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Spatial distribution and source apportionment of PCBs in sediments around İzmit industrial complexes, Turkey

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ABSTRACT

The spatial distribution, degree of pollution and major sources of PCBs were evaluated in surficial sediments within the heavily urbanized and industrialized İzmit Bay and its main freshwater inputs. ΣPCB concentrations range from 2.90 to 85.4 ng g^{-1} in marine sediments and from ND to 47.7 ng g^{-1} in freshwater sediments. Results suggest that high concentrations of ΣPCBs were localized around a chlor-alkali plant and an industry that handles bulk liquid, dry and drummed chemicals, and petroleum products in the Bay. Using a chemical mass balance receptor model (CMB), major sources of PCBs in the region were investigated. The CMB model identified Aroclor 1254 and 1260 to be the major PCB sources in marine sediments and the less chlorinated Aroclor 1248 and 1242 as the major PCB sources in freshwater sediments. The potential sources for the PCBs were briefly discussed in terms of their use in various industrial applications.

1. Introduction

Polychlorinated biphenyls (PCBs) are xenobiotic compounds of anthropogenic origin that are ubiquitous, toxic and persistent in the environment (Erickson, 1997). Owing to their properties of industrial interest, PCBs were extensively used in various applications as dielectric fluids, plasticizers, additives, among others, in many countries starting from the 1930s. Starting with the early work by Jensen (1966), it was realized that PCBs resulted in widespread pollution by being accumulated in soil, sediments and aquatic fauna as well as being transported long distances in the atmosphere (Wania and Mackay, 1993; Meijer et al., 2003). Although their production was banned worldwide by the Stockholm Convention on POPs, they are still in use especially in closed applications, and hence, pose a threat to the environment and human health if handled improperly. Contrary to the extensive information on PCB use, inventory and disposal over the world, fairly little is known about the status of PCBs in Turkey, who became an official party of the Stockholm Convention in January, 2010. According to a comprehensive study on the global distribution and budget of PCBs in background surface soils by Meijer et al. (2003), Turkey is in a global source region defined by the coordinates between 30 and 60°N where 86% of the total global PCB usage occurred. In addition, it is also in a region where relatively higher emissions of PCBs would be expected on a global scale (Breivik et al., 2007). Nevertheless, limited attention was given to the investigation of contamination of soil and aquatic environment by persistent organic pollutants (POPs) in Turkey. A recent study by the authors provides a comprehensive review of available information on spatial distribution of PCBs in the environment (Gedik and Imamoglu, 2010). The presence of a number of potentially important local PCB contamination sources especially in or around industrial regions was revealed as a result of this assessment; the industrial complexes in İzmit are among them.

İzmit Bay is a semi-closed industrial region spreading over an area of about 310 km^2, length of 50 km and width of 2–10 km on the southeastern part of the Marmara Sea (Morkoc et al., 2008). The Bay is typically divided as western, central and eastern sections; a number of large industries (chlor-alkali, paper mill, oil refinery, etc.) were located throughout the coastline. The Bay system receives freshwater from two main branches (Dil creek and Sarı creek) carrying most of the domestic, agricultural and industrial wastes into the Bay. There are also direct inputs from a number of industrial activities to the Bay. Over the past decades, the region has been under the influence of many types of organic and inorganic pollutants (Morkoc et al., 2008). Two relatively recent studies by Telli-Karakoc et al. (2002) and Tolun et al. (2008) investigate POPs, including PCBs in sea water and mussels of İzmit Bay.

Establishment of effective control strategies necessitates comprehensive environmental data. Characterizing areas of contamination and apportionment of pollution sources, therefore,

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preclude any legislative steps for prevention of further pollution. In this context, receptor models have been used for more than two decades to find out the number and composition of contaminant sources in environmental forensic investigations (Johnson and Ehrlich, 2002). The receptor model, namely, chemical mass balance (CMB) model has been applied in a great number of pollution studies commonly in air resources management (Watson et al., 2002; Cetin et al., 2007). CMB has also been applied successfully for quantitative identification of PCB sources in sediments in recent years (Imamoglu and Christensen, 2002; Imamoglu et al., 2002; Ogura et al., 2005; Honda et al., 2008). Meanwhile, to our knowledge, evaluation of PCB contamination and sources based on congener specific analysis and receptor modeling has not been attempted in the aquatic environment of Turkey. Thus, the aim of this study is to assess the distribution of PCBs in the surficial sediments around industrial complexes in İzmit Bay and main freshwater inputs, and to identify the contribution of possible sources using the chemical mass balance model.

2. Materials and methods

2.1. Sampling

Surface sediments (upper 10 cm) from İzmit Bay and its surrounding freshwater branches (Fig. 1) were taken during September–October 2008 using a dipper or a grab sampler. Samples were homogenized and placed into clean amber glass jars with Teflon-lined lids and kept in coolers during sampling. Upon return to the laboratory, samples were split into two fractions of which, in the first fraction, moisture and organic matter content was determined gravimetrically by drying for 24 h at 105 °C and for 4 h at 550 °C (Heiri et al., 2001), respectively. The other fraction was stored at -20 °C until extraction for PCB analysis. While the moisture content ranged from 6.82% to 59.6% with an average of 33.4 ± 16.8%, organic matter content ranged from 1.87% to 12.8% with an average of 6.27 ± 3.64% in all sediment samples.

