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Baseline

Evaluation of sediment contamination by monoaromatic hydrocarbons in the coastal lagoons of Gulf of Saros, NE Aegean Sea

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ABSTRACT

The concentrations and distribution of monoaromatic hydrocarbons (benzene, toluene, ethyl benzene and the sum of *m*-, *p*- and *o*-, xylenes) were determined in the sediments of coastal lagoons of the Gulf of Saros, using a static headspace GC–MS. The total concentrations of BTEX compounds ranged from 368.5 to below detection limit 0.6 μg kg^{-1} dw, with a mean value of 61.5 μg kg^{-1} dw. The light aromatic fraction of *m*-, *p*-xylene was the most abundant compound (57.1% in average), and followed by toluene (38.1%) > ethylbenzene (4.1%) > o-xylene (2.5%) > benzene (1.1%). The factor analysis indicated that the levels and distribution of BTEX compounds depend on the type of contaminant source (mobile/point), absorbance of compounds in sediment, and mobility of benzene compound and degradation processes. Point sources are mainly related to agricultural facilities and port activities while the dispersion of compounds are related with their solubility, volatility and effect of sea/saline waters on lagoons.

Monoaromatic hydrocarbons represent a significant part of volatile organic compounds, a collective name for benzene, toluene, ethyl benzene, and xylenes (BTEX compounds). Monoaromatic hydrocarbons are the most mobile and toxic hydrocarbon constituents and present various aquatic environments (Bianchi et al., 1991). These compounds are often found in discharges and petroleum products such as gasoline, and other common environmental contaminants and acutely toxic to aquatic organisms if contact is maintained (Wang and Fingas, 1998). They may be yielded by uncompleted burning of organic matter and their major sources to the environment include vehicle exhaust (mobile source), coal/waste burning, oil refining processes, etc. (point sources). In addition, monoaromatic hydrocarbons are used extensively in manufacturing processes, production of synthetic materials and consumer products, such as plastics, insecticides and paints. They are included in the US Environmental Protection Agency (EPA) purgeable priority pollutants list (USEPA, 1989).

The coastal areas of the Gulf of Saros, NW Turkey, are important places in daily life, providing contributions to regional and national economy in terms of conservation biological diversity, particularly fisheries, livestock, salt production, reed cutting and recreational activities. These areas are mostly characterized by coastal lagoons (Fig. 1), which form ecotones between freshwater, marine and terrestrial biotopes under the control of coastal geomorphological processes. These lagoons have been partially affected over time by anthropogenic pollution; mainly related with the increasing population and recreational activities around them. Only a few researches have addressed the role of the anthropogenic impacts in some of these lagoons around the Gulf of Saros (e.g. Yılmaz and Serbest, 2005; Yaşar, 2010; Barut et al., 2015). No published papers or available data was found on the monoaromatic hydrocarbons in these lagoons. Therefore, the present study aims to assess the concentrations of monoaromatic hydrocarbons, their distribution and possible sources in the bottom sediment of these coastal lagoons.

Beginning from the border with Greece and down to the western coasts of the Gelibolu (Gallipoli) Peninsula, many small coastal lagoons are situated at the coastal regions (Fig. 1). All these lagoons, usually located on places where coastal and shelf areas are relatively wider, are characterized by shallow coastal salt lakes, partially or completely separated from the sea by some barriers. Their salinity may vary depending on balance between precipitation and evaporation and feeding watercourses.

One of the most important wetlands of the world is located on the Enez-Evros delta and represents key environments for the sustainable development of the economy with abandoned channel mouths, dunes, marshlands, lagoons and saltpans (Alpar, 2001). This was an important settlement region during the Hellenic, Roman, Byzantine and Ottoman periods, and an important port dating back to the 12th century BC. Shifting riverbed of Maritza and siltation turned the ancient estuary into adjacent large and small lakes and lagoons (Fig. 1a); namely Enez (S_1), Işık/Bücürmene (S_2 and S_3), Kuvalak (S_4), Küçükgöl (S_5), Dalyan ($S_{6–10}$) and Taşaltı ($S_{11–12}$).

