Distribution of Fragrances and PAHs in the Surface Seawater of the Sicily Channel, Central Mediterranean.

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Keywords: Fragrance Materials (FMs); Personal Care Products (PCPs); Polycyclic Aromatic Hydrocarbons (PAHs); Seawater; Mediterranean.

Highlights

First study on PCPs in Mediterranean open seawater.

Detailed distribution of PAHs in the Sicily Channel.

Salicylates result the most abundant FMs.

Pyrogenic sources of PAHs.

Marine currents and atmospheric transport are major drivers.

Abstract

The Mediterranean Sea is highly influenced by several anthropic pressures, including different kinds of organic pollutants. Fragrance Materials (FMs) and Polycyclic Aromatic Hydrocarbons (PAHs) were investigated in the surface seawater of the Sicily Channel in offshore and coastal areas. Total concentrations of FMs and PAHs resulted respectively up to 112 ng L^{-1} and 43 ng L^{-1}, with similar distributions of both classes of analytes: lower values were detected in some coastal samples, due to the upwelling of deep and unpolluted waters, while the presence of gyres probably accumulates contaminants in offshore areas. Confirming previous works, the allergenic and oestrogenic Salicylates generally resulted the most abundant FMs and diagnostic ratios indicated combustion processes as the sources of PAHs. The coupling of the well-known PAHs with a new class of Personal Care Products (PCPs) helped the identification of the major environmental drivers: the results highlighted the role of mesoscale hydrodynamics and suggested long-range atmospheric transport as key factors. The first detection of the selected FMs in open sea areas support the hypothesis of their environmental persistence.

1. Introduction

The Mediterranean Sea is a semi-enclosed basin surrounded by highly populated regions (Berrojalbiz et al., 2011). Anthropic pressures largely influence the environment, deriving from industrialization, urbanization and agriculture, as well as fishing, maritime traffic, harbor activities and tourism (Castro-Jiménez et al., 2012; Er-Raioui et al., 2009). The rapid increase of the demographic pressure and of the economic evolution lead to a large number of organic pollutant sources constituting a threat to the environment and biodiversity of the area (Castro-Jiménez et al., 2012). The Mediterranean Sea is therefore a region of special interest to study the factors controlling distribution, transport and fate of pollutants in marine waters (Berrojalbiz et al., 2011). However there are major knowledge gaps, since, in comparison to offshore waters, most studies focus on sediments and on local coastal areas influenced by proximity to inputs and runoff from land-based sources (Berrojalbiz et al., 2011; Giuliani et al., 2015). In the open sea other key factors, such as atmospheric transport and deposition, become important drivers as significant diffuse sources (Tsapakis et al., 2006).

Among organic pollutants, very little is known about the presence of Personal Care Products (PCPs) in the Mediterranean: few studies report the presence of PCPs in surface waters, Wastewater Treatment Plants (WWTPs), sediments and organisms (Arpin-Pont et al., 2016) and this information is limited to coastal marine environments. Fragrance Materials (FMs) are widespread used ingredients of PCPs and previously synthetic musks represent a category of contaminants whose environmental fate was mainly investigated by the literature (Daughton and Ternes, 1999). However, little is known about other different FMs and in this study we focus on 17 long-lasting and stable fragrances that are commercially available (Vecchiato et al., 2016). The trade names (Givaudan®) of the selected FMs are: Amberketal, Ambrofix, Amyl Salicylate, Benzyl Salicylate, Bourgeonal, Dupical,