2.2. Extraction, cleanup and instrumental analysis

During extraction and cleanup, United States Environmental Protection Agency (US EPA) methods 3540C (Soxhlet extraction), 3630C (Silica gel cleanup), 3660B (Sulfur cleanup), 3665A (Sulfuric acid cleanup) were applied. Samples were analyzed both in terms of 41 individual PCB congeners (Accustandard Inc./C-QME-01, New Haven, CT, USA) and Aroclor mixtures (1016:1260 = 1:1) (Chem Service Inc., West Chester, PA, USA). Details about the extraction, cleanup and instrumental methods are provided in Supplementary material (SM).

2.3. Quality assurance/control

Quality assurance/control protocols include regular check of blanks, analysis of laboratory control samples, matrix spike/matrix spike duplicates (MS/MSD), and the CRM141-050 certified reference material (Resource Technology Corp., Wyoming, USA) concurrently with the environmental samples. A total of 41 individual PCB congeners were analyzed (IUPAC No: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 201, 205, 206, 208, 209). More details about the QA/QC procedures are provided in SM.

2.4. Chemical mass balance (CMB) modeling

The CMB model used in this study is described in detail by Christensen et al. (1997) and Gedik (2010). CMB is a receptor model that uses a mass balance approach to find out the pollutant

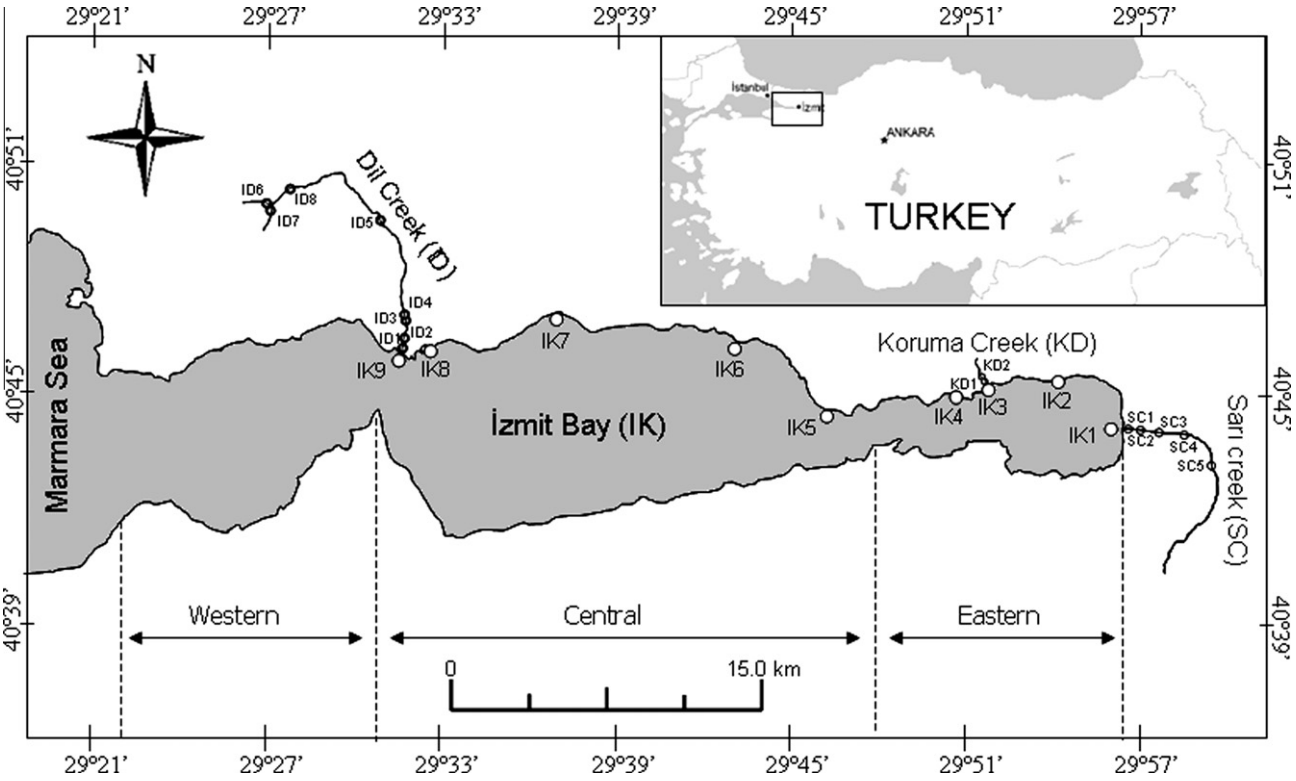

Fig. 1. Sampling sites on İzmit Bay and its surrounding freshwater branches.