ENVIRONMENTAL INVESTIGATIONS IN THE GULF OF POZZUOLI (NAPLES) IN RELATION TO PAHs CONTAMINATION

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Abstract – The Gulf of Pozzuoli (GoP) is a marginal sub-basin of the SE Tyrrhenian Sea, characterized by a strong anthropogenic impact, due to high population density and intense commercial and tourist traffic. Historically, the GoP is dedicated to the farming of bivalve mollusks, and mussels are constantly subject to chemical and microbiological monitoring to protect the health of consumers. Data from this monitoring show high levels of polycyclic aromatic hydrocarbons (PAHs) in mussels from the Lucrino area during the winter season. This study reports the activities carried out to investigate the levels and sources of contamination by PAHs in this area focusing also on the different PAH profiles and on the sea surface currents of the Gulf of Pozzuoli (Naples).

Introduction

The Gulf of Pozzuoli (GoP) is a marginal sub-basin of the south-eastern Tyrrhenian Sea (TYS), that is semi-enclosed by the Cape Miseno in the northern part of the GoP, and by the Island of Nisida in the southern part. This area is characterized by a strong anthropogenic impact, due to high population density and intense commercial and tourist traffic [Arienzo et al., 2017].

Historically, the GoP is dedicated to the farming of bivalve mollusks which are constantly subject to chemical and microbiological monitoring to protect the health of consumers. The monitoring plans detected high levels of polycyclic aromatic hydrocarbons (PAHs) in the mussels collected in the Lucrino area [Esposito et al., 2020].

PAHs are a large group of organic compounds comprised of two or more fused benzene rings arranged in various configurations. These compounds are widespread pollutants all over the world characterized by hydrophobicity, thermostability and highly persistent in the environment. PAHs have been determined to be highly toxic, mutagenic, carcinogenic, teratogenic, and immuno-toxic to various life forms.

The analysis on seasonality shows that PAH concentrations tend to be higher in specimens sampled in cold months (October–March), and this trend is statistically significant as reported in other studies [De Giovanni et al., 2022; Esposito et al., 2017].

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Figure 1 – Sampling station in the Gulf of Pozzuoli.

Literature studies suggest that contamination could be associated to the pyrolytic source of PAHs from the brownfield site of Bagnoli [Arienzo et al., 2017]. The area of Bagnoli located in the southern side of the GoP hosted important industrial plants (steel mills, cement factories, production of asbestos and fertilizers) until the end of the 20th century. These anthropogenic activities caused high levels of environmental pollutants and potentially hazardous chemicals, which affected the quality of marine ecosystems and, as a consequence, the human health. Toxic and potentially toxic metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are the main contaminants found out in the soil and along the shoreline area [Ausili et al., 2020].

This study presents a set of multidisciplinary activities carried out to investigate the levels and sources of contamination by PAHs in the area of Lucrino basing on data from different scientific fields and samples including sediments, biological data and sea surface currents. In particular, data on the presence of PAHs in marine sediments along the entire coast of the GoP from Bagnoli to Baia, including the low depth areas next to the shoreline, are used as shown in Figure 1.

Sea surface current pattern during specific periods is obtained through oceanographic datafrom the modeling system ROMS (Regional Ocean Model System).

The GoP is in the Northwest area of the Gulf of Naples (GoN). The latter, inlet of the TYS, has a superficial circulation which is partly influenced by the large-scale circulation of the TYS. The circulation of the GoN is dominated by the complex interaction between factors acting on different spatial and temporal scales. Two classes of forcers have been identified that act on the pelvis and influence its circulation: remote and local [Gravili et al., 2001]. The main remote forcing is represented by the southern Tyrrhenian Sea, whose circulation can guide the movement of the water mass inside the GoN [Gravili et al., 2001]. Among the local factors, the main factor that gives the surface circulation of the Gulf the greatest spatial and temporal dynamic variability is wind stress [Moretti et al., 1976-1977; de Maio, 1985; Menna et al., 2007]. By virtue of this differentiation, it is possible to identify different circulation pattern developing in the GoN, each representative of the combination of specific seasonal and dynamic conditions [Cianelli et al., 2011].

