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Organic and heavy metal pollution in shipbreaking yards

Atilla Yılmaz [a,*], Burak Karacık [a], Sevil D. Yakan [a], Bernhard Henkelmann [b], Karl-Werner Schramm [b,c], Oya S. Okay [a]

[a] Department of Naval Architecture and Ocean Engineering, Istanbul Technical University, 34469, Turkey
[b] Molecular Exposomics (MEX), Helmholtz Zentrum München, 85764, Germany
[c] Department für Biowissenschaften, Technische Universität München, 80333, Germany

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ABSTRACT

Sediment samples were collected from five stations in Aliağa Shipbreaking Yard which is located in the coastal area of the Aegean Sea. To determine the pollution levels in marine environment resulting from the shipbreaking activities, organic pollutant and metal levels were investigated in the collected samples. Organic pollutants of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were analysed and found between the concentrations of 585–25000, 17–847 and 11–118 μg/kg in dry weight, respectively. In addition, eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were determined in the sediment samples. The metal concentrations were found relatively higher compared to the values measured in the reference sampling station. The pollutant levels were compared with the concentrations in the sediment quality guidelines to assess the probable effects on marine ecosystems.

1. Introduction

Shipbreaking is a feasible way of recycling and it enables the reuse of materials in several industries, considering the worldwide depletion of natural resources. Offering ship owners the possibility of realizing their old ships, shipbreaking provides employment and contributes to the economy in remarkable amounts. Due to regulatory restrictions and arising environmental problems in developed countries, the shipbreaking activities are generally performed in developing countries such as India, Bangladesh, Pakistan, China and Turkey (Demaria, 2010). In the developing countries, environmental issues, human health problems and work safety are mostly ignored at the expense of economical income (Rousmaniere and Raj, 2013). Although the Far East countries offer the opportunity of low-cost labour, the expedient location makes Turkey more desirable for European and surrounding countries. The ship dismantling activities in Turkey are executed at Aliağa Shipbreaking Yard (İzmir) which is located at the coastal region of the Aegean Sea. A remarkable amount of the scrap iron demand of Turkey is supplied from the shipbreaking activities in Aliağa Shipbreaking Yard which has an annual shipbreaking capacity of 600,000 LDT (Neşer et al., 2008).

Shipbreaking activities threaten the marine environment and the human health by potential release of many different organic and inorganic pollutants (Neşer et al., 2012a; Siddiquee et al., 2012). Cutting, blasting, tank cleaning activities, bilge and ballast water discharges, asbestos removal, burning of electrical cables and plastic materials are examples of pollution sources in shipbreaking yards (Hossain and Islam, 2006; Sarraf et al., 2010). For the sustainability of shipbreaking and the safety of human health and environment, elaborative examinations of those facilities are required.

Organic pollutants mainly polycyclic aromatic carbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are important chemical groups released from the shipbreaking industries. It is well known that these pollutants have hazardous effects both on the human and the environmental health (Rastogi et al., 2009; Solomon and Schettler, 2000; Yoon et al., 2007). The main sources of PAH compounds in the environment may be petrogenic (oily wastes and spills, bilge water etc.) or pyrolytic (emissions from fossil fuel combustion) (Soclo et al., 2000). The production of PCBs was banned throughout the world since 1970s. However, they are still found in the various environmental matrices due to their persistency to degradation (de Boer et al., 2010; Syakti et al., 2012). Due to their stability in high temperatures and good electric conductivity, PCB congeners were widely used in several components of old ships (hoses, plastic foam insulation, cables, hull bottom plates, hull paints etc.) (Hossain and Islam, 2006; Walker, 2008). Like PCBs, the usage of

* Corresponding author.
E-mail address: atillayilmaz@itu.edu.tr (A. Yılmaz).

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OCP compounds were either limited or banned in developed countries, after the hazardous effects on human health were revealed (Alavanja et al., 2004; Beard, 2006; Coumoul et al., 2002). OCPs were used for insect and rodent control and in hull paints as an antifouling agent.

Organic pollutants are hydrophobic and accumulate mainly in the sediments and biota in the aquatic ecosystem. Sediments, formed by the accumulation of particles, accurately represent levels and patterns of present and historical marine pollution (Pereira et al., 1996; Sakan et al., 2009). Hosting many organisms in the aquatic food chain, sediments are the vital components of the marine environments.

In this study, sediment samples were collected from Aliağa Shipbreaking Yard in order to determine the organic pollutant and heavy metal levels and patterns to assess the impact of shipbreaking activities to the marine environment.