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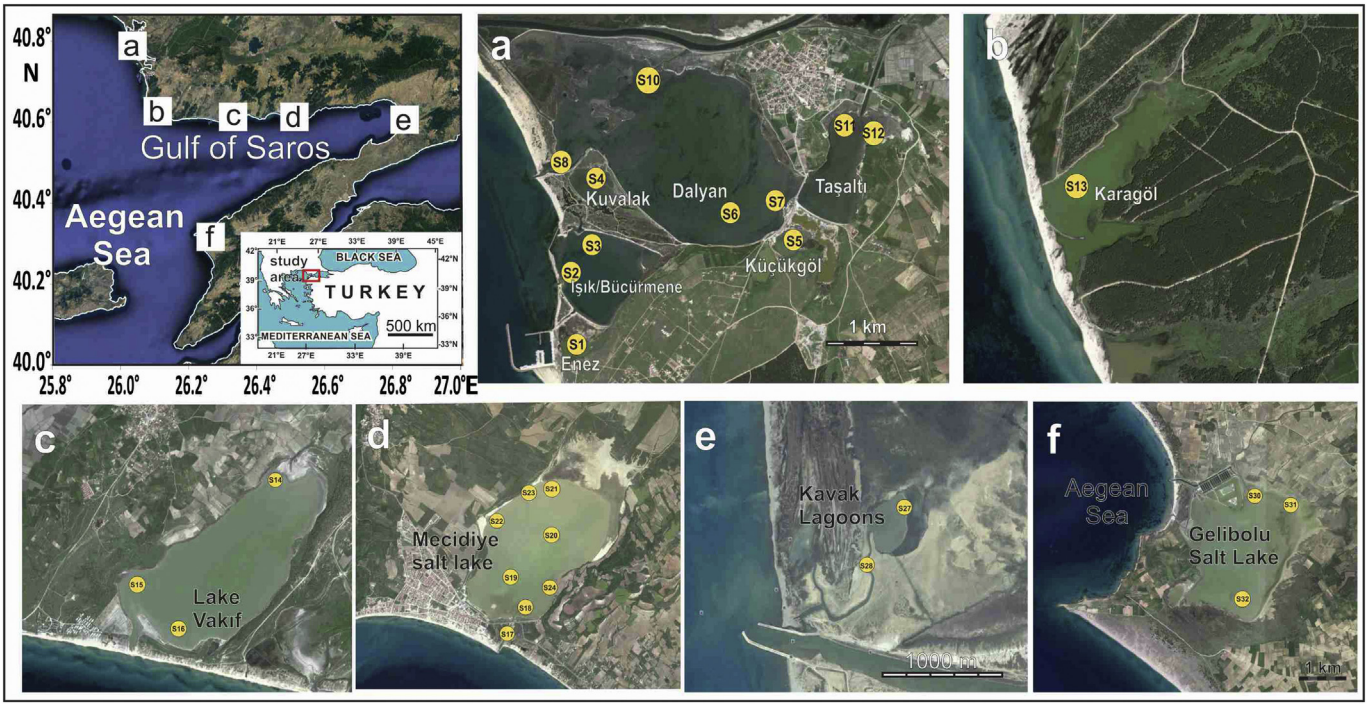

Fig. 1. Locations of coastal lagoons with sampling sites; a: Enez (S_1), Işık/Bücürmene (S_{2-3}), Kuvalak (S_4), Küçükgöl (S_5), Dalyan (S_{6-10}) and Taşaltı (S_{11-12}), b: Karagöl (S_{13}), c: Lake Vakıf (S_{14-16}), d: Mecidiye (Erikli) salt lake (S_{17}–S_{24}), e: Kavak Lagoons (S_{27-28}) and f: Gelibolu salt lake (S_{30-32}).

