

# The PAH composition of surface sediments from Stagnone coastal lagoon, Marsala (Italy)

Loredana Culotta<sup>a</sup>, Concetta De Stefano<sup>b</sup>, Antonio Gianguzza<sup>a</sup>,  
Maria Rosaria Mannino<sup>a</sup>, Santino Orecchio<sup>a,\*</sup>

<sup>a</sup> *Dipartimento di Chimica Inorganica, Università di Palermo, Viale delle Scienze, Parco D'Orleans II, I-90128, Palermo, Italy*

<sup>b</sup> *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, I-98166 Messina Vill. S. Agata, Italy*

Received 6 December 2004; received in revised form 22 March 2005; accepted 5 May 2005

Available online 18 January 2006

## Abstract

This paper examines the presence, distribution, nature and sources of 22 Aromatic Hydrocarbons (PAHs), which are important environmentally and toxicologically, in sediments from the Stagnone coastal lagoon at Marsala (Italy). Analysis was performed by gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM). The total concentration of polycyclic aromatic hydrocarbons ranged from 72 to 18381 µg/kg of dry matrix. The relative standard deviation (RSD) of the replicates on the concentrations of individual compounds ranged from 5% to 20%. The accuracy of method was estimated by analyzing “blank” samples added of known quantities of analytes and the recover percentage was  $88 \pm 9\%$ . The detection limit (LOD) of analytical procedure was less than 0.2 µg/kg d.w. for all analytes. The quantification limit (LOQ) of analytical procedure was less than 0.7 µg/kg d.w.

The resulting distributions and weight ratios of specific compounds are discussed in terms of sampling location and origin of organic matter. A comparison with other studies of total PAHs suggests that the levels are within the concentration ranges already reported by other authors. From an eco-toxicological point of view, total PAH concentrations at seven out of the eight sites studied represent a relatively clean environment when compared to other sites.

Organic matter content and PAH concentrations were found to be correlated and the compounds present in Stagnone sediments were shown to be mainly of pyrolytic origin, while a negligible quantity of PAHs may derive from biogenic sources since all the sediments contain pyrene traces. There is no evidence of coal-tar contamination.

Cluster analysis was carried out in order to discriminate between different PAH origins.

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*Keywords:* PAHs; Sediments; Environmental chemistry; Coastal lagoon; Stagnone; Marsala

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) include aromatic molecules containing fused aromatic rings

and are of special concern because of their widespread distribution throughout the environment and their often toxic and carcinogenic properties (Hoffman et al., 1984; Pruell and Quinn, 1985). Some PAHs are persistent and toxic to aquatic organisms and bioaccumulate. Fish and higher organisms in the food chain tend to metabolise and excrete PAHs relatively rapidly. PAHs

\* Corresponding author.

*E-mail address:* [orecchio@unipa.it](mailto:orecchio@unipa.it) (S. Orecchio).

can influence the development of liver tumours in several fish species and may adversely affect the reproductive process in fish and other aquatic species.

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. In general the two main sources of PAHs in the environment are fossil fuels, mainly crude oil, and the incomplete combustion of organic materials such as wood, coal and oil. PAHs enter the sea by both atmospheric and aquatic routes, though little information exists on riverine input. In addition to the many domestic and industrial combustion processes in use today, coal-tar containing coating systems are also a major source of PAHs. To these may be added offshore activities, oil spills, offshore installations and shipping exhausts (Howsam and Jones, 1998).

Under anaerobic conditions some PAHs can also be derived from biogenic precursors such as pigments and steroids (Wakeham et al., 1979, 1980). PAHs formed by natural processes include perylene, retene, and phenanthrene homologues. They are also formed naturally in forest fires and volcanic eruptions.

Background levels of PAHs in the marine environment are a result of biosynthesis and natural oil seeps. Anthropogenic activities are generally recognised to be the most important source of PAH release into the environment.

Background values for PAHs in sediments appear to be within the range 0.01 to approximately 1 mg/kg d.w. The highest levels of oil in bottom sediments typically occur in river mouths, estuaries and bays, as well as in areas of regular shipping, oil production and transportation.

The purpose of this study was to determine the distribution of PAHs in the superficial sediments of the *Stagnone* coastal lagoon at Marsala (Italy), to provide data for comparison with other marine systems and to establish whether the compounds are of biogenic or anthropogenic derivation.

Because of the favourable physical and environmental conditions it enjoys, *Stagnone* lagoon is used for salt production and fish farming. The lagoon is characterized by abundant organic detritus, deriving from aquagenic and anthropogenic inputs and anoxic/reduced sediments make it a preferential site for the uptake and preservation of PAHs. Moreover, the coal-tar and/or creosote used in the fish farming process may be a source of polycyclic aromatic compounds.

In the present study, investigations were carried out into the sixteen PAHs identified by the US-EPA as

requiring priority monitoring action within the framework of environmental quality control (Simoneit, 1998). Other non-US-EPA listed PAHs, namely perylene and some methyl derivatives, were also investigated in order to obtain further information on their origins. Perylene is usually considered a marker of the terrestrial origin of organic matter in the sediments (Sportsol et al., 1983; Colombo et al., 1989; Budzinski et al., 1997).

In this work, together with PAHs, we analyzed water and organic contents because it has been demonstrated that the concentrations of PAHs in sediments were affected by chemical composition of the samples such organic matter and water content (Kim et al., 1999). Generally, sediments with high water content (40%=muddy) were characterised by high values of PAHs, while sandy (about 20% water) sediments with low PAH content (Belahcen et al., 1997), sediments with high organic content were characterised by high values of PAHs (Witt, 1995).

Relationships between PAH concentration and distribution, which are useful for evaluating possible sources of contamination, were defined by comparing the profiles of 22 PAH compounds recovered from sediments.

## 2. Experimental procedure

### 2.1. Study site

The *Stagnone* lagoon at Marsala is a shallow basin in western Sicily (37° 52' north; 12° 28' east) (Fig. 1) with a surface area of about 2000 ha and an average depth of 1.5 m. It is separated from the open sea by a calcarenite platform (Isola Longa). The northern (Bocca S. Teodoro) and southern (Bocca Grande) mouths allow water exchange. Water temperatures (min. 11.2 °C, max. 29.1 °C) and salinities (min. 32.8, max. 47.1) have broader annual amplitudes than the surrounding sea (temperature: min. 14.1 °C and max. 26.4 °C; salinity close to 37). The basin is oligotrophic. No freshwater input is present (Sarà et al., 1999).

### 2.2. Sampling

Eight sediment samples were collected in the spring of 2004. Fig. 1 shows the location of the sampling sites. A total of 200 g of surface sediment were manually collected from each site using a glass container and placed in plastic bags. The samples were immediately refrigerated (4 °C) on site, stored avoiding exposure to light, and then rapidly transported to the laboratory where they were frozen prior to analysis.

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