2. Materials and methods

2.1. Sampling

Sediment were sampled from four different locations (Fig. 1) along the coastal area of Aliağa Shipbreaking Yard in February 2013. In addition, a reference point was selected in Aliağa town which is remote from the shipbreaking activities. S4 and S-Ref stations were relatively shallow stations (~0.5 m), whereas the depth of the other stations (S1, S2 and S3) were approximately 15 m. An approximate amount of 1000 g of surface sediment (0–10 cm) were collected by van Veen grab sampler. Collected samples were immediately transferred to the laboratory and stored at −20 °C until the chemical analysis were performed.

2.2. Total organic carbon and particle size analyses

Total organic carbon (TOC) was determined by using a LECO CNS2000 Carbon Analyzer. Approximately 0.5 g of sediment samples were dried and treated with HCl to remove $CaCO_3$. Particle size distribution and classifications were performed according to the ASTM D-2487 standard method (ASTM, 1993).

2.3. Chemical analyses

For organic pollutant analyses, the samples were homogenised and mixed with diatomaceous earth for the removal of water. Then, the samples were extracted by using accelerated solvent extraction system (DIONEX ASE 200). The extracts were purified using silica gel and alumina mixed column and C-18 solid phase extraction (SPE) cartridges. The purified samples were analysed by high resolution gas chromatography coupled with a high resolution mass spectrometry (HRGC-HRMS) system. 16 PAH, 18 PCB and 29 OCP compounds were analysed in the sediment samples. During the analyses, Agilent 6890 GC equipped with a 60 m capillary column Rtx-Dioxin2 (Restek, Germany) was used. A quality management system according to DIN EN ISO/IEC 17025 is operated in the accredited laboratory. ^{13}C isotope dilution method was used for quantification of the analytes. Internal reference materials and international interlaboratory comparison studies were used for the validation of the procedures (Okay et al., 2014).

HNO_3/H_2O_2 based digestion test protocol (US EPA, 1996) was followed for the analysis of metals. The sediment samples were sieved with a 2-mm mesh sized sieve, stored in desiccator and dried at 60 °C for 24 h prior to analysis. The dried and weighed samples (1 g) were placed in a Teflon cup and 6 mL of HNO_3 and 4 mL of HCl were added. Then the cups were capped and digested in microwave digestion system (CEM MARS-5). The metal analyses were performed by using inductively coupled plasma-optically emission spectrometry (ICP-OES, Varian, model 725). The instrument was calibrated with mixed metal standards. A known concentration of yttrium was added to the standards for the determination of instrumental variations during the analysis (Bradford et al., 2009).

3. Results and discussion

Sixteen PAH compounds, which are identified as primary pollutants according to United States Environmental Protection Agency (USEPA) (Keith and Telliard, 1979), were measured in the sampling area. Total PAH concentrations (Table 1) in shipbreaking yard area ranged between 2499 (S1) and 24,934 μg/kg dry weight

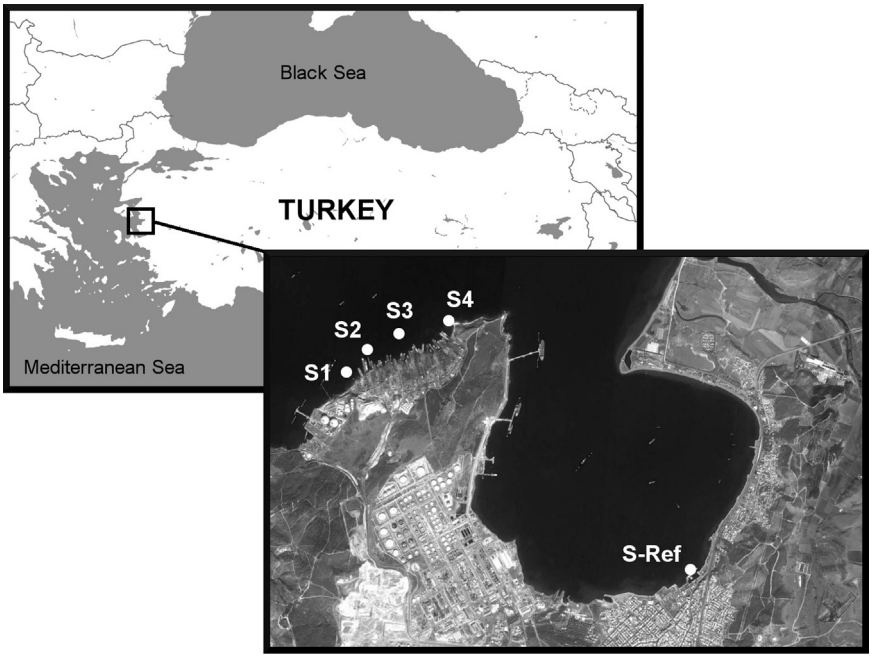

Fig. 1. Sampling stations.