Hexyl Salicylate, Isobutavan, Lemonile, Mefranal, Myraldene, Okoumal, Oranger Crystals, Pelargene, Peonile, Tridecene-2-Nitrile, Ultravanil (Table SI1). The common features of these FMs are a long persistence as fragrances (tenacity on blotter) and a chemical stability that allows their application in very different commercial products (eindex.givaudan.com). Such characteristics are possible indications of their persistence in the environment. The selected FMs were recently found as contaminants in the Venice Lagoon, where sewage outlets largely emit these compounds into the surface seawater, with concentrations up to 10 μg L^{-1} in the innermost urban canals (Vecchiato et al., 2016). Traces were found also in the coastal surface seawater of Terra Nova Bay, Antarctica, where emissions from the nearby research station, as well as a contribution from atmospheric transport were hypothesized (Vecchiato et al., 2017). Amongst the 17 fragrances, Benzyl, Hexyl and Amyl Salicylates were investigated by a limited literature: because of their low prices (under $5/kg), these FMs are High Production Volume (HPV) chemicals with an worldwide annual consumption well over 5000 tons (Belsito et al., 2007; Gaudin, 2014). Benzyl Salicylate is also an allergenic UV-filter agent (Heisterberg et al., 2011; Kameda et al., 2011), with an oestrogenic activity comparable to bisphenol A (BPA) (Zhang et al., 2012) and giving oestrogenic responses in human breast cancer cells (Charles and Darbre, 2009). Benzyl and Hexyl Salicylates were detected in different WWTPs (Godayol et al., 2015; Kameda et al., 2011; Negreira et al., 2010; Simonich et al., 2002, 2000), while fewer data are reported about Benzyl Salicylate in river waters (Kameda et al., 2011; Negreira et al., 2010; Vila et al., 2016).

More studies are available regarding Polycyclic Aromatic Hydrocarbons (PAHs) in the Mediterranean: the distribution of these compounds (deriving from incomplete combustions, direct dispersions of oil products and biogenic natural sources) was mainly investigated in coastal environments, while less studies considered the open sea areas (Berrojalbiz et al., 2011; Castro-Jiménez et al., 2012). The

available information shows that the occurrence of PAHs in offshore waters is dependent from atmospheric transport and deposition, particle and plankton settling processes in the water column and the presence of mesoscale variability associated with gyres (Berrojalbiz et al., 2011; Castro-Jiménez et al., 2012; Parinos and Gogou, 2016).

The aim of this work is to study the distribution of fragrances and PAHs in the surface seawater of the Mediterranean: the coupling of a new class of pollutants with well-known tracers, as PAHs, could help the interpretation of the processes governing their environmental presence. In particular, the detection of the selected FMs in open sea areas far from direct sources would highlight the role of the long-range atmospheric or oceanic transport, involving the possible environmental persistence of these contaminants. The study area is located in the Sicily Channel, which is the central connection between the Eastern and Western Mediterranean and the samplings were aimed to distinguish contamination in offshore and coastal areas. To the best of our knowledge this is the first survey investigating PCPs in offshore Mediterranean surface seawater and the first study focused on PAHs in the Sicily Channel, where only previous scarce data were available.

2. Materials and methods

Surface seawater samples (Table SI2) were collected in July 2016 during the oceanographic cruise BANSIC 2016 (CNR R/V “Minerva Uno”) in solvent-rinsed glass bottles at the sites shown in Figure 1.

