Microbial processes and organic priority substances in marine coastal sediments (Adriatic Sea, Italy)

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Introduction

The western Adriatic margin receives large inputs of organic matter from both terrestrial and marine sources and potentially sequesters a significant fraction of organic carbon in his seabed. Recently, based on elemental and isotopic data, Boldrin et al. (2005) and Miserocchi et al. (2007) identified the estuarine-derived organic matter as a further important source.

Sediments are an important compartment of the aquatic environment acting as sink or source of organic matter, nutrients and pollutants. Sediments are not currently monitored for the definition of the environmental quality standard and no organic pollutants thresholds are given by EC for the quality definition . Conversely Environmental Quality Standards (EQS) are given by the Directive 2008/105/EC for surface waters, on the base of a list of 33 organic priority substances.

Benthic microbial communities are posed at the base of the heterotrophic chain and play an important role in driving the biological processes including the biodegradation. However in the current version of the MSFD (2008/56/EC) the microbial component is neglected.

Scarce are the information on the organic pollutants in the sediments of the Adriatic Sea, with the exception of the North-West area (e.g . Perugini et al. 2007), as well as scarce are the information on the microbial processes (e.g. Danovaro et al. 2001). Moreover to define the "good environmental status" the MSFD takes into account several descriptors including the "sea-floor integrity" (n. 6) and "contaminants" (n. 8) whereas the benthic communities are at the moment neglected.

In the frame of the PERSEUS Project (subtask 1.3.3 ADREX: Adriatic and Ionian Seas Experiment), two cruises were conducted in the Adriatic Sea (Italy) in order to verify the occurrence patterns of selected classes of organic priority substances (WFD, 2008/105/EC) in sediments together with the structural and functional parameters of the native bacterial communities. Then, three classes of organic pollutants of environmental concern were selected: 15 congeners of Polycyclic Aromatic Hydrocarbons (PAHs), Nonylphenols (4-NP and two ethoxylates NPEO1, NPEO2), Bisphenol A (BPA). The sampling areas are of interest for the project and sited in a gradient of anthropogenic pressure (Fig.1).

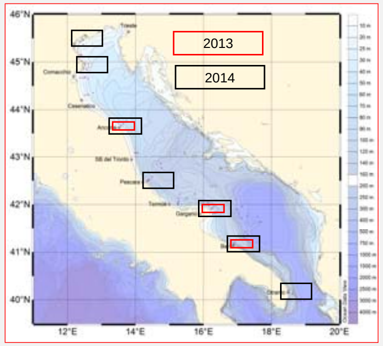


Fig.1

Materials and Methods

Sediment samples were collected in several coastal areas impacted by a gradient of anthropogenic pressure . The samplings were performed on board of R/V Dallaporta (CNR) (Nov-2013) and R/V Explora (OGS) (Oct-2014) (Fig.1). The data are relative to surface sediments, collected by a box corer, and cores collected in selected sites by a corer SW104. In this investigation were collected a total of 80 sediment samples of which 68 superficial and 12 cores. Polycyclic aromatic hydrocarbons (PAHs), Nonylphenol (4-NP, NPEO1, NPEO2) and Bisphenol A (BPA), were extracted by ultrasonic bath with the appropriate solvent, followed by analytical determination with LC-MS and HPLC UV-fluorescence (Patrolecco et al., 2010). The bacterial cell abundance was determined by epifluorescence microscopy (DAPI) and the rate of bacterial carbon production (BCP) was determined by measuring the ^{3}H-leucine uptake rate as described in Amalfitano et al. (2008). The community respiration rate (CR) was estimated by the measurement of the electron transport system activity (ETS, Houri-Davignon et al., 1989, Romanì et al., 1998). All data were normalized according to the sediment dry weight. Some of the analyses of the last cruise (Octb-14) are still running.

PAHs in surface sediments

The highest mean concentrations of ∑PAHs (as sum of 15 congeners) were observed in the coastal area sited in front of the lagoon of Venice (831 ng ∑PAHs/g) (Fig.2). A decreasing trend in PAHs concentration was observed southward, up to reach the lowest mean concentration in the sites posed in front of Otranto (23 ng ∑PAHs/g). These contamination levels are considered in the literature as moderate (<1000 ng g-1, Baumard et al., 1998) when compared to highly urbanized coastal areas in the Mediterranean Sea Gómez-Gutiérrez et al., 2007). .

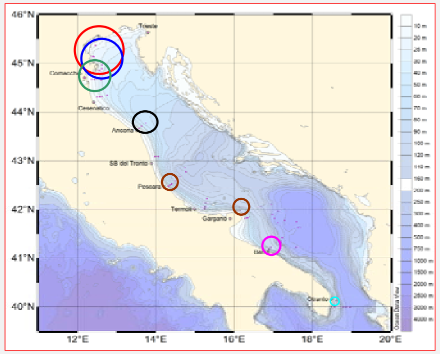


Fig. 2

sampling area	∑PAHs mean conc.(ng/g)
Venice	831±300
Adige Rver mouth	522±286
Po River mouth	356±98
Ancona	134±90
Pescara -Gargano	87±14
Bari	102±61
Otranto	23±7

PAHs in sediment cores

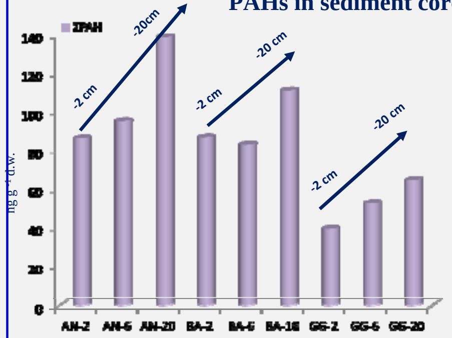


Fig. 3

The depositional setting varies between the study areas. The sediment cores represent the environmental images of 60-150 years and are a suitable tool to analyse the trend in the levels of contamination throughout the time. The concentrations of PAHs were in the same order as those of box cores. The increase of contamination between the layers -2/-20 cm was observed in all the sites.

