1} of domestic wastewater were discharged to the bay without significant treatment (UNEP, 1993) until 2000. In early 2000, the wastewater treatment plant (WTP) began to treat domestic and industrial wastes. Eutrophication of the inner bay is a serious problem throughout the year and red tide events are becoming more frequent (UNEP, 1993; IMST, 1988; IMST, 1991; Kontas et al., 2004).

Heavy metals, as defined by Nieboer and Richardson (1980), are normal constituents of the marine environment. At least 11 are known to be essential to marine organisms: Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se and Ni (Bryan, 1979). These metals always function in combination with organic molecules, usually proteins. Metals occur normally at low concentrations yet are capable of exerting considerable biological effects even at such levels (Rainbow, 1992). All metals are toxic above some threshold bioavailable level. Ag, Hg, Cu, Cd and Pb are particularly toxic (Bryan, 1979). The elucidation of the comparative pollution of aquatic environments by heavy metals is possible by analysis of water, sediments and members of indigenous biota, i.e. biomonitors (Phillips and Rainbow, 1993).

Sediments are composite materials consisting of inorganic components, mineral particulates and organic matter in various stages of decomposition. It is well known that they are sensitive indicators between natural and anthropogenic variables (Salamons, 1995; Calmano et al., 1996). Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic contaminants of marine coastal sediments (NOAA, 1988; Raoux et al., 1999). PAHs show a marked hydrophobic character, resistance to biodegradation (Soclo et al., 2000) and adverse effects on health (carcinogenic and/or mutagenic activity) (Henner et al., 1997; Singh et al., 1998) and ecosystem (Varanasi et al., 1985; Long et al., 1995).

Metal pollution of the sea is less visible and direct than other types of marine pollution but its effects on marine ecosystems and humans are intensive and very extensive. As an indirect measure of the abundance and availability of metals in the marine environment, the bioaccumulation of metals by the tissues of marine organisms is studied. The bioaccumulation studies led to the adoption of the bio-indicator concept (Langston and Spence, 1995). Fish are widely used as bio-indicators of marine pollution by metals (Evans et al., 1993).

A number of studies have been carried out on the concentrations of nutrients and heavy metals in the bay for 1 year periods (Demirkurt et al., 1990; Parlak and Demirkurt, 1990; Kucuksezgin and Balci, 1994; Balci et al., 1995; Kucuksezgin, 1996; Kucuksezgin et al., 2002), but no long-term and seasonal data are available. No published data are available on petroleum hydrocarbon concentrations in the sediments from the Izmir Bay. The main aim of this study was to monitor levels, temporal variability and distribution of nutrients, heavy metals in edible fishes and sediments of Izmir Bay before and after installation of a wastewater treatment plant. This is the first time that the total petroleum hydrocarbon data has been collected (November 2000), quantified and evaluated in the bay.

2. Materials and methods

Nutrient and heavy metal data were collected during cruises of R/V *K. Piri Reis* during 1996–2003 at sampling stations. The study area and the positions of the sampling stations located between the longitudes 26°30′–27°08E and latitudes 38°41′–38°21N are shown in Fig. 1. Seawater samples were collected with General Oceanic Go-Flo Rosette bottles attached to the CTD system from the following depths: 0, 10, 20, 30, 40, 50 and 60 m. Nutrient analysis was carried out within 1 week of the completion of the cruise, using a Skalar (two-channel) Autoanalyzer. Intercalibration of seawater samples (from QUASIMEME, Plymouth Marine Laboratory, Round 22) was used as a control for the analytical methods of nutrients. The colorimetric methods adopted were similar to those described by Stricland and Parsons (1972) and Grasshoff et al. (1983). Water samples for chlorophyll-*a* (Chl-*a*) were collected from water column and were filtered through GF/F filters, Chl-*a* were measured, using a Sequoia-Turner Fluorometer (Stricland and Parsons, 1972).

Sediment samples were taken using Van-Veen Grab from surface sediments. Samples were digested in microwave digestion system (Milestone 1200) with a HNO_3–HF–$HClO_4$–HCl acid mixture for heavy metals (UNEP, 1985b,c,d,e).

Mullus barbatus, being bottom dwellers to a certain extent, are species that tend to concentrate contaminants to a higher degree than other species due to high mobility. For this reason, it was recommended by FAO/UNEP (1993) as monitoring species. *Solea vulgaris* was also selected as monitoring species because it is important commercially and commonly consumed by humans. Samples were collected from Foca, Mordogan and Gediz River estuary in the outer part of the bay. Tissues were homogenised in a blender; approximately 5–7 g of homogenate was then digested with 5:1 HNO_3/$HClO_4$ in a microwave oven (UNEP, 1982, 1984, 1985a). All analyses were performed by flame (Cr), cold vapour