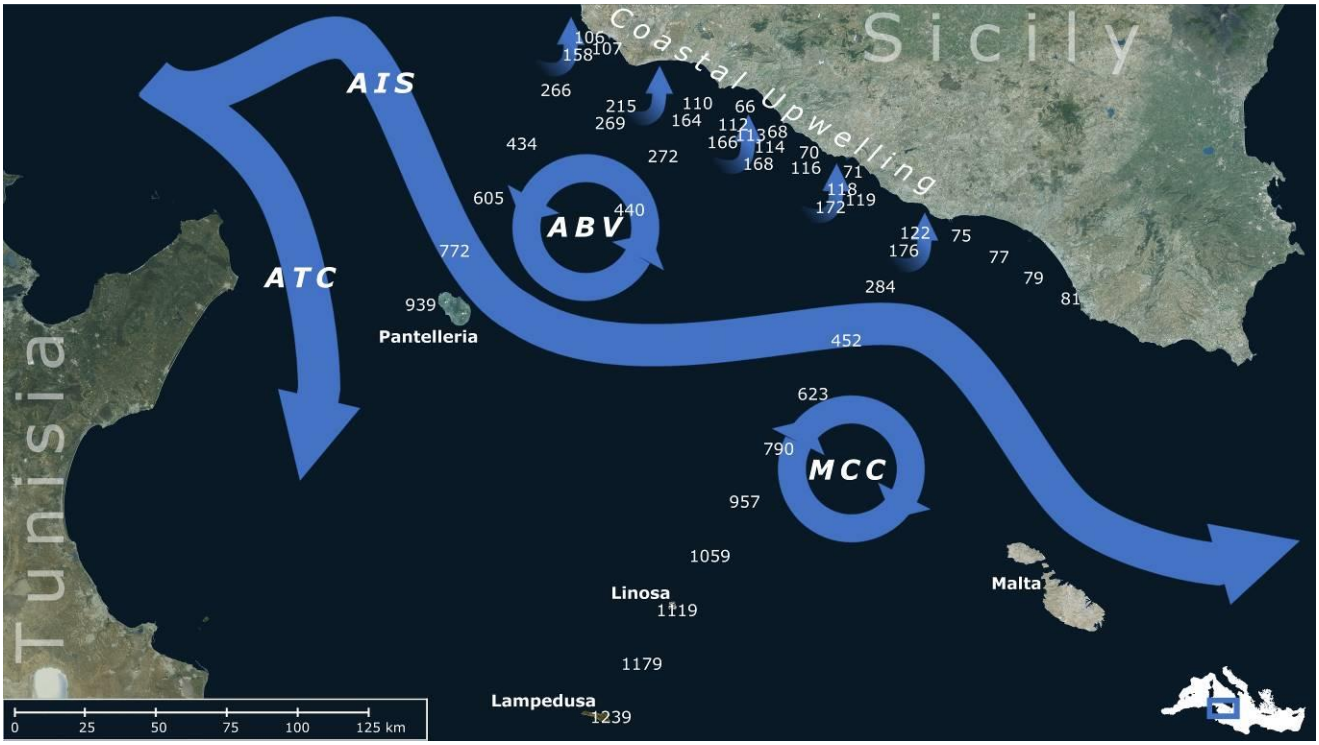

Figure 1: Sampling locations of the surface seawater and principal surface currents in the Sicily Channel, Mediterranean. Modified from (Ciappa, 2009; Falcini et al., 2015).

In the Sicily Channel the surface Atlantic Water (AW) is advected by the Atlantic Ionian Stream (AIS) and the Atlantic Tunisian Current (ATC) (Figure 1). In summer the meandering AIS flows round semi-permanent structures: the cyclonic Adventure Bank Vortex (ABV), the anticyclonic Maltese Channel Crest (MCC) (Ciappa, 2009; Falcini et al., 2015). An important spatial variability exists in terms of shape, position and strength of these currents (Bonanno et al., 2014) and summer westerly winds cause upwelling along the southern coast of Sicily (Ciappa, 2009; Patti et al., 2010). A deeper westward current transports water of eastern origin at an intermediate layer (Bonanno et al., 2014) and these hydrodynamic conditions also influence the distribution of biota in the area (Cuttitta et al., 2017).

Details of the analytical method were previously described (Vecchiato et al., 2016, 2015). Briefly, water samples (1 L) were spiked with ^{13}C internal standards and extracted using 200 mg Oasis® HLB cartridges (Waters Corp., Milford, MA USA) previously conditioned with 10 mL of dichloromethane followed by 10 mL of ultrapure water (ELGA, High Wycombe, UK). Pesticide-grade dichloromethane, toluene, acetone and *n*-hexane (Romil Ltd., Cambridge, UK) were used. Isotope-labelled standard solutions (CLM-2477, CLM-2451, CLM-2722), were purchased from CIL (Cambridge Isotope Laboratories, Inc., Andover, MA USA), while PAHs native standard solutions (Naphtalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(*a*)anthracene (B(*a*)A), chrysene (CHR), retene (RET), benzo(*b*)fluoranthene (B(*b*)F), benzo(*k*)fluoranthene (B(*k*)F), benzo(*a*)pyrene (B(*a*)P), benzo(*ghi*)perylene (B(*ghi*)P), indeno(1,2,3-*c,d*)pyrene (I*cd*P) and dibenzo(*a,h*)anthracene (D(*a,h*)A)) were acquired from Dr. Ehrenstorfer (Augsburg, Germany). The results of the fragrances are expressed as a concentration of the commercial product standards (Givaudan, Vernier, Switzerland), since most of the 17 FMs are not available at analytical or reagent grade. Cartridges were eluted with 1 mL of toluene, 15 mL of dichloromethane followed by 10 ml of *n*-hexane. Eluates were dried with Na_2SO_4 and reduced to 100 µL under a gentle nitrogen flow at 23 °C (Turbovap II®, Caliper Life Science, Hopkinton, MA, USA). Instrumental analyses were conducted by GC-MS (7890A-5975C, Agilent Technologies) on a 60-m HP-5MS column (0.25 mm I.D., 0.25 µm; Agilent Technologies, Avondale, USA) in Single Ion Monitoring (SIM). Crude results were corrected using the instrumental response factors and procedural field blanks (n=3). The Method Detection Limit (MLD) was calculated as three times the standard deviation of the blank signal and details are reported in Table SI3.

