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Biogeochemical cycle of Hg and heavy metals in the highly contaminated Augusta Bay (Sicily, southern Italy)

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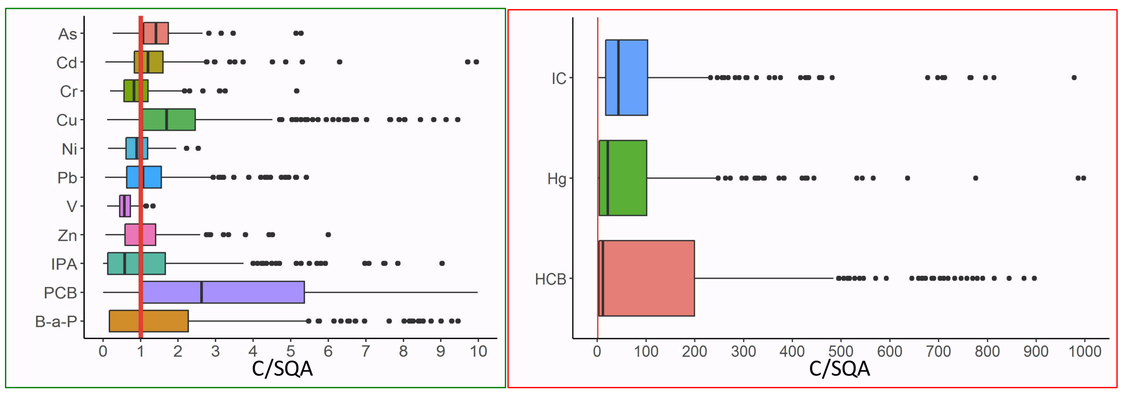
Introduction Augusta Bay is one of the three highly contaminated areas on the Italian cost selected as natural laboratory within the CISAS project. Comprehensive investigation of biogeochemical dynamics of traditional and emerging contaminants has been carried out in all the environmental matrices (air, seawater, soils, sediments and food) to verify sources, pathways and fate in the studied system and transfer mechanisms to the ecosystem and humans. This work a short presentation of the scientific approach followed to investigate on heavy metals (with a particular focus on Hg) in the marine environment of Augusta Bay offers the methodological view adpted in the other study areas of CISAS and, specifically, an ensemble of new results about the biogeochemical cycles of contaminants in coastal marine system in order to identify possible transfer mechanisms from environment to human.

Study area Augusta Bay is a semi-enclosed marine area (extended ~23.5 km^2 and averagely deep 15 m) located on the eastern Sicilian coast (Ionian Sea, Italy). It is delimited by artificial dams and with two main restricted inlets allow the connection with the open sea. Outside the bay, a very narrow shelf develops until 110-130 m depth, with an average slope value of ~3° which abruptly terminates with a steep slope characterized by a dense net of canyons dropping to the deep end of the Ionian basin.

The bay hosts one of the most important harbours of the Mediterranean Sea and a one of the largest petrochemical hub in Europe, where oil refineries and petrochemical industries were active, since 1950s. In particular, from 1958 to 2005, a chlor-alkali plant, using mercury cells, operated in the area, and discharged sewages without pre-treatment, until late 1970s.

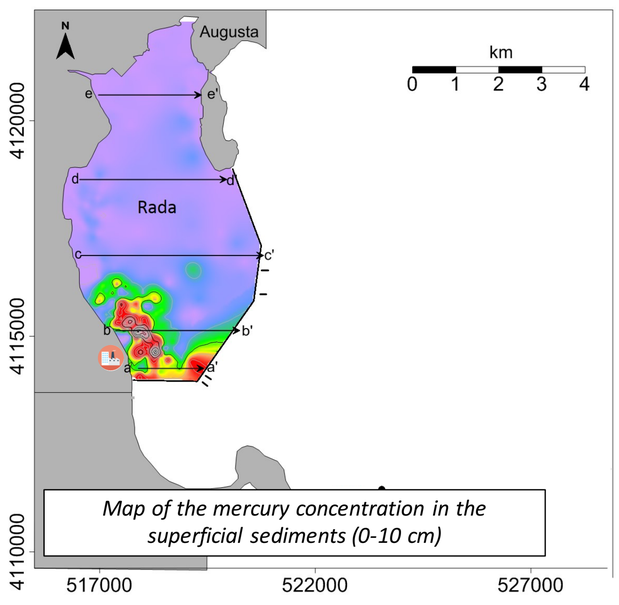
Sediment pollution Uncontrolled discharges from the industries led to significant contamination in the bottom sediments. Owing to this state, Augusta Bay is included in the National Remediation Plan by the Italian Environmental Ministry (Law 426/98, Ministerial Decree 10.01.2000).

