HYDROCARBON CONCENTRATIONS IN SURFACE SEDIMENTS FROM AMBARLI HARBOR (SEA OF MARMARA, TURKEY)

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Abstract
Surface sediments collected from 33 stations along the Ambarli Harbor, the Sea of Marmara, were analyzed for petroleum aromatic hydrocarbons by UV-fluorescence. Higher concentrations of total aromatic hydrocarbons were found of all the samples collected during May 2009, with levels ranging 1860 and 72 µg/g eq oil (205 and 7 µg/g chrysene eq.). The spectra indicate dominant pyrolytic origins in some stations of pyrolysis reactions of fossil fuels where the 3-4 ring PAHs are dominant. The pyrolytic contamination of these stations could be attributed to fossil fuel oil particulates emission by commercial vessels, heavy maritime traffic, particularly involving petroleum transports and fishing boats, and the improper disposal of ballast and bilge waters.
Keywords: Petroleum, Pah, Sediments, Marmara Sea, Pollution

Introduction
Sources of contaminants in the Harbor include municipal and industrial discharges, atmospheric inputs, non-point source runoff, hazardous waste sites, landfills, combined sewer overflows and accidental spills. The important sea pollutants originated from ship and seaport are as follows: oil-products, crew-disposals (i.e., shower, sink and toilet), bilge water, ballast, washing water for ballast, liquid-, and solid type poisonous materials carried by the ships and garbage of the ships. It is known that these anthropogenic pollutants arrive at the sediments, then, negatively affect the quality of the sediment.
Ambarli Harbor in Marmara region has an important position as a seaport especially for the city of Istanbul. It serves to the ships such as container-, cargo-, RoRo- and tanker types. Analyzing of the data from 2007 shows that totally 4959 ships has made use of the seaport.
The purpose of this study was to determine the concentration of the total hydrocarbons in the surface sediments in and offshore Ambarli Harbor to provide data for comparison by different reference materials and to get understand whether pyrolytic or petrogenic inputs come from anthropogenic processes.

Material and Method
Sampling
The sediments were taken by using the grab sampler, in May 2009 on board of R/V ARAR from 33 stations. The sampling depths were between 11 and 78m. The topmost 0-5 cm of the grab sample was carefully removed using clean spatula. The samples were stored in a freezer at -20°C until analysis.
Analytical procedure
The methods used in this study have been described in detail [1] and will only be summarized here. TOC contents were measured by means of the Walkey-Black Method [2]. Extraction of samples with a Soxhlet apparatus and analyses by UV fluorescence spectroscopy (Jasco-6300, Shimadzu) were given in detail by Ünlü [1]. Considering spectrofluorometer conditions, excitation and emission wave-lengths were fixed to 310 and 360 nm for single measurement, respectively.

Results and Discussion
The TOC content of the sediment samples, which accounts for most of the variation in the uptake of contaminants by the sediment, is variable and ranges from 0.37% to 3.82%.Total aromatic hydrocarbon concentrations in samples varied between, 1860 µg/g and 72 µg/g equivalents of oil (205 µg/g and 7 µg/g chrysene eq.). An acceptable upper limit is 50 µg/g for clean sea floor sediments [3] and the concentrations higher than 100 (µg/g dry weight) are mainly related with terrestrial (riverine) inputs or port activities, on the basis of classification adapted by Readman [4]. According to fluorescence synchronous spectra of the sediment extracts containing >100 µg/g confirm the existence of a chronic oil pollution in the sampling region and suggest the presence of high potential hazards to aquatic organisms in the study area.
Although in general UV fluorescence technique has been replaced by more specific methods it is still being used for monitoring spatial and temporal concentration gradients of petroleum hydrocarbons in sediment. Because of its simplicity, sensitivity and easy application, UV fluorescence in synchronous excitation-emission technique constitutes a promising tool to be used in determination the polyaromatic structure of a compound since Lloyd has developed this method [5]. It simplifies the emission of each component of a mixture and gives a better-resolved spectrum for the whole of the mixture components [5]. According to the number of aromatic rings (spectral region from 220-700 nm), the USEPA priority PAH compounds were divided into three groups, representing two-, and three-, four-, and five-, and more ring PAHs.
Petroleum hydrocarbons in crude oil and light refined products are dominated by the lowest molecular weight PAHs with only trace levels of the penta- and hexa- aromatics present. However, 1-2 rings PAHs have not been encountered in the sediment samples. It appears likely that the more volatile PAHs are rapidly lost in this environment, through evaporation and photo-decomposition.
Our results indicate dominant pyrolytic origins in all samples with small amount of pyrolysis reactions of fossil fuels at some stations (e.g. A1, A3, A7, A8, A12, A13, A18, A23, A27 and A28) where the 3-4 ring PAHs such as pyrene derivatives are dominant. The pyrolytic contamination of these stations could be attributed to fossil fuel oil particulates emission by commercial vessels.
In sediment, the major problems are the land based and ship-based pollution. The sediments from the Sea of Marmara, show that the port activities are the most serious source of pollution in the around of Ambarli Harbor region. In this study area in which are determined the elevated contents of total aromatic hydrocarbons sediment is also polluted with larger amount of pyrogenic fossil fuel compounds. Therefore the marine sediments are very important in our estimating the degree of the damage given to the ecosystem by such inputs. The results deduced in this study, which for the first fundamental dataset for the region to be used as reference in future.

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