3. Results and Discussion

Fragrances

Fragrances were detected in 27 out of 42 samples of surface seawater of the Sicily Channel, with the sum of the concentrations up to 112 ng L^{-1} (Table SI4). Those compounds that were never detected in any sample (Amberketal, Dupical, Isobutavan, Lemonile Mefranal, Myraldene, Tridecene-2-Nitrile, Ultravanil) were excluded from the following discussion.

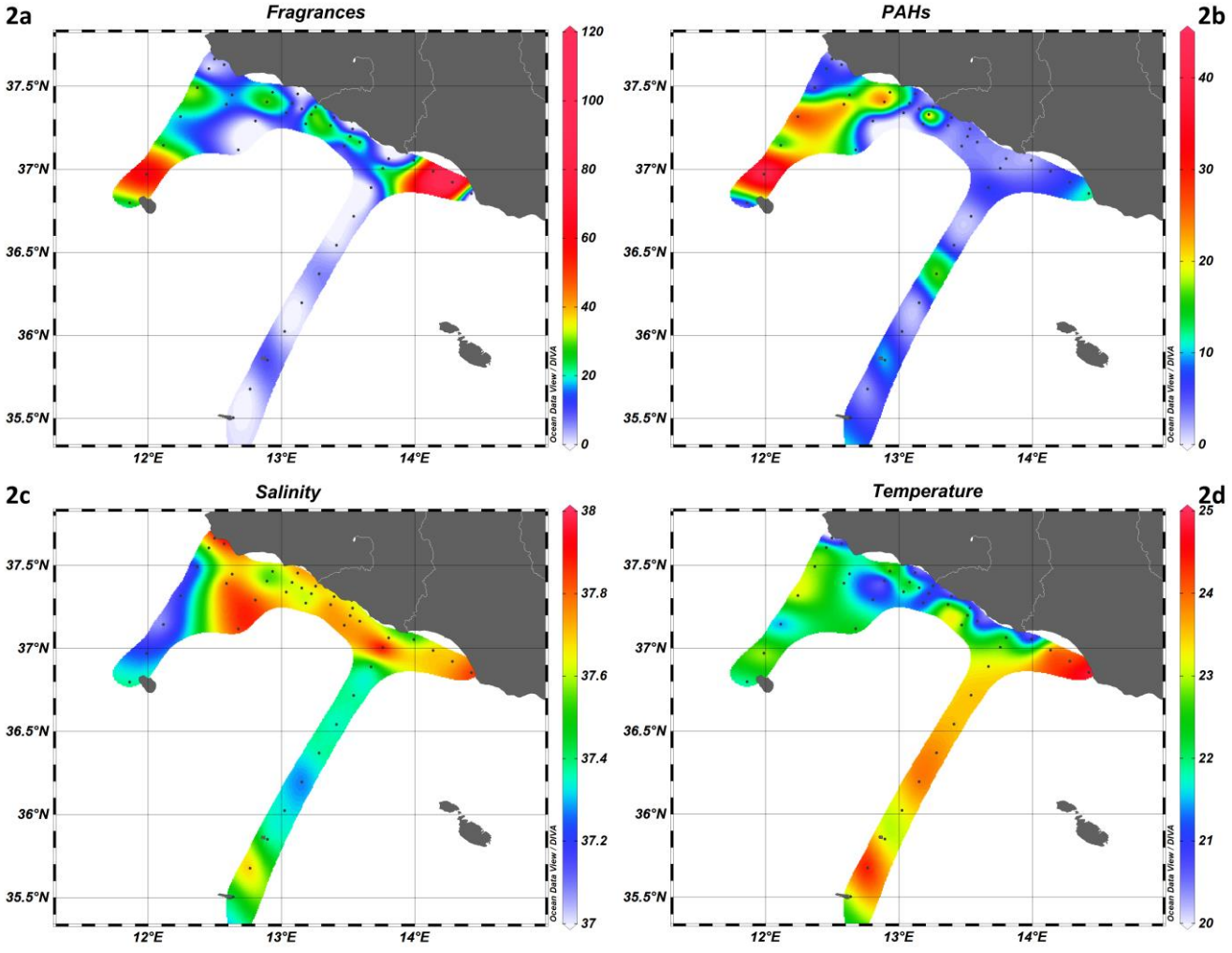

Figure 2a, b, c, d: Concentrations of Fragrances (ng L^{-1}; 2a), PAHs (ng L^{-1}; 2b), Salinity (PSU; 2c) and Temperature (°C; 2d) in seawater samples of the Sicily Channel. Refer to Figure 1 for sample stations (black dots) and to Tables SI4 and SI5 for other details. Data were interpolated using Ocean Data View - Diva Gridding.

159

160 Focusing on the western transect towards Pantelleria Island, the coastal samples resulted with lower
161 levels of FMs in comparison to offshore waters, where concentrations relatively peaked in the
162 sample 772 (64 ng L^{-1}; Figure 2a) and in the near samples 605 and 939, resulting respectively 27 and
163 26 ng L^{-1}. A similar pattern marks also the coastal area between approximately 3 to 30 km from the
164 Sicilian shore, where no or low FMs were found generally in correspondence to colder and saltier
165 water masses (Figure 2c, 2d): concentrations ranging from 20 to 30 ng L^{-1} were found at
166 intermediate distance to the shore (samples 110, 164, 114, 116, 118, 119) in comparison to the
167 samples 66, 70 and 71, resulting ldl-10 ng L^{-1} (Figure 3). Samples 68 and 113 except from this
168 scheme. The different distribution between coastal and open sea areas is likely due to the
169 occurrence of phenomena of wind-driven coastal upwelling raising deep and unpolluted waters
170 (Ciappa, 2009; Patti et al., 2010), while the presence of gyres, as the cyclonic ABV, probably
