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SHORT COMMUNICATION

Polycyclic aromatic hydrocarbons (PAH) in marine sediment of the northwestern Mediterranean Sea (Italy)

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Abstract

The presence and distribution of the 16 polycyclic aromatic hydrocarbons (PAHs) priority pollutant listed by US EPA (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenzo[a,h]anthracene, Benzo[g,h,i]perylene, Indeno[1,2,3-c,d]pyrene) were investigated in sediments from 35 stations of the Ligurian coast (Northern Italy). Results were shown as total PAH concentrations (PAHs) and molecular indices based on ratios of selected PAH concentrations were used to differentiate PAHs from pyrogenic and petrogenic origin. Analysis was performed by gas/chromatography mass spectrometry (GC/MS) with selected ion monitoring (SIM). Total PAHs concentrations ranged from 1113 to 17006 ng/g of dry matrix. PAH profiles varied according to the nature of the site and its proximity to sources; in general, the contamination levels of total PAHs were similar to those observed in contaminated and slightly contaminated sediments of the Mediterranean Sea. In some cases the concentration of contaminants is influenced by physical circulation processes that raise the concentrations of anthropogenic pollutants offshore an order of magnitude higher than those near industrial and harbors activities.

Keywords: PAHs, sediment, Ligurian Sea, GC-MS, pollution

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds listed as priority pollutants by international environmental protection agencies due to their carcinogenic, mutagenic, and toxic effects. Arising from both natural and anthropogenic sources, PAHs are ubiquitous in the environment (Usenko *et al*. 2007). As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly tend to become associated with particulate matter. Sediments therefore represent the most important reservoir of PAHs in the

marine environment, and contaminant concentrations in bottom marine sediments represent a critical measure of health for any coastal ecosystem.

PAHs are present as a complex mixture of alkylated and non-alkylated homologues: lower molecular weight molecules are generated by low temperature combustion, whereas high molecular weights are derived from high temperature combustion, without smoke, post combustion, or quenching. Usually the ratio of alkyl/non-alkylated aromatic homologues is used to identify sources of PAHs pollution (Soclo *et al*. 2000). The interest in these ratios is due to the fact that PAHs distribution is governed by thermodynamics in low-temperature processes (*e.g*. petroleum formation). Instead, kinetics factors are predominant in high-temperature processes (*e.g*. organic matter pyrolysis).Then the PAH isomeric distribution is temperature dependent. PAHs of petrogenic input are generally characterized by a high phenantrene/anthracene ratio (Gui Peng 2000), whereas high levels of five- and four-ring hydrocarbons are distinctive of mixture formed by the combustion of fossil fuel (Gogou *et al*. 2000). Whereas pyrolytic sources include combustion processes the petrogenic input is related to petroleum products and this is largely prevalent in aquatic environment.

The Ligurian Sea belongs to the northern part of the western Mediterranean. The limited width of the coastal zone determines a gathering of the urban areas with a consequent concentration of both civil and industrial presence in a narrow but highly populated territory. Oil shipping operations continue to be the main source of PAHs causing significant decline in seawater quality in the northwestern Mediterranean, where coasts are dotted by pollution hot spots, usually located in semi-enclosed bays close to big cities, harbors and industrial areas. PAHs presence is often due to shipping operations such as deballasting, tank-washing, dry-docking, fuel and bilge oil.

Surface and intermediate currents that follow a cyclonic circulation dominate the circulation of the Ligurian Sea. However, local circulation is responsible for the dispersion of sediment material along the coast, and these alongshore currents often cause an eastward oriented transport (Bertolotto *et al*. 2003).

The purpose of this study was to determine the distribution of PAHs in the superficial sediments of the Ligurian coastal area (Italy), to provide data for comparison with other marine systems and to establish whether the compounds are of biogenic or anthropogenic derivation. Our sampling was carried out in 35 stations situated between Recco and Sestri Levante, two Mediterranean tourist harbors of the Ligurian coast.

The sampling program for PAHs in sediments was undertaken along the Ligurian Coast from Recco to Sestri Levante.

