

POLYCYCLIC AROMATIC HYDROCARBONS IN THE AREA OF A GREEK PETROLEUM REFINERY

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) in coastal areas commonly originate from petroleum extraction, transport and refining processes. They may pose a risk to marine life, as they can be both carcinogenic and mutagenic.

In this study, the 16 PAHs on the EPA's priority pollutant list were determined in the wastewater of the petroleum refinery of Motoroil Hellas, as well as in the seawater of the nearby area.

Keywords: *PAH, Aegean Sea, Petroleum, Coastal Waters*

Introduction

The main sources of PAHs in the environment are natural and intentional combustion of organic matter and petroleum manipulation (extraction, transport and refining) [1]. Solid phase extraction (SPE) [2] and ultrasonic extraction [3,4] are frequently used for the pre-concentration of PAHs from environmental matrices, while high performance liquid chromatography (HPLC) is often used for the analytical determination of PAHs [2,3,4]. Motoroil Hellas, an important Greek refinery, is located on the NW coast of Saronikos Gulf, about 80 km from Athens. In this study, the 16 PAHs on the EPA's priority pollutant list were determined in the treated industrial effluent (IE), sewage effluent (SE), cooling waters (CW) of the refinery, as well as in the seawater of the nearby area (stations S1, S2, S3).

Methodology

The samples were collected in March and September 2007. They were filtered using glass fibre filters within a few hours of sampling for the separation of the aqueous and the particulate matter fractions. The filtered water samples were pre-concentrated by SPE using C18 cartridges. The filters were solvent extracted using an ultrasonic bath and SPE cleanup was performed. An internal standard was added to all samples before their respective extraction techniques. After elution from the cartridges and final concentration by nitrogen blow-down, the PAHs were determined by HPLC with photo-diode array and fluorescence detectors. Gradient elution was used, as well as fluorescence wavelength programming. The only PAH not determined with the fluorescence detector was acenaphthylene, which has a fluorescence close to zero.

Results

Some determined PAH concentrations for both sampling periods are given in the tables below:

Tab. 1. PAH concentrations

| March 2007 | | | | | | |
|-----------------------|------|------|------|------|------|-----|
| Σ(water+part.matter) | S1 | S2 | S3 | IE | SE | CW |
| naphthalene | 19.5 | 19.0 | <LD | 88.5 | 20.3 | <LD |
| phenanthrene | 24.6 | 25.4 | 21.0 | 73.8 | 11.0 | <LD |
| fluoranthene | 7.0 | 5.3 | 4.9 | 59.7 | <LD | <LD |
| pyrene | 8.0 | 7.0 | 24.0 | 4.7 | 9.0 | <LD |
| benzo(b)fluoranthene | <LD | 3.8 | <LD | 18.8 | <LD | <LD |
| benzo(k)fluoranthene | <LD | <LD | <LD | <LD | <LD | <LD |
| dibenz(a,h)anthracene | <LD | <LD | <LD | 24.1 | <LD | <LD |
| September 2007 | | | | | | |
| Σ(water+part.matter) | S1 | S2 | S3 | IE | SE | CW |
| naphthalene | <LD | <LD | 20.8 | 79.3 | <LD | <LD |
| phenanthrene | 18.9 | 13.6 | 18.6 | 62.4 | 16.5 | 8.4 |
| fluoranthene | 7.7 | 6.9 | <LD | 6.0 | <LD | 6.3 |
| pyrene | 13.6 | 25.9 | 5.3 | 15.0 | 5.4 | <LD |
| benzo(b)fluoranthene | <LD | <LD | <LD | 10.6 | <LD | <LD |
| benzo(k)fluoranthene | <LD | <LD | <LD | 3.9 | <LD | <LD |
| dibenz(a,h)anthracene | <LD | <LD | <LD | 9.0 | <LD | <LD |

Discussion

Individual PAH concentrations in the filtered water samples ranged from 2.9 ng/L for fluoranthene to 29.1 ng/L for phenanthrene, while in the particulate matter they ranged from 3.8 ng/L for benzo(b)fluoranthene to 88.5 ng/L for naphthalene. Two- to four-ring PAHs were more abundant; the highest concentrations were found for naphthalene (88.5 ng/L), phenanthrene (73.8

ng/L) and fluoranthene (56.8 ng/L) respectively in the particulate matter of the industrial effluent. Five- and six-ring PAHs were only detected in the particulate matter; the highest concentrations were found for dibenz(a,h)anthracene (24.1 ng/L) and benzo(b)fluoranthene (18.8 ng/L) respectively in the industrial effluent. The concentrations of individual PAHs as well as total PAHs for March in the seawater samples were overall slightly higher than those determined for September. Although concentrations of individual PAHs were generally low, it is essential to continue environmental monitoring in the area on a regular basis.

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References

- 1 - UNEP, 2002. Regionally Based Assessment of Persistent Toxic Substances, Mediterranean Regional Report, UNEP Chemicals, Switzerland.
- 2 - Triantafyllaki S., Dassenakis M. and Psaroudakis N., 2005. Determination of Polycyclic Aromatic Hydrocarbons in Seawater by High Performance Liquid Chromatography with Photo Diode Array and Fluorescence Detection, *CEST: 9th Int. Conf. on Env. Sc. and Tech.*, 1-3/9/2005, Rhodes.
- 3 - Fan S.-L., Zhao L. and Lin J.-M., 2007. Flocculation-ultrasonic assisted extraction and solid phase clean-up for determination of polycyclic aromatic hydrocarbons in water rich in colloidal particulate with high performance liquid chromatography and ultraviolet-fluorescence detection, *Talanta*, 72: 1618-1624.
- 4 - Sun F., Littlejohn D. and Gibson M.D., 1998. Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection, *Anal. Chim. Acta*, 364: 1-11.