Materials and Methods

Specimens of *Mytilus galloprovincialis* were collected from sea farms located along the coastal area of the GoP (Fig.1) The samples were transferred to the laboratory of Istituto Zooprofilattico Sperimentale del Mezzogiorno. Mollusks were washed with ultrapure water to remove any sludge or adhering particles, and the soft tissue of the shells was excised with a plastic knife. The PAHs analysis was performed by using a method developed in accordance with the criteria performance fixed by Regulation EU 836/2011; the method involves the saponification of the sample followed by extraction, purification and analysis by HPLC-FLD. The method allowed the quantification of four PAHs required by European legislation: benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbFA), benzo[a]pyrene (BaP). PAH concentrations and sum of BaA, CRY, BaP and BbFA (PAH4) were expressed in μg kg^{-1} wet weight (ww). The limit of quantification (LOQ) of the method was 0.2 μg kg^{-1} for each PAH analysed.

The sediment samples were collected and analysed from the Agenzia Regionale Protezione Ambientale della Campania (ARPAC). Twenty sampling stations were identified along the GoP coastline, from Bagnoli (Naples) to Baia (Bacoli), where surface sediment samples were taken. Additionally, three stations in correspondence of higher depth and at larger distance from the coastline were selected in the framework of Legislative Decree 152/06. Depth, geographical coordinates and distance from the coast are reported in Table 1.

Table 1 – Sampling stations along the Gulf of Pozzuoli.

Code	LAT. Nord	LONG. Est	depth (m)	distance from the coast (m)
CRIPA 1	40.80294	14.17031	5	245
CRIPA 2	40.80715	14.16724	6	340
CRIPA 3	40.80959	14.16558	5	280
CRIPA 4	40.80800	14.16101	13	690
CRIPA 5	40.80647	14.15863	20	955
CRIPA 6	40.81110	14.16373	5	195
CRIPA 7	40.81375	14.16012	4	254
CRIPA 8	40.81631	14.15332	5	170
CRIPA 9	40.81689	14.14820	8	170
CRIPA 10	40.81919	14.13053	5	148
CRIPA 11	40.81901	14.12191	7	167
CRIPA 12	40.81949	14.12158	5	155
CRIPA 13	40.81979	14.12167	3	188
CRIPA 14	40.82022	14.12107	3	230
CRIPA 15	40.82782	14.09512	3	370
CRIPA 16	40.82816	14.08759	5	229
IT15-LC036	40.80032	14.10533	70	3600
IT15-PZ	40.80907	14.12087	40	1200
IT15-BG039	40.80417	14.15083	55	1500

The extraction of PAHs from sediment samples was carried out with cyclohexane/acetone solution in ultrasonic bath. The organic solvent was removed by means a rotary evaporator and the dry residue was redissolved in n-hexane and injected in a GC-MS system. All samples were analyzed for the 16 US EPA priority PAHs.

To study the variability of surface currents, output of Regional Ocean Modeling System (ROMS) implemented by the marine and meteorological forecasting and observation center of the Dipartimento di Scienze e Tecnologie of the Università degli Studi di Napoli Parthenope, was used.

ROMS is a free surface hydrostatic model, widely used by the scientific community for a set of applications for the observation of surface sea currents, cryosphere dynamics, sediment transport, tidal cycles, biogeochemical cycles, and dispersion of pollutants. ROMS uses vertical terrain-following coordinates (they allow greater resolution in areas of main interest such as, for example, the thermocline or the friction layer on the bottom) and orthogonal curvilinear horizontally on a staggered Arakawa C calculation grid. Thanks to this characteristic, it was possible to increase the vertical resolution of the model in special interest areas as the layer depth where the mussel farms are located (between 5- and 25-meters depth). The ROMS circulation model presents a single computation domain with a spatial resolution of about 160 m and for 11 depth levels (from 0 to 10). In this study, only surface variables have been used

Results and Discussion

The results of the monitoring PAHs in mussels collected in the GoP, show a very different situation for the sampling stations.

In the Monte di Procida and Lake Fusaro plants, the concentrations of Benzo[a]pyrene (BaP) and other PAHs were almost always lower or slightly higher than the quantification limit, regardless of the withdrawal season. The area near the Island of Nisida may also be considered at low risk, since no non-compliant value was found and concentrations were generally low. On the contrary the areas of Punta Terone and Punta Pennata at the north end of the Gulf, showed appreciable concentrations of PAHs without exceeding the maximum limit (ML), except for three samples. It should be noted that these cases always occurred in the winter season (years 2016, 2019, 2020). Moving towards the center of the GoP, in the area of Lucrino, the concentrations of PAHs in mussels were significantly higher than those measured in the other sites. In particular, during the winter season, the levels of Bap and PAH4 exceeded the ML in 17 samples out of 100 and the average concentrations of Bap and PAH4 were 3.1 and 14.0 μg/kg, respectively.

