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Spatial and seasonal variabilities of dissolved hydrocarbons in surface waters from the Northwestern Mediterranean Sea: Results from one year intensive sampling

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HIGHLIGHTS

- Spatio-temporal distribution of dissolved hydrocarbons in the NW Mediterranean Sea
- Sources, transport and removing processes affecting AHs and PAHs are uncoupled.
- Anthropogenic signatures (both petrogenic and pyrogenic) increased in winter.
- Dissolved hydrocarbons originated mainly from the Rhône River and the atmosphere.

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ABSTRACT

Dissolved aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs) were analysed from surface water collected in continental, harbour and off-shore marine sites from Marseilles coastal area (Northwestern Mediterranean Sea) from February 2011 to February 2012. AH and PAH concentrations were in the range of 0.04–0.53 $\mu g\ l^{-1}$ and 8.1–405 $ng\ l^{-1}$, respectively. They both displayed seasonal and spatial variations in their concentrations and molecular composition. The lowest AH concentrations were found in summer and the highest PAH concentrations in winter. Both natural and anthropogenic (pyrogenic and petrogenic) hydrocarbon sources were identified. In winter, concentrations and composition patterns highlighted an increase in the signature of unburned and combusted fossil fuels, while they suggested an enhancement of weathering processes in summer months. Hydrocarbon inputs to the dissolved phase seemed to originate mainly from the atmosphere and the Rhône River. Hydrocarbon additional sources were identified only at the harbour site, emphasising the intense shipping traffic and industrial activities occurring in one of the most important Mediterranean harbours. This study underscores the strong dynamics of dissolved hydrocarbons and the uncoupling of the sources, transport and removing processes affecting AHs and PAHs. It also demonstrates the pertinence of taking this dynamics into account for the budget assessments of organic pollutants in coastal environments.

1. Introduction

Hydrocarbons, including aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs), are among the most widespread organic contaminants found in the marine environment. Some of them are harmful to living organisms with reprotoxic, carcinogenic and mutagenic effects (Kennish, 1992; Scarlett et al., 2007). Hydrocarbons are introduced in the coastal marine waters mainly through atmospheric exchanges/depositions, rivers, municipal/industrial effluents and surface runoffs (Tolosa et al., 1996; Lipiatou et al., 1997; Castro-Jiménez et al., 2012). AHs and PAHs may be both of biogenic or anthropogenic origin, although PAHs are almost exclusively considered of anthropogenic origin, especially in highly urbanised and industrialised areas. Moreover, PAHs are sensitive indicators of petrogenic (uncombusted petroleum) and pyrogenic (incomplete combustion of fossil fuels) sources (see reviews by Wang et al., 1999; Wurl and Obbard, 2004). The uncoupling of the sources, transport and removing processes affecting these two hydrocarbon classes has already been evoked (Bouloubassi and Saliot, 1993; Wakeham, 1996). Thus, the simultaneous analysis of AHs and PAHs constitutes a powerful and indispensable approach for the comprehensive assessment of various inputs as well as for the

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determination of their environmental behaviour, especially in estuarine and coastal regions.

Because of their low water solubility, AHs and PAHs are considered to be preferentially associated with particles in the coastal marine waters. This is highlighted by the large number of studies dealing with hydrocarbons in coastal sediments and particles while hydrocarbons in the dissolved phase of the water column have been much less investigated. However, in some systems with a low suspended matter load, the concentrations of PAHs in the dissolved phase were similar or even higher than those recorded in the particulate phase (Bouloubassi and Saliot, 1991; Guigue et al., 2011). In addition, dissolved hydrocarbons in the marine coastal environment are subjected to various transformation processes including evaporation, interactions with dissolved organic matter, bio-degradation and photo-degradation (Jordan and Payne, 1980; Schwarzenbach et al., 1993; Tsapakis et al., 2006). A better knowledge of the distribution and fate of hydrocarbons in the dissolved phase of the water column is essential for a more accurate estimation of their fluxes and budgets within marine ecosystems.

Dissolved hydrocarbons and their degradation products bioconcentrate into organisms by passive diffusion and respiration (Berrojalbiz et al., 2009, 2011). For small organisms at the basis of many marine trophic chains, dissolved hydrocarbons are much more bio-available and therefore more likely to have toxic effects on the biota than hydrocarbons present in particles, which are bioaccumulated through ingestion (Tilseth et al., 1984; Akkanen et al., 2012). Documenting dissolved hydrocarbon concentrations, which are presently scarce in marine waters, is relevant for assessments of toxicological effects within coastal marine ecosystems.

Marseilles (Southern France) is the first Mediterranean harbour for goods traffic and the Marseilles–Fos petrochemical complex is the world's third oil port. Marseilles is also the second most populated city in France, and thus generates important industrial, shipping, nautical and tourism activities. Hence, the Marseilles coastal area (Northwestern Mediterranean Sea) is exposed to numerous sources of contamination such as urban and industrial wastes, petroleum inputs and atmospheric depositions from transports, pyrogenic residues, and industrial and harbour activities. Moreover, the Marseilles coastal area is highly influenced by the Rhône River, which is the most significant source of freshwater in the Mediterranean Sea (Durrieu de Madron et al., 2003; Pairaud et al., 2011). Indeed, the Rhône River is the largest French river in terms of water discharge, and represents a considerable transport pathway for contaminants to the marine environment.

