Sedimentary record of PAHs pollution in the Gulf of Trieste (Northern Adriatic Sea)

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic contaminates in coastal sediments derived from natural and anthropogenic sources. The waters of the Gulf of Trieste are extensively used for tourism and Maricultural purposes. Hence, extensive areas of the Gulf are affected by organic pollution. In addition, fresh water inflows of the tributary rivers, draining industrial and agricultural areas are another source of pollution.

In this work the authors present a historical reconstruction of PAH contamination in the Gulf of Trieste. For this, two long (~ 2 m) sediment cores taken from the central part of the Gulf, were collected and analysed.

MATERIALS AND METHODS

Cores GT1 (200 cm long) and GT3 (120 cm long) were taken by gravity core sampler and sediments extruded and subsampled at 1 cm intervals. Samples were freeze-dried and ground to a fine powder for analysis. Organic carbon ($C_{org.}$) and total nitrogen (N_{tot}) contents were determined by a Carlo Erba elemental analyzer (model EA 1108) after acidification with 1N HCl. The precision of the measurements was ±3 %. The isotopic composition of sedimentary C_{org} was determined after treatment with 1M HCl to remove carbonate material, while isotopic composition of N_{tot} was determined directly on bulk powdered samples. The $\delta^{13}C$ and $\delta^{15}N$ of C_{org} and N_{tot} fractions were analysed using a Europa 20-20 continuous-flow stable isotope analyser with ANCA-SL preparation module. Isotopic ratios are expressed in the usual δ-notation in parts per mil (‰). For carbon, the standard is the V-PDB carbonate, while for nitrogen the standard is atmospheric (air) nitrogen. The overall analytical precision was ±0.2 ‰ for $\delta^{13}C$ values and ±0.3 ‰ for $\delta^{15}N$ values. The ^{14}C ages of bulk sedimentary $C_{org.}$ were determined at the National Ocean Sciences Accelerator Mass Spectrometer Facility (Woods Hole Oceanographic Institution, MA, USA). The counting error in the reported ^{14}C measurements averaged ±2 % of the measured “age”.

To determine the PAH concentration in the sediment samples the authors used gas chromatography with mass spectrometric detec-

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tion (GC/MSD) combined accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE). For extraction an ISCO (Lincoln, NE, USA) supercritical fluid extractor (SFX2-10) was adopted in our study. Detailed extraction is published in details elsewhere (NOTAR & LESKOVŠEK, 2000). For extraction we used 10 mL disposable high temperature crystalline polymer extraction cartridges (ISCO, Lincoln, NE, USA) that were packed with 5g of sediment sample, 2 g of activated copper powder (to reduce the amount of sulphur present) and 2 g of wet support. Extracts were collected in glass-stopped 100 mL vials. Qualitative and quantitative analysis of PAHs in marine sediment extracts were performed by gas chromatograph equipped with split/splitless injection port and mass selective detector operating in the selected ion monitoring (SIM) mode using a Hewlett-Packard model 6890 GC/MSD with automatic liquid sampler. The GC was equipped with a HP5-MS cross-linked 5 % phenyl-methyl-siloxane capillary column (30m x 0.25 mm i.d., 0.25 mm film thickness). An internal standard mixture containing four deuterated PAHs (acenaphthene-d10, chrysene-d12, phenantherne-d10, perylene-d12) was added directly to the sample prior to extraction. Response factors