The seasonal variability in the PAHs concentration in mussels has been previously related to the seasonal variability of the circulation in the Gulf of Naples [Perugini et al., 2007]. In particular, it has been suggested that the presence of a northward current outside the Gulf of Naples might favour the increase in PAH levels in mussels through remobilization, suspension and transport of contaminated sediments.

Previous studies on sediment samples in the GoP show that the concentrations of Σ16PAHs in all sediment samples from the Bagnoli brownfield site were above the limit values [Albanese et al., 2017]. In our study, the percentage distribution of PAHs in the GoP shows large variability according to the different sub-areas or stations. Figure 2 and 3 show the percentage of each congener in relation to the total PAHs, and for each station, percentages are show along concentric rings. Then, each ring represents the PAHs of a station, and the arc of each PAH is proportional to its percentage. This representation allows to define a pattern characteristic of the type of contamination of each station.

The results of sediment analysis demonstrate that the first eight stations (CRIPA stations from 1 to 8) located in the Bagnoli area have the same pattern of contamination (Fig. 2). On the other hand, CRPA stations from 10 to 14, located around the northern part of GoP and around the town of Pozzuoli, are characterized by different PAH percentages and distribution (Fig. 3).

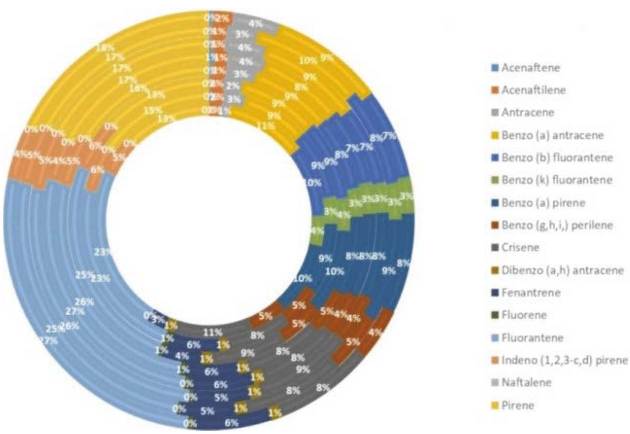

Figure 2 – Ring chart of the percentage distribution of PAHs in stations from CRIPA1 (innermost ring) to CRIPA8 (outermost ring).

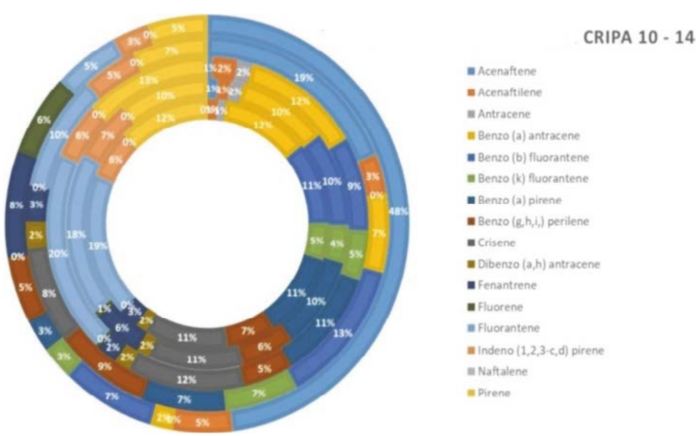

Figure 3 – Ring chart of the percentage distribution of PAHs in stations from CRIPA10 (innermost ring) to CRIPA14 (outermost ring).

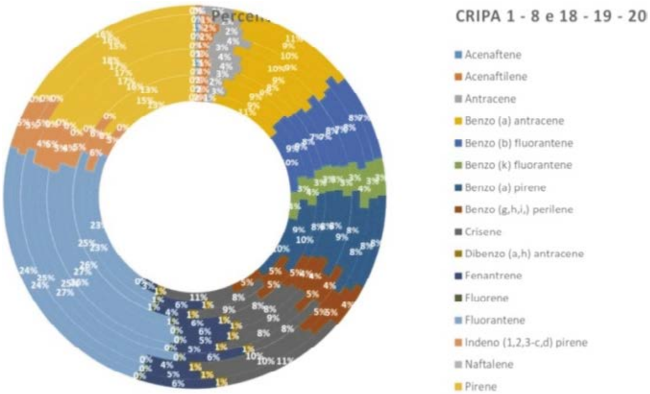

Figure 4 – Comparison ring chart between CRIPA 1-8 (innermost ring) and CRIPA 18-20 (outermost ring) stations.