171 accumulates fragrances at their offshore borders, depending on the variability of the hydrodynamic
172 patterns (Bonanno et al., 2014). However, the influence of the near Pantelleria island and/or the
173 advection of AW from Northern Tunisian coastal areas cannot be ruled out. Different water masses,
174 such as the anticyclonic MCC, influence the samples of the eastern transect towards Lampedusa
175 Island, where, with few exceptions, fragrances resulted below detection limits. The highest
176 concentrations of FMs were found in the samples 77 and 79 facing the gulf of Gela, resulting
177 respectively 81 and 112 ng L^{-1}. In this case it is possible to hypothesize the role of local land-based
178 pollution, since in this area the upwelling is known to weaken (Piccioni et al., 1988), and marine
179 currents transport eastwardly offshore the waters from the outlet of the Salso river, outflowing
180 north-west to the gulf of Gela.

181 As in previous works (Vecchiato et al., 2017, 2016), Salicylates generally resulted the most abundant

and frequently detected compounds, with the sum of Amyl and Hexyl Salicylate constituting the 25-100% of the total fragrances (Table SI4). Conversely, Benzyl Salicylate was detected only in 8 samples at 0.7-5.6 ng L^{-1}: this differs with seawaters influenced by direct untreated discharges in the Venice lagoon (Vecchiato et al., 2016), but it is more similar to remote Antarctic samples, where atmospheric transport was hypothesized (Vecchiato et al., 2017). Higher levels of Benzyl Salicylate were found in wastewaters and rivers (Godayol et al., 2015; Kameda et al., 2011; Negreira et al., 2010; Simonich et al., 2002, 2000; Vila et al., 2016). The concentrations of this allergenic and oestrogenic compound (Charles and Darbre, 2009; Zhang et al., 2012) resulted far below possible ecotoxic damages to *Daphnia* and other species (Belsito et al., 2007).