Numerous works have reported on the concentrations of hydrocarbons in waters and sediments from the Northwestern Mediterranean Sea (Benlahcen et al., 1997; Lipiatou et al., 1997; Dachs et al., 1997, 1999; Pérez et al., 2003; Mille et al., 2007; Berrojalbiz et al., 2011). However, little is known about the concentrations of dissolved AHs and PAHs in surface water of the Rhône River (Sicre et al., 2008), the Rhône Delta (Bouloubassi and Saliot, 1991, 1993) and the Bay of Marseilles (Marty and Saliot, 1976; Siron et al., 1987; Guigue et al., 2011). The main objectives of the present work are (i) to assess the spatial and temporal variabilities of dissolved AHs and PAHs in the surface waters of the Marseilles coastal area in term of concentration, molecular composition, origin and fate and (ii) to better understand the influence of the Rhône River on their distribution.

2. Material and methods

2.1. Study sites

Two continental (Arles and Vaccarès) and three marine (Port-de-Bouc, Couronne and Sofcom) sites were studied in the Marseilles coastal area neighbouring according to their different potential levels and sources of contamination (Fig. 1; Table 1). Arles station (AR) is located in the Rhône River, which is 812 km long and has a drainage basin of approximately 97,800 km^2. The Rhône delta has a surface area of ~1750 km^2 and is composed mainly of wetlands, ponds and salt marshes. The central part of the delta, known as the ‘Camargue’ (~750 km^2), comprises farmlands and salted ponds. The Vaccarès pond (VA, 12 km long, 6500 km^2, <2 m depth) is the largest pond of Camargue. It is the main element of the control system of the Rhône delta waters. VA is thus directly under the influence of the Rhône River. It is also subjected to pesticides and hydrocarbons from agricultural operation and nearby industrial areas such as the Marseilles–Fos petrochemical complex through atmospheric transport.

Port-de-Bouc (PB) is a harbour situated in the Gulf of Fos-sur-mer and surrounded by the Marseilles–Fos petrochemical complex, which includes several chemical, petroleum and steel-work plants. The Gulf of Fos-sur-mer receives some freshwater inputs coming from the Rhône River and the Berre Lagoon (Ulses et al., 2005). In addition, PB is positioned on the route of oil cargo ships going to the Berre Lagoon through the Caronte channel. Couronne (COU) is a nearshore site off PB. COU is located close to the Rhône River plume whose extent depends on Rhône water discharges and wind conditions (Pairaud et al., 2011). Sofcom (SOF), situated in the Bay of Marseilles near the Frioul Islands (~7 km off Marseilles), is a nearshore observation site of the national Service d'Observation en Milieu LITtoral (SOMLIT; http://www.domino.u-bordeaux.fr/somlit_national/). It is located much farther from the Rhône River and was selected as marine reference by comparison to the other anthropogenically impacted sites.

2.2. Sampling strategy

All sites were sampled ca bi-monthly from February 2011 to February 2012 in the morning between 8:00 and 12:00 am (Table 1). Freshwater samples (AR and VP) were taken directly from the edge while marine samples (PB, COU and SOF) were collected from the R/V Antédon II. AR, VA and PB were sampled only at 0.1 m depth (subsurface water, SSW) whereas offshore marine sites (COU and SOF) were sampled at 0.1 and 5 m depths. SSW samples were collected directly in 4 l Nalgene® polycarbonate bottles. The bottles were opened below the water surface to avoid the sampling of the surface microlayer. Five m depth samples were taken by means of a 5 l Niskin bottle equipped with silicon ribbons and Viton o-rings. They were then transferred into Nalgene® bottles. The bottles were washed with 1 M hydrochloric acid (HCl) and ultrapure water (i.e., Milli-Q water from Millipore system, final resistivity: 18.2 $M\Omega\ cm^{-1}$) before use, rinsed three times with the respective sample before filling and stored in the dark in the cold (4–8 °C).

2.3. Filtration of samples

Back in the laboratory, samples were immediately filtered under a low vacuum (<50 mm Hg) through precombusted (500 °C, 4 h) GF/F (~0.7 μm) glass fibre filters (47 mm diameter, Whatman) using polysulfone filtering systems for hydrocarbons (AHs and PAHs) and all-glassware systems for biogeochemical parameters, i.e., nitrates (NO_3^-), chlorophyll *a* (Chl-*a*) and particulate organic carbon (POC). The hydrocarbons present in the particulate matter, which was retained on the filters, are not presented here. The material that passes through GF/F filters consists in truly dissolved and colloidal matters, which can be each subjected to specific processes (Gustafsson and Gschwend, 1997). However, as it is difficult to separate operationally these two fractions, most of the environmental studies (including the present one) consider the material presents in GF/F filtered water simply as the ‘dissolved matter’. It is worth noting that hydrocarbon concentrations in the truly dissolved phase would be lower than those reported here. Filtered samples for dissolved hydrocarbon analyses were stored in 2 l SCHOTT® glass bottles with 50 ml dichloromethane (CH_2Cl_2) at 4 °C in the dark before solvent extraction (within 48 h). Filtered samples for NO_3^- and filters for Chl-*a* and POC were stored frozen until