Finally, the results, in terms of percentages of individual PAHs from sampling stations next to mussel farms in Lucrino area of GoP (CRIPA 18-19-20) show almost the same PAHs distribution of Bagnoli stations (Fig.4).

These similarities seem to suggest a common source of contamination between the sediments from the Bagnoli area and those collected close to the mussel farms.

To investigate the possible effect of marine currents on the transport of PAHs from the Bagnoli area to the Lucrino Mussels farms, the output of the ROMS have been analyzed for a limited number of events from 2018 to 2021. Figure 5 shows the surface current pattern that was modelled for three days before the biological sampling of 14th January 2021, when the concentration of PHAs (BaP:16,5 μg/kg; Σ16PAHs: 71,8 μg/kg) in the biological samples of Lucrino exceeded the law limits.

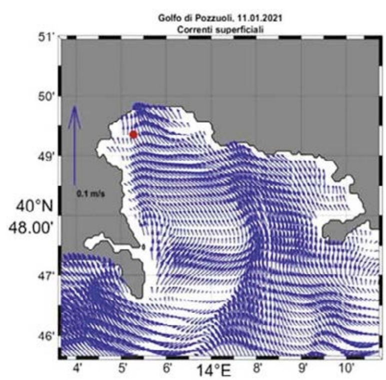

Figure 5 – Surface currents map 3 days before the exceeding event on 14th January 2021. The red dot indicates the position of the mussel farms, in the Lucrino area, where the samples were taken by the ASL.

The same scheme (Fig. 6) has been adopted when the concentration of PHAs in three mussel samples of Lucrino (BaP= 12.6- 14.2- 33.4 μg/kg; Σ4PAHs= 42.1- 49.3- 99.2 μg/kg) exceeded the law limits. The time step of three days was defined on the basis of the dimension of the GoP (average depth of about 60 m, maximum depth of 110 m, surface of 33 km^2) and of the mean surface currents (about 6 cm/s) modelled on hourly basis from 2019 to 2021.

To highlight the difference in the pattern of currents between events of exceeding the legal limits and events of not exceeding the legal limits, the map of the surface currents was made 3 days before a sampling in which no values of BaP above the LOQ were recorded. Figure 7 shows the map of the currents three days before 27th July 2021 when the concentration of PAHs in mussels was low (BaP= <0.2 μg/kg; Σ4PAHs= 2.7 μg/kg).

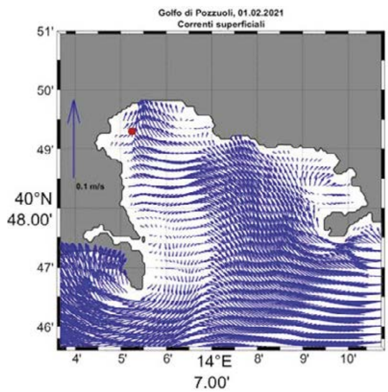

Figure 6 – Surface currents map 3 days before the event of exceeding legal limits on 04th February 2021. The red dot indicates the position of the mussel farms, in the Lucrino area, where the samples were taken by the ASL.

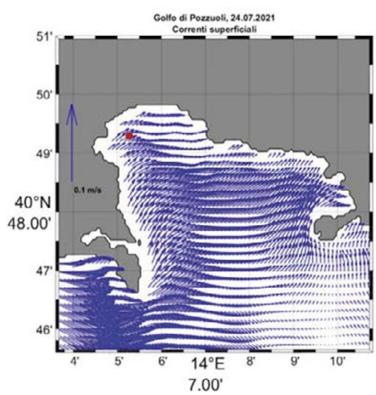

Figure 7 – Surface currents map 3 days before the event of not exceeding legal limits on 27th July 2021. The red dot indicates the position of the mussel farms, in the Lucrino area, where the samples were taken by the ASL.