Also Pelargene and Ambrofix were frequently detected in the samples, resulting respectively below 6.3 and 7.2 ng L^{-1}, while the occurrence of Bourgeonal, Oranger Crystals, Peonile an Okoumal was only occasional (Table SI4). In particular the last compound was found only in the sample 215, which was characterized by a peculiar composition, with amyl salicylate resulting below detection limits and a relatively higher proportion of the “minor” fragrances: it can be supposed that, considering the heavy maritime traffic in the area (Romagnoli et al., 2016), this specific sample reflects possible direct discharges from the previous passage of a ship.

The results of the FMs are in the same range of concentration of various PCPs globally detected in open sea environments (Arpin-Pont et al., 2016). Focusing on the Mediterranean region, the levels of FMs in the Sicily Channel are comparable to musk fragrances, UV-filters and other PCPs in environmental waters, resulting lower than samples from WWTPs and polluted hotspots (Cabeza et al., 2012; Celano et al., 2014; Gracia-Lor et al., 2012; Martínez Bueno et al., 2012; Negreira et al., 2010; Villa et al., 2012). The occurrence of PCPs also in biota (Cunha et al., 2015; Trabalón et al., 2015) and sediment matrices (Combi et al., 2016; Pintado-Herrera et al., 2016) accounts for the

205 ubiquitous presence of this class of compounds in the Mediterranean, with consequent concerns
206 about their environmental fate.

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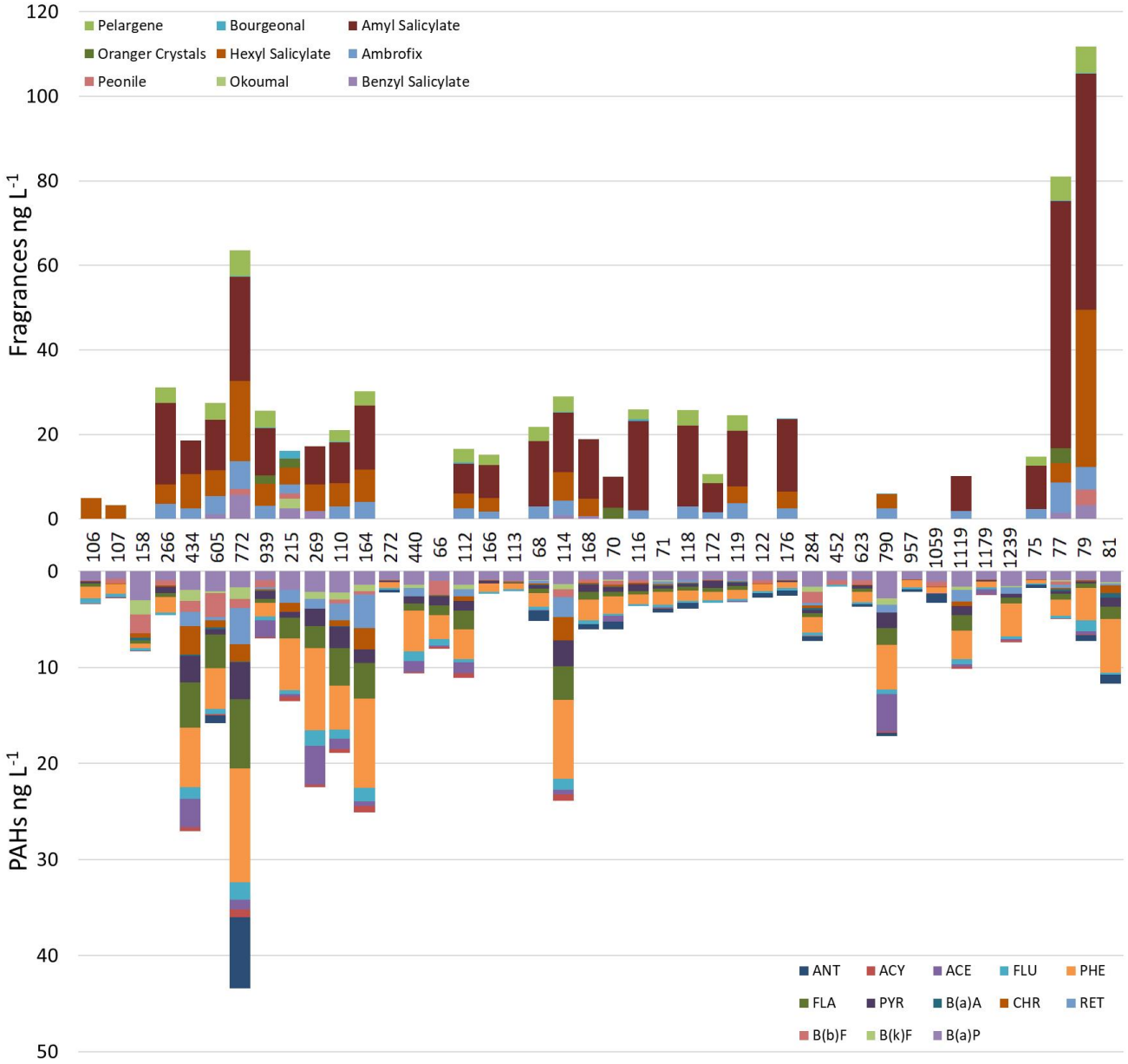

