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Particulate PAHs and *n*-alkanes in the air over Southern and Eastern Mediterranean Sea

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HIGHLIGHTS

- The patterns of PAH_s and *n*-alkanes over Mediterranean Sea were investigated.
- Vehicles exhausts seemed to be the principal PAH source over Mediterranean Sea.
- Relevant differences were observed among *n*-alkane concentrations in marine sites.
- This study underlined the role of anthropogenic sources near harbors.

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ABSTRACT

Particulate polycyclic aromatic hydrocarbons, *n*-alkanes and polar organic compounds were investigated in the marine atmosphere of Southern and Eastern Mediterranean Sea, in the frame of the scientific cruise of Urania ship between 27 July and 11 August 2013. The PM_{10} fraction of aerosol to which most organic substances are associated, were collected daily; contemporarily, gaseous regulated toxicants (ozone, nitrogen oxides and carbon oxide) and carbonyls were recorded. Samplings were carried out in front of Palermo and Messina, respectively the start and end harbors, and along the cruise, both in movement (*transects*, N = 14) and at stops (N = 11). Total PAHs ranged from 0.06 ng/m^3 up to 1.8 ng/m^3, with the maximums observed close to harbors. Unlike total concentrations that were in general comparable, the percent composition of PAHs was distinct for harbors, transects and stops, which allowed to draw insights about the pollution sources impact. Concentrations of *n*-alkanes (C_{18}–C_{35}) ranging from 6.7 to 43 ng/m^3 were quantified. The carbonyls evaluation revealed relatively high concentrations of formaldehyde (~4–24 μg/m^3) and acetone (~5–35 μg/m^3) near harbors, and of acrolein (up to 12 μg/m^3) offshore, while benzaldehyde was quite independent of the site type (≈0.5 μg/m^3). Nicotine and caffeine were detected, at different extents (0.0–2.2 ng/m^3 and 0.01–0.17 ng/m^3, respectively), in ca. 70% and 100% of samples. Alkyl phthalates ranged from 2.7 to 67 ng/m^3 and showed variable percentages in the samples. Finally, traces of *N*,*N*-diethyl-*meta*-toluene amide (up to 0.4 ng/m^3) were found at all sites.

1. Introduction

Seas and oceans, covering ¾ of Earth surface, play a key role with regard to chemistry of the troposphere. Marine regions not only undergo the long-range transport of polluted air, but also directly contribute to the release of chemicals from ocean surface through spray raised by winds, and to their removal by deposition. Moreover, marine atmosphere is reach of ozone and oxidants, able to decompose reactive gaseous species and favor the formation of secondary aerosols. Mediterranean Sea coasts in particular host megacities as well as intense industrial and agricultural activities in Europe, Middle-East Asia and Africa countries; which are interested by a huge inter-exchanges of goods, petrol and people. Alongside, the geography of the surrounding regions regulates the wind, temperature and rain regimes.

Marine aerosols are complex mixtures of chemicals, among which organic species have gained concern thanks to their impact on trends of global climate, chemistry of the atmosphere and biogeochemical cycling of nutrients (Fu et al., 2013). Studies dealing with composition of marine aerosols started at rural locations over the coasts more than 30 years ago, (Sicre et al., 1987; Gogou et al., 1998; Gigliotti et al., 2000; Kavouras and Stephanou, 2002; Almeida

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Abbreviations

PAH symbols

BaA	benz[*a*]anthracene
CH	chrysene
BbF	benzo[*b*]fluoranthene
BjF	benzo[*j*]fluoranthene
BkF	benzo[*k*]fluoranthene
BeP	benzo[*e*]pyrene
BaP	benzo[*a*]pyrene
PE	perylene
IP	indeno[1,2,3-*cd*]pyrene
DBA	dibenz[ah]anthracene
BPE	benzo[*ghi*]perylene
∑PAHs	total PAHs

Carbonyl compounds

L_1	formaldehyde
L_2	acetaldehyde
ACE	acetone
ACR	acrolein
L_3	propanal
MAC	methylacrolein
L_4	butanal
L_{Bz}	benzaldehyde
L_5	pentanal
L_{To}	*para*-tolualdehyde
MGl	methylglyoxal
L_6	hexanal