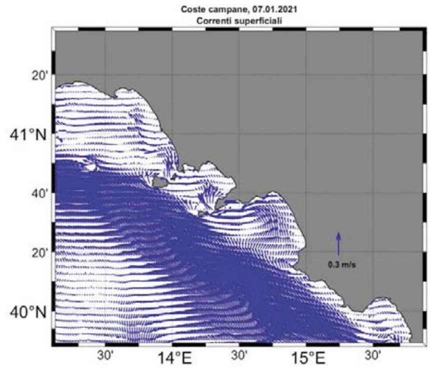

Figure 8 – Map of the Campania coasts with surface currents 7 days before the event of exceeding the legal limits of 14th January 2021.

As the surface circulation of the Gulf of Naples is influenced by the Tyrrhenian offshore currents, maps of the surface currents of the Campania coasts have been made for the same events. Sea surface currents during the winter period, when the concentration of PAHs in mussels is higher, are mainly directed from Bagnoli area to Lucrino mussel farm in the coastal area of the GoP. While the open sea area (i.e. the external limit of the GoP) is mainly influenced by a northward current [Iacono et al., 2013] of the area of the Tyrrhenian Sea focused on the Campania Coasts (Fig. 8).

During 27th July 2021 the sea surface currents in the Gop there are no direct currents from East to West, as for events in which the concentration of PAHs exceeded the law limits, but direct currents from West to East. This condition contributes to the non-accumulation of contaminants in the area where the mussel farms are located. In the same period the circulation of the Tyrrhenian Sea is characterized by a coastal current towards the south and outgoing from the Gulf of Naples (Fig. 9).

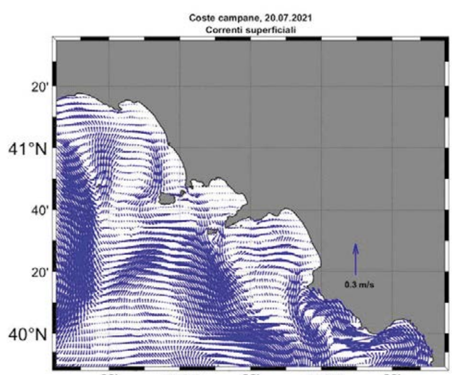

Figure 9 – Map of the Campania coasts with surface currents 7 days before the event of not exceeding the legal limits of 27th July 2021.

Accordingly, we suggest that during winter, when the East-West circulation pattern is more often verified, the contamination of mussels is favoured by the possible transport of PAHs from the Bagnoli area toward the Lucrino mussel farms. This is in agreement with previous studies, showing that the main remote forcing is represented by the southern Tyrrhenian Sea, whose circulation shows a large seasonal variability [Aulicino et al., 2016; Iacono et al., 2021] and that can guide the movement of the water mass inside the GoN [Gravili et al., 2001]. Here, when the dynamics of the surface currents depends on the offshore Tyrrhenian currents, two different scenarios can be outlined the Tyrrhenian current is directed towards the Northwest or towards the Southeast. In the first case an intense flow almost parallel to the Bocca Grande which enters the GoN from the Bocca Piccola and moves towards the island of Ischia. At the basin scale, when the current enters the GoN it creates a cyclonic structure while in the Gulf of Castellammare an anticyclonic structure is formed [Castagno et al., 2020, Aulicino et al., 2016].

According to the studies by de Ruggiero et al., 2020, in winter and autumn the main remote forcing is the offshore Tyrrhenian current directed towards the north-west. If the Tyrrhenian current moves south-east, the external part of the GoN has a cyclonic structure, while the Gulf of Naples and the Gulf of Castellammare have anticyclonic structures.

Conclusion

This study confirms the use of bivalve molluscs as good bioindicators to assess levels and trends of seawater contamination, due to their filter-feeding behaviour and sedentary life, that lead to the accumulation of pollutants in their tissues.

The results of sediment analysis seem to confirm the hypothesis that the contamination of molluscs raised in the Lucrino area of the GoP could be attributed to contaminated sediments of the Bagnoli area. Moreover, the seasonality of the phenomenon may be related to the recurrence of specific surface current patterns that could transport pollutants from the source area (Bagnoli) toward the mussel farms area of Lucrino.

Further efforts are necessary to confirm our hypothesis. In particular this study highlights the need for in situ current data along the water column, in order to test the model performances as well as the need for a higher frequency of the biological sampling.

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