208

209 Figure 3: Fragrances and PAHs in the surface seawater of the Sicily Channel (ng L^{-1}). Only detected
210 compounds are displayed.

211

PAHs

The presence of PAHs was detected in every sample of seawater, with concentrations ranging from 1.6 to 43 ng L^{-1} (Table SI5). NAP, B(*ghi*)P, I(*cd*)P and D(*ah*)A resulted below detection limits and were not considered in the discussion. The distribution of PAHs is similar to fragrances (Figure 2b and 3): the highest levels were found in the sample 772 (43 ng L^{-1}) along the transect towards Pantelleria, corresponding to the peak of FMs, followed by the sample 434 (27 ng L^{-1}), while low concentrations were found near the coast, mainly due to upwelling phenomena. This is replicated at intermediate distance to the Sicilian shore, with peaks of concentrations in the samples 164 (25 ng L^{-1}) and 114 (24 ng L^{-1}). Focusing on the eastern transect towards Lampedusa, relatively higher concentrations were found in the samples 790 (17 ng L^{-1}) and 1119 (10 ng L^{-1}), where also FMs resulted above detection limits. This pattern indicates that the processes of transport of both PAHs and FMs follow similar schemes and the presence of currents of water masses, as the ABV and the coastal upwelling, likely influences the distribution of these pollutants in the surface seawater. However, a remarkable exception is represented by the samples facing the gulf of Gela, where low levels of PAHs were found in the samples 77 and 79, contrary to the high concentrations of fragrances. This supports the hypothesis of a case of local pollution as a source of PCPs for these samples, in comparison to marine or atmospheric transport. Nevertheless, in Gela are located important petrochemical industries that might constitute a source of contamination to the surrounding environment, which is apparently in contrast with the relatively low levels of PAHs in our samples (Orecchio et al., 2010).

Concentration of PAHs in surface seawater are comparable to data from open sea areas of the Mediterranean (Berrojalbiz et al., 2011; Dachs et al., 1997; Ehrhardt and Petrick, 1993; Parinos and Gogou, 2016). In particular in the Sicily Channel, Dachs et al. found 1.1 ng L^{-1} of PAHs, while Berrojalbiz et al. detected 0.25-0.76 ng L^{-1} as a sum of dissolved and particulate fractions. Higher

levels (22.5 ng L^{-1}) were found by Ehrhardt and Petrick as the mean concentration of transect in the same area (Berrojalbiz et al., 2011; Dachs et al., 1997; Ehrhardt and Petrick, 1993). In the coastal environments levels of ∑(PAHs)<100 ng L^{-1} are frequently found (El Nemr and Abd-Allah, 2003; Guigue et al., 2014; Guitart et al., 2010, 2004; Karacik et al., 2013; Lammel et al., 2015), however concentrations could rise substantially in presence of specific sources, river outlets and harbors (Bihari et al., 2007; Bouloubassi and Saliot, 1991; Er-Raioui et al., 2009; Marrucci et al., 2013; Montuori et al., 2016; Montuori and Triassi, 2012; Mzoughi and Chouba, 2011; Yilmaz et al., 1998).