Polar compounds

NIC	nicotine
COT	cotinine
CAF	caffeine
DEET	*meta*-*N*,*N*-diethyl toluamide
DMP	dimethylphthalate
DEP	diethylphthalate
DiBuP	diisobutylphthalate
DnBuP	dibutylphthalate
BuBzP	butylbenzylphthalate
DEHP	diethylhexylphthalate
ΣAPs	total alkyl phthalates

et al., 2005; Tsapakis and Stephanou, 2007; Wang et al., 2013), and continued by means of ship cruises across seas (Tsapakis and Stephanou, 2005; Moreno et al., 2010; Velchev et al., 2011) and oceans (Jaward et al., 2004; Ding et al., 2007; Xu et al., 2012; Lohmann et al., 2013; Liu et al., 2014). These investigations were focused on both macro and micro-components, inorganic and organic substances, gaseous compounds, semi-volatile and particulate species. Nevertheless, rather than to marine air attention was overall paid to sea water (dissolved and suspended materials: Maldonado et al., 1999; Campanelli et al., 2004; Nizzetto et al., 2008; Berrojalbiz et al., 2011; Castro-Jiménez et al., 2012; Marrucci et al., 2013; Siemers et al., 2015), sediments (Gogou et al., 2000; Tsapakis et al., 2006; Cardellicchio et al., 2007; Perra et al., 2011; Acquavita et al., 2012, 2014; Marini and Frapiccini, 2013; Net et al., 2015) and sea/air interface (Marty et al., 1988; Manodori et al., 2006; Lohmann et al., 2009; Guitart et al., 2010; Mulder et al., 2014).

In recent years, little has been made about organic air contaminants. Hence, this study aimed at better understanding the composition of organic substances in marine aerosols above the Mediterranean Sea, undertaken within the *Fenice 2013* scientific cruise of CNR Research Vessel *Urania* [from SO.PRO.MAR, Fiumicino (RM), Italy. See Supplementary Table S1 for boat facilities]. A list of compounds were investigated, occurring both in particulate (polycyclic aromatic hydrocarbons with molecular weights ranging from 226 to 278 a.m.u., C_{18}–C_{35} *n*-alkanes, polar substances) and gaseous phase (ozone, nitrogen oxides, carbon monoxide, C_1–C_7 aldehydes and ketones). Our investigation allowed collecting new information on chemicals that affect the marine atmosphere, including carcinogenic polycyclic aromatic hydrocarbons (PAHs). PAHs arise primarily from natural and anthropogenic sources such as oil spills, vehicle exhausts, industrial wastes, biomass burning, and coal and wood combustion (Ravindra et al., 2008; Zhang and Tao, 2009). Marine environments, relatively far from emission sources, are traditionally viewed as an ultimate sink for these toxicants, as air masses transport them over long distances.

Limited environmental data sets of non-polar and low-polar compounds in marine regions are available (Gogou et al., 1996; Gigliotti et al., 2000; Castro-Jiménez et al., 2012) and very little is known about polar organics, about which original information was collected during the *Fenice 2013* cruise.

2. Materials and methods

2.1. The Fenice cruise 2013 and sampling sites

The oceanographic campaign *Fenice 2013* was conducted as a part of MED-OCEANOR (Integrate Atmospheric Water Measurements to Assess the Mercury Cycle Over in the Mediterranean Sea). The cruise started from Palermo (38°10′N, 13°26′E) on 26 July 2013 and finished in Messina (38° 11′ N, 15° 33′ E) on 12 August (Fig. 1). At almost all the sampling stations, the sea area was free of important stationary anthropogenic emission source (open sea) and atmospheric transport was expected to be the principal source of pollution. In front of ports the environment might be affected by the transport of contaminants from mainland and from human activity. In addition, near the Malta Island the relatively high contamination could depend on the intense maritime traffic for commercial activities. The Mediterranean climate is typically characterized by hot and dry summers; during the cruise period meteorological conditions were represented by a high pressure system (daily average 1011–1022 mbar) with moderate wind (mean daily speed ranging 12–15 km h^{-1}) and elevated values of temperature (daily maximums 24–38 °C) and humidity (mean period value 84%).

A total of 26 sampling intervals of three distinct categories were established during the cruise, depending on geographical and shipping situation, i.e. in front of the two harbors (ca. 2 km from coast), offshore at stops (N = 11) and during transects between stops (N = 13). In addition, 24 h samplings were carried out all over the cruise, each starting at ~08:00 h. Table 1 lists the sampling dates and intervals with the site symbols.

$PM_{2.5}$ fraction of particulate was examined, since organics are associated with it (Moller and Alfheim, 1980; Kameda et al., 2005), and ultra-fine and fine aerosols are responsible of ambient toxicity together with a handful of gaseous species (ozone, nitrogen dioxide