Figure 1. Sampling area in the northwestern Mediterranean (Italy)

Samples were collected from 35 stations using a Schipeck grab sampler that picks up surficial sediments (0-2 cm). Sediments were freeze-dried and sieved to remove the raw fraction. A Hewlett Packard 7680 T (HP 1050) extraction module, coupled with an isocratic pump as supercritical fluid was utilised to process samples, then concentration of PAHs were detected by a Finnigan SSQ 710 quadrupole mass spectrometer coupled to a Varian 3400 gas chromatograph equipped with a splitless injector and AS200 auto sampler. The assessment of the accuracy relative to PAHs was based on the analysis of a certified standard (BCR CRM 535 Freshwater harbor sediment) supplied by NIST (USA). The accuracy ranged from 79.8% (benzo(a)anthracene) to 96.1% (benzo(b) fluoranthene).

Results and Conclusions

The total concentration of the 16 compounds investigated was expressed as the sum of concentrations (ΣPAHs), ranged from 1113 to 17006 ng/g of dry matrix (mean value 3663 ng/g and median value 2170 ng/g). The concentration levels of aromatic hydrocarbons are directly proportional to the distance from anthropogenic activities, highest near the port of Sestri Levante, results that fit with other data registered in this area (Benlahcen *et al.* 1997). Surface sediment concentrations of organic micro pollutant PAHs were within the range of concentrations reported for the Mediterranean area: 48-595 ng/g for benzo(a)pyrene (Bertolotto *et al.* 2003).

All the surface sediment samples show a high content of low molecular weight PAH (2-3-ring PAH) with phenanthrene as dominant compound in most cases. It is generally accepted that low values of Phe/An (<10) and high values of Flt/Py (>1) are related to pyrolytic origins. The PAHs of petrogenic input are generally characterized by high Phe/values. In our study, only in three stations Phe/An ratio values lower than 10 were registered. In the others locations ratio values ranged from 12.4 to 29.1. In the case of Flt/Py, their ratio is also discriminating. Fluoranthene is less thermodynamically stable than pyrene and a

predominance of the first compound over the second one is characteristic of pyrolytic products. In our study only in one station Flt/Py ratio was lower than 1 (0.97); in the other stations the ratio ranged from 1.38 to 3.4.

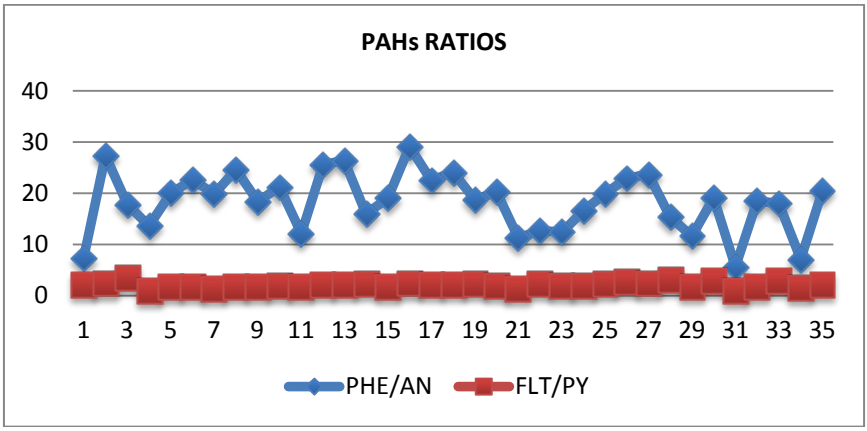

Figure 2. PAHs ratios at 35 sampling locations in the Ligurian Sea

PAHs found in the analyzed sediments were probably caused by mixed petrogenic and pyrogenic contaminations. In fact, most stations exhibited the same pattern of distribution with ratios values of Phe/An > 10 and Flt/Py > 1. The coastal environment could be subject to contamination by several sources of PAHs that can explain this mixed origin: industrial wastes containing combustion derived PAHs, oil spillage, emission of atmospheric particles enriched with combustion-derived PAHs that may be deposited into sediments.

As a conclusion, the contamination levels of PAHs in the study area were similar to those observed in polluted and slightly polluted sediments of the Mediterranean Sea. Major PAHs sources inferred from diagnostic indices were both pyrogenic and petrogenic. In some cases we found that PAHs concentrations are influenced by physical circulation processes that can lead to deposits of contaminants an order of magnitude higher offshore that those near the source of pollutants.

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