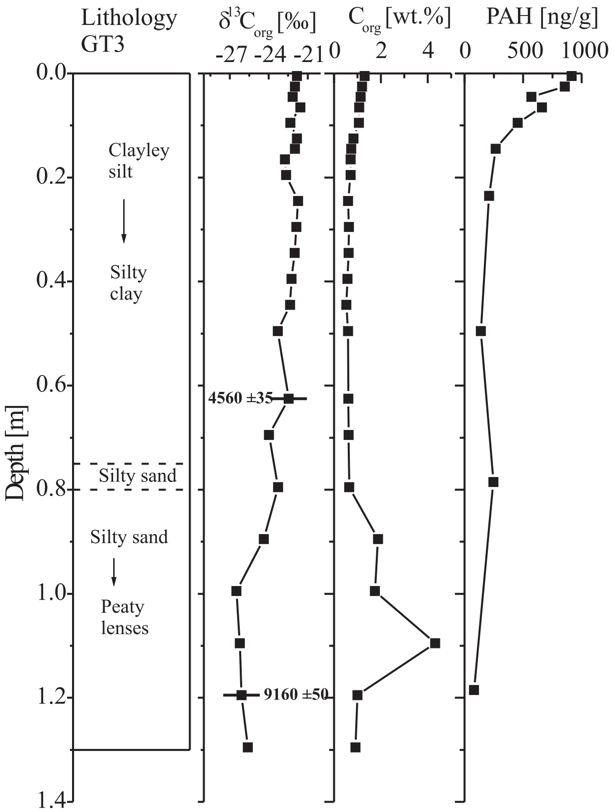

Figure 1. Vertical profiles of lithology, organic carbon (C_{org}) content, $\delta^{13}C_{org}$ values and polycyclic aromatic hydrocarbons (PAH) content in sediment core GT3. Conventional $^{14}C_{org}$ ages are also shown.

and retention times were determined relative to four deuterated internal standards and a standard PAH test mixture. The recovery data, precision, accuracy and method detection limits (MDL) were evaluated statistically and are presented elsewhere (NOTAR & LESKOVŠEK, 2000).

RESULTS AND DISCUSSION

The vertical profiles of C_{org} show a decrease in the upper part of the core until reaching a nearly constant value of about 0.6 %. The average $\delta^{13}C_{org}$ value and C/N ratio of -22.3 ± 0.6 ‰ and 9.2 ± 1.9, respectively indicate that ~70 % of organic material is of marine origin. The $^{14}C_{org}$ dating shows the presence of old sedimentary organic matter in the upper predominantly marine sequence of the core (Fig. 1). The terrigenous sequence starts below a depth of 150 and 90 cm in GT1 and GT3 cores, respectively, which has the characteristic higher C_{org} contents, low $\delta^{13}C_{org}$ values, and high C/N ratios. These parameters indicate that sedimentary organic matter originates from terrestrial plant material and according to $^{14}C_{org}$ dating is approximately 9000 years old (OGRINC ET AL., 2005). The mean sedimentation rate from the upper 65 cm marine part of the core GT3 is 0.14 mm yr^{-1} and is more than 10-fold lower than the value of 1.8 mm yr^{-1} calculated from the Hg content (COVELLI ET AL., in prep.). Mercury was previously correlated with ^{210}Pb and can be used as a geochronological tracer in recent sediments of the Gulf of Trieste (COVELLI ET AL., 2001). This difference is a likely result of a recent increase in the rate of sedimentation.

Concentrations of PAH decrease from the surface to deeper layers in the core (Figure 1). Concentrations vs. depth profiles of three representative pyrogenic PAHs; pyrene, benzofluoranthenes and phenantrene are similar to that of total PAHs. Using Hg as a recent geochronological tracer it emerges that the sediment layer in the core GT3 located at the depth of 10 cm dated to about 50 years BP, i.e. after the Second World War. Below this depth only low levels of PAHs were observed. The concentration of retene, considered as a product of the burning of coniferous timber, increases indicating an increased terrigenous input, about 50 years BP, and in the Middle Age. Geochronology suggests that the present-day PAHs accumulation flux amounts to about 0.1 mg cm^{-2} yr^{-1} while in sediments deposited before the Second World War the flux average was <0.03 mg cm^{-2} yr^{-1}. The PAH contents in the terrigenous peat layer dated to about 9000 years BP are about 3-fold lower than in the pre-industrial marine sediments. There was no significant correlation between the total PAH and C_{org} contents observed probably indicating relatively polluted sediment. No correlation was found between PAHs and black C (BC) vertical distribution in the core GT1 either suggesting a lack of association between both substances. The ratios of methylphenentrenes to phenantrene, as an indicator of anthropogenic influences such as combustion of organic matter around the gulf, were low (<0.5). Therefore, the high combustion processes as the main sources of PAHs in the gulf are through fresh water inflows and atmospheric inputs. The same conclusion appears from the predominance of high molecular weight (4, 5, 6 rings) over low molecular weight (2, 3 rings) PAHs in upper layers of both cores. Also, phenantrene /anthracene ratios of about 10 and lower, and fluorantene/pyrene ratios of about 1 and lower suggest pyrolytic contamination of sediments. The lower phenantrene/anthracene ratios in the surficial layer probably indicate that the PAHs received by the sediment in the 20th Century came from nearby sources.

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