Farther to the east and south, the geomorphologic units around the Gulf of Saros represent different stages of development such as sandy beaches, mudflats, marshes, shallow lagoons, small lakes and channels. The Karagöl (S_{13}) is a very small lagoon with a surface area of 0.1–0.3 km^2 depending on the seasons (Fig. 1b). Along the northern coasts of the Gulf of Saros, the salt lakes of Vakıf (S_{14-16}) and Mecidiye-Erikli (S_{17-24}) are the most important lagoons located at the river mouths and marsh areas (Fig. 1c and d). Their waters are pungent and salty. The Lake Vakıf (S_{14-16}) is small (1.8 km^2). The salt lake on Mecidiye-Erikli coastal beach zone (2.5–3.3 km^2) was mentioned in Ottoman archives as the source of salt to meet Istanbul's needs. The Kavak Lagoons (S_{27-28}) at the easternmost part of the Gulf of Saros are rather small (<0.1 km^2) (Fig. 1e). The Gelibolu salt lake (S_{30-32}) is located at the western tip of the Gallipoli Peninsula (2.5 km^2) (Fig. 1f). This salt lake has greatly influenced by a fish farm that has been opened to operation in recent years.

The samples were collected from 26 stations in the coastal lakes around the Gulf of Saros on October 2004 (Fig. 1). The samples were removed manually with PVC pipes from 10 to 20 cm depth below the bottom surface. The sampling vessels were capped and stored on a dry-ice bed inside the collection box. The samples were frozen immediately after sampling and analysed within 48 h of collection.

The concentrations in the sediment samples were determined at MERLAB Central Research Laboratory of Istanbul University. A static headspace autosampler (Thermo Finnigan model HS 2000) equipped with standard glass vials of an internal volume 10 ml was employed. HS-GC–MS reference procedure set was in accordance with the description of a literature (Esteve-Turrillas et al., 2007). Standard solutions containing benzene (99.99%), toluene (99.5%), ethyl benzene (99.97%), *m*-xylene (99.8%), *p*-xylene (99.9%) and *o*-xylene (99.3%) were purchased from Merck (Darmstadt, Germany). For qualitative and quantitative identification of the BTEX compounds in the sediment samples, standard curves have been generated for different concentration ranges using benzene, toluene, ethyl benzene, *m*-, *p*- and *o*-xylene standards in hexane. Detection limits and recoveries were obtained from analysis of three replicates standard solutions at concentrations of 1.5, 3.12, 6.25, 12.5, 25 and 50 μg/l, respectively.

One gram of sediment sample was weighted in a 10 ml standard glass vial. The sample heated in headspace autosampler at 90 °C for 10 min with shaking. The syringe temperature was selected at 100 °C. The oven temperature program started from 40 °C held for 10 min, increased at a rate of 20 °C/min, up to 200 °C and finally held for 2 min. Electron impact ionization (EI) was used at 70 eV and helium flow is 1 ml/min. Transfer line temperature were fixed was held at 250 °C. The detector temperature was set to 230 °C. A Hewlett Packard HP 5MS column (Palo Alto, CA, USA) (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used to obtain the reference data by chromatography.

For instrumental control and intensity measurements, it was employed using vendor software Xcalibur from Thermo (Waltham, MA, USA). Calibration data were developed with the help of TurboQuant Analyst 6.0 software (Thermo Nicolet Corp. Madison, USA).

The mass spectra were obtained at a mass-to charge ratio (m/z) scan range from 75 to 200. The specific ions generated at m/z 77 and 78 for benzene, m/z 91 and 92 for toluene and m/z 91 and 106 for ethylbenzene and xylenes. The recoveries of compounds were found to be between 70 and 130%. The mean level of relative percentage difference (RPD) duplicate sample was <15%. The limit of detection (LOD) was between 0.25 and 0.5 μg kg^{-1} dw for each component.

Pearson's correlation coefficients (r) calculated the strength of relationships between the monoaromatic hydrocarbon concentrations, and principal component analysis (PCA) quantified spatial/temporal variability of BTEX sources for lagoon sediment samples (n = 26). As a whole, the first few components explain the inherent variation of the data to the maximum possible extent (Varmuza and Filzmoser, 2008). In the present study, PCA was conducted with varimax rotation. The first three eigenvalues retained were 3.2, 1.3 and 0.8.

The granulometric analysis was performed using petrographic procedures adapted from Folk (1980), as described by GERG SOP-8908. The bottom sediments in the lakes are under the control of material supplied with river alluvium, surficial water flows. They are composed of mainly sand and mud mixtures depending on their locality (Table 1). The contents of water in the samples range between 15.6% and 67.1%, with an average of 31.3%.

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