Focusing on the individual compounds, FLU, PHE, FLA, PYR, CHR and B(*a*)P were detected in more than 70% of the samples and their sum constitutes the 53-99% of the total concentrations (Table SI5). PHE was the most abundant compound (up to 12 ng L^{-1}), which is in agreement with previous data (Berrojalbiz et al., 2011). The average relative pattern of the major PAHs of the Sicily Channel is in accordance with that found in the seawater (Berrojalbiz et al., 2011) and in the aerosol (Castro-Jiménez et al., 2012; Tsapakis et al., 2006) collected in open sea areas, supporting the hypothesis of the role of the atmospheric transport leading net inputs of PAHs to open waters.

Retene (1-methyl-7-isopropyl phenanthrene) is a natural diterpenoid PAH deriving from the digenetic degradation of abietic acid, a constituent of plant resins, but RET is also used as a molecular marker typical of combustion of coniferous wood (Bouloubassi and Saliot, 1993; Lipiatou and Saliot, 1991). The levels of RET in the surface seawater samples (l.d.l - 3.7 ng L^{-1}) are comparable to previous data in the western Mediterranean (Bouloubassi and Saliot, 1993) and the occurrence of this compound suggests the role of biomass combustion as a major source of PAHs. This is also supported by the application of the diagnostic molecular ratios ANT/(ANT+PHE) and FLA/(FLA+ PYR) (Tobiszewski and Namieśnik, 2012), resulting in most samples respectively >0.1 and >0.5 (Figure SI1). These values indicate a clear prevalence of pyrogenic sources (mainly from combustion of

258 grass, wood and coal) upon petrogenic sources, which is in accordance with the distribution of PAH
259 in the atmosphere over the open sea Mediterranean (Castro-Jiménez et al., 2012). Conversely
260 petrogenic inputs are generally found to become more relevant in coastal areas (Gregoris et al.,
261 2014). This suggests for PAHs a predominance of the atmospheric transport processes upon local
262 pollution, e.g. fuel leaks from ships.
263
264 **4. Conclusions**
265 This study represents the first detection of the selected FMs in open sea environment. The distance
266 from direct sources evidences the previously hypothesized persistence of these contaminants
267 (Vecchiato et al., 2017, 2016) involving processes of long-range transport. Both atmospheric and
268 marine phenomena probably constitute key factors: on one hand the spatial distribution of the
269 FMs, together with PAHs, can be explained considering the presence of hydrodynamic currents, as
270 AW, ABV and coastal upwelling, on the other diagnostic ratios and literature data highlight the role
271 of the atmospheric transport. With the exception of few coastal samples, the general concordance
272 of the distribution of fragrances and PAHs indicates that both classes of compounds are depending
273 from the same environmental drivers, as suggested also by the similarity of the range of their
274 physico-chemical properties (Vecchiato et al., 2016). Consequently, if likely the PAHs detected in
275 the samples were originally emitted directly in the atmosphere by combustion processes, the FMs,
276 as other PCPs, are generally supposed to enter in the environment through discharges in the water
277 compartment (Vecchiato et al., 2016). Therefore, if an atmospheric transport is hypothesized, the
278 volatilization probably occurs from wastewaters containing FMs, as well as directly from the
279 household and personal good where these products are used, since the semi-volatility is a
280 fundamental commercial characteristic to give a persistent perfuming. Future studies should

disentangle the questions about the fate of the fragrances in the atmospheric compartment. Nevertheless, the peculiar concentrations of FMs found in the samples 77 and 79 plausibly reflect a local land-based pollution. The results highlight the role of mesoscale phenomena governing the distribution of organic pollutants between offshore and coastal areas, providing a first insight about the presence of fragrances in open seawater and improving the information available about the presence of PAHs in the Sicily Channel. This knowledge can help to achieve the challenging goal of the protection of the Mediterranean environment.

Acknowledgments

This work was supported by the Italian Ministry for Education, University and Research's RITMARE flagship project. The authors gratefully acknowledge all the researchers, the crew of the r/v "Minerva 1" and his Captain Emanuele Gentile (Oceanographic Cruise BANSIC-2016). We also wish to thank Francesco Calore and Andrea Bertin from the chemical laboratory of S.E.S.A. SpA, who gave an invaluable technical support. Givaudan and the International Express Service (IES-Ingredients) provided the commercial standards of FMs free of charge. Elga Lab water, High Wycombe UK, supplied the pure water system used in this study.

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