PAHs, Nonilphenols (4-NP, NPEO1, NPEO2) and Biphenol A in surface sediments

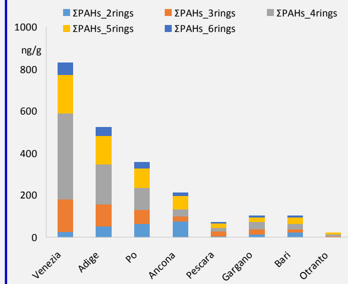


Fig. 4

The 15 congeners of PAHs quantified were divided according to the number of aromatic rings in the molecule. The contribution of the congeners with four, five and six rings (pyrolytic) accounted for 53-80% of the total PAH concentration, while the contribution of the two, three rings (petrogenic) accounted for only 21-46%.

Overall the composition of PAHs suggested a pyrolytic source in the study area althought specific sites (Po, Ancona and Bari) showed a shift versus the petrogenic input due probably to the intensive maritime activities. Moreover the relationship between fluoranthene and pyrene concentrations (r= 0.98, p<0.01) indicated that PAHs in the Adriatic Sea had presumably undergone similar environmental processes independent of the sampling sites.

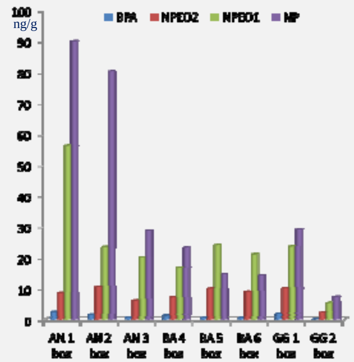


Fig. 5

The concentrations of 4-Nonilphenol (NP), NP-ethossylates (NPEO1, NPEO2) and Bisphenol A (BPA), in the Ancona (AN), Bari (BA) and Gargano (GG) sediments, from cost to offshore, were in the range of values reported in the literature and lower than those reported for the Venice lagoon (Pojana et al. 2007). In this set of data we observed a gradient in the NP concentrations from Ancona (90 ng/g) to Gargano (7 ng/g). The NP/NPEO1 ratio was >1 in all the sites except in the Bari sediments, where NPEO1 appears to be the most abundant compound and the ratio value dropped to 0.6. Overall, NP/NPEO1 ratio is low near the sewage treatment plant, where NPEO1 results the prevalent compound, and tends to increase moving away from the effluents, probably due to the occurrence of ethoxylic chain degradation.

Microbial processes and pollutant concentrations

Fig. 6

Changes in the concentration of ∑PAHs in the surface sediments were positively related to changes in the microbial community respiration rates (R^2=0.69, p<0.05), when eliminating the most polluted sediments from the northern area (Venice, Adige and Po river mouth). No significant trend was observed between respiration rates (CR) vs cell abundance and bacterial C production (BCP) (p> 0.05). The relationship between the bacterial growth efficiency (BGE=BCP/CR+BCP) and PAHs, highlights a reduction of the efficiency by which microbes use the substrate with the increasing pollution.

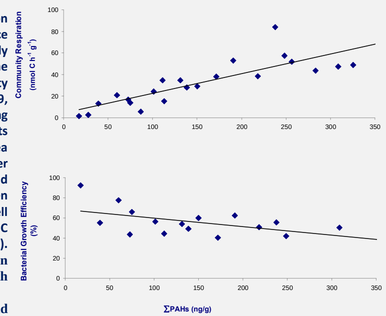
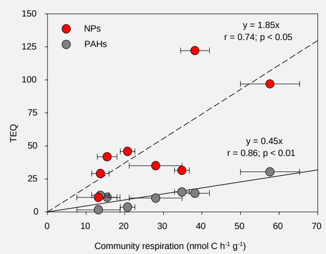


Fig. 7

The potential toxicity of sediment was evaluated using the total Toxic Equivalent (TEQ) approach for PAH and NP mixtures (USEPA, 1993). We observed a positive and significant correlation with the community respiration rates and the potential toxicity of the sediments.



Preliminary conclusions These preliminary results help us to shed light on aspects poorly studied on the effect of pollution on a component of the benthic microbial community. The adverse effects of pollution seems to undermine the basis of the food chain of marine ecosystems by shifting the microbial metabolism toward the catabolic processes (loss of energy by the CO_2 emission). This trend may result in a reduction of productivity for organisms places at higher levels of the trophic chain with consequences on the entire ecosystem. In the context of the MSFD this result should draw greater attention to the importance to study sediments in their chemical and microbial characteristics for a better definition of GES. By combining the chemical and biological information we can meet the criteria defined in the MS in the frame of the descriptor 6: Sea-floor integrity and descriptor 8: Contaminants.