Concentrations of heavy metals and organic contaminants measured in the sediments (C) resulted from 2 to 10^3 higher than threshold values (SQA) require by Italian Legislation (Decree Law 172/2015). Particularly, mercury (Hg), hexachlorobenzene (HBC) and hydrocarbons (IC>12) were from 1 to 3 order of magnitude higher than above law limits.

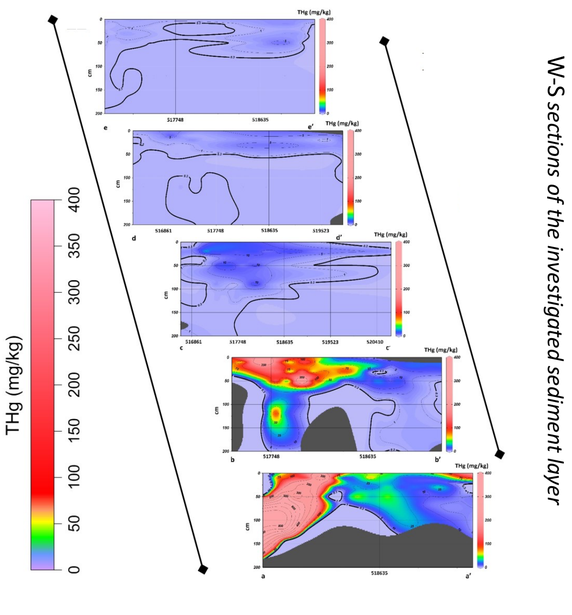


Despite the de-mercurization plant came into use since late 1970s - early 1980s, the superficial sediments (0-10 cm) result to be still heavily contaminated, after about 40 years. High mercury concentrations, up to 3 orders of magnitude higher than threshold value reported as sediment quality guidelines (0.3 mg kg^{-1}; Legislation Decree 172/2015), were recorded in the upper part of the cores collected from the south-western area, showing as Hg pollution in Augusta Bay continues to be a relevant environmental threat.

On the base of statistical interpolation of Hg data relative to the analyses of 350 cores sampled in 2005 (ICRAM, 2008) and 2017 (this study), a polluted sediment volume of about 700.000 m^3 was estimated. In the south-western area of the bay the highest Hg concentrations were found and the entire investigated sediment layer (0-200 cm) resulted to be contaminated.



Map of the mercury concentration in the superficial sediments (0-10 cm)

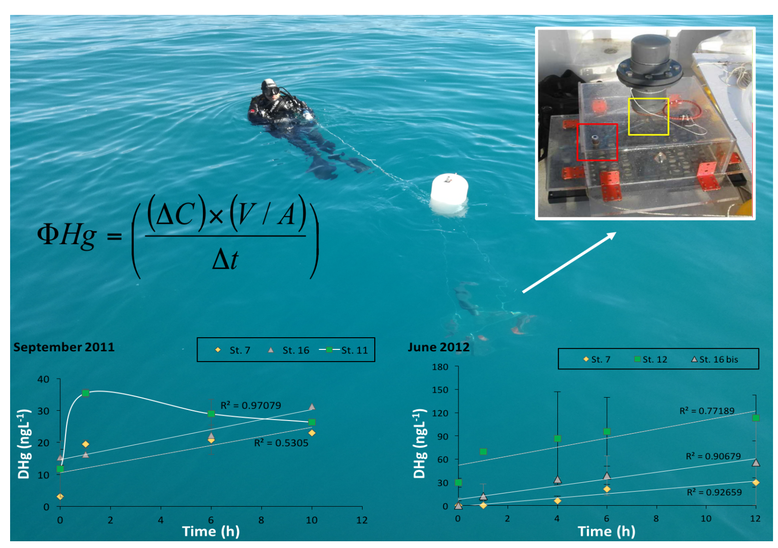


W-S sections of the investigated sediment layer

Chemical speciation analysis, carried out on the cores sampled between 2016-2017, showed that about 1% of total Hg in the superficial sediments is in methylated form (methylmercury, MeHg). It is the most toxic and bioavailable (about sex times more than inorganic mercury) chemical species of the Hg, particularly dangerous for the human health because characterized by a high biomagnification rate through the aquatic food web. Comparison with other polluted areas testifies a significant level of MeHg in the Augusta Bay sediments.

Mercury polluted area	MeHg (µg kg^{-1})	Reference
Bay of Augusta	0.30 - 59.7	This study
Bay of Castela *(Adriatic Sea)*	6.10 - 36.7	Kwokal et al. (2002)
Gulf of Trieste *(Adriatic Sea)*	0.20 - 60.1	Covelli et al. (2001)
Gulf of Taranto *(Ionian Sea)*	1.00 - 40.0	Spada et al. (2012)

Releasing processes at sediment-seawater interface Mercury fluxes at the sediment-seawater interface were investigated using an in-situ benthic chamber. The calculated fluxes were extended to a yearly estimation and then over the entire area using the territorial distribution model proposed by Aurenhammer (1991) (Voronoi Polygons method). Estimated value of 1.3 kmol y^{-1} clearly emphasizes the role of the sediments as source of the metal for the overlying water.

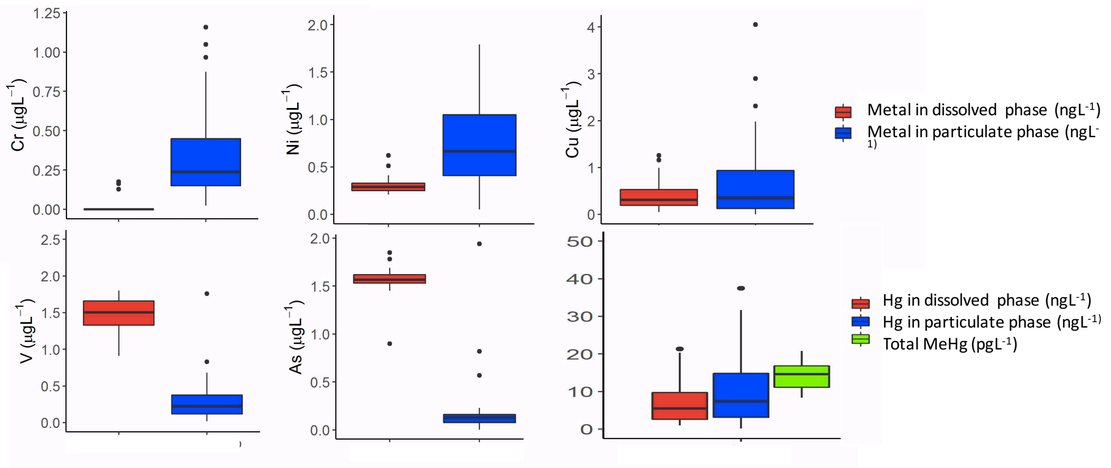


Heavy metals and MeHg in the seawater In the period 2018-2019, Augusta Bay seawater was seasonally collected at different quote from 20 stations. Concentrations of As, Cu, Cd, Cr, Hg, MeHg, Ni, Pb and V were measured in the samples, in both dissolved and particulate phases. Metals concentrations found in dissolved phase were lower than threshold values (SQA) indicated by the Legislation Decree, 172/2015, although it is important to highlight that both Hg and Ni showed concentrations significantly higher than relative background values. The total (dissolved+particulate) MeHg concentrations resulted quite comparable with values reported for the Mediterranean Sea.

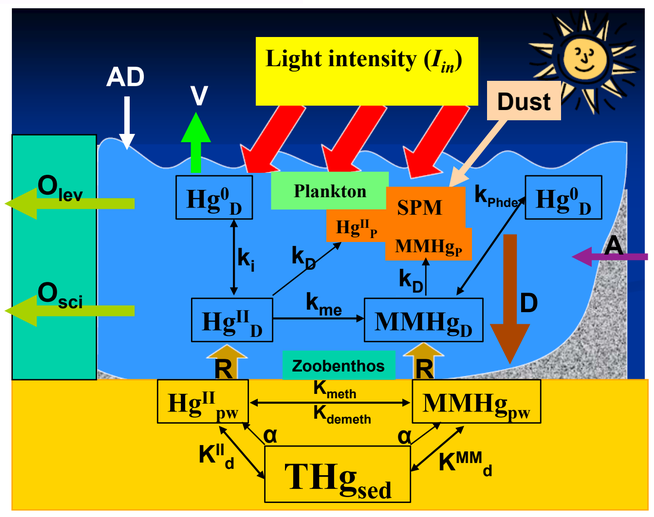
	As	Cu	Ni	V	Cr	Cd	Pb	Hg	MeHg
	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	ng L^{-1}	pg L^{-1}
mim-Max	0.9-1.9	0.05-1.3	0.2-0.6	0.9-3.4	<0.1	<0.02	<0.1	1-21	0.1- 21
Median	1.6	0.30	0.30	1.7	<0.1	<0.02	<0.1	6.0	12.0
SQA	**5**		**8.6**		**4**	**0.2**	**1.3**	**70**	
Mediterranean Sea			0.09-0.13	1.6**				0.1-0.8*	<20*

*Cossa and Coquery, 2005; Covelli et al., 2009; Horvat et al., 1999, 2003; Tessier et. al., 2004; Faganeli et al., 2003
** Morley, 1997; Sherrel and Boyle, 1988,

V and As showed higher affinity for the dissolved phase, conversely, Cr and Ni were more associated to the suspended particulate matter, while Cu and Hg resulted more homogeneously distributed between the two phases. On the basis of the partition in seawater, different pathways of transfer of the metals from water to biota may be assumed. Specifically, As, V, Cu, Hg, being in dissolved phase (as ions or organic/inorganic complexes), would be potentially more bioavaible than Cr and Ni, and easily uptake into organisms at the base of the pelagic food web. The check of this hypothesis is of crucial importance to understand the transfer of metals from the aquatic environment to human, also at the light of recent studies (e.g. Wu et al., 2019) showing that bioconcentration of Hg at the base of the pelagic web food (e.g., small algae and bacteria) is a significant predictor of Hg in fish.



A biogeochemical dynamic model to explore the Hg biogeochemical cycle in Augusta Bay The biogeochemical dynamics of Hg, and specifically of its three species Hg^0, Hg^{II} and MeHg, in the marine coastal area of Augusta Bay has been explored by an advection-diffusion-reaction model for mercury in the seawater compartment coupled with i) a diffusion-reaction model for mercury in the pore water of sediments and ii) a sorption/de-sorption model for mercury in the sediments. The model parameters were calibrated considering multiple field observations and experimental data (Oliveri et al., 2016; Salvagio Manta et., 2016; Sprovieri et al., 2011, this study). Specifically, the spatio-temporal variability of the Hg chemical species in seawater and superficial sediments and the Hg fluxes at the boundaries of the 3D model domain were reproduced, showing an excellent agreement with the experimental data. The mass-balance of the different Hg species in seawater has been calculated for the Augusta Bay improving the previous estimation. Also, a recycling of Hg inside the bay corresponding to about 70% of the whole budget has been calculated, highlighting a crucial role of internal processes in the dynamics of this element and a specific threat for the fish compartments in terms of biomagnification effect through the food web.



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