Corso di Dottorato di Ricerca in Scienze della Vita e dell'Ambiente, Ciclo XXXVII

Biogeochemycal cycling of contaminants in marine waters

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Introduction

From the 20th century, the increment and intensification of the industrial activities resulted to an alteration of the matter balances in many biogeochemical cycles due to the emission in the environment, distant from the natural emission sources, of pollutants in the form of products, sub-products of production processes (i.e. industries) or anthropic activities (i.e. marine traffic), waste disposal or bad waste management.

This disequilibrium in geochemical processes has resulted in an increase in the concentration of elements (such as metals) in various environmental receiving matrices. In recent years, research has intensified to collect data and understand the problem better. The relevance of this issue grows, especially concerning Potentially Toxic Elements (PTEs), a class of persistent inorganic pollutants that include both metals and metalloids. These elements can bioaccumulate in the tissues of organisms and, in some cases (such as mercury), biomagnify along the trophic chain. Lead (Pb), cadmium (Cd), and mercury (Hg) are classified as priority pollutants according to the Water Framework Directive due to their ability to cause toxicity in receiving organisms even at very low environmental concentrations.

PTEs can be used as tracers of different emission sources. For instance, besides the well-known Na, Mg, K, and Ca as markers of primary marine aerosol sources, elements like Al and Fe can serve as valuable indicators of crustal inputs. Moreover, metals such as As, Pb, Cd, Cr, and Ni are tracers of anthropogenic pollution[1]. The study aims to evaluate (1) the characterization of PTEs in seawater and surface sediments; (2) the possible influence of atmospheric pollution on the marine biogeochemical cycle of PTEs; (3) the partitioning and interaction between different matrices; and (4) the seasonal evolution of pollutant contents in various matrices.

Materials and Methods

Study area & sampling

Seawater and Sediments

Three sites along the coast of Ancona. Sampling frequency: monthly.

Sites	Anthropogenic pressures
Palombina (Pal), depth 0.5m	Oil Refinery, tourism, untreated sewage discharges
Marina Dorica (MD), depth 4m	Port area, maritime traffic
Portonovo (PN)*, depth 14m	Maritime traffic

*surface and bottom; Conero regional park

Atmospheric depositions:

sampling once a month.

Port area of Ancona, CNR rooftop.

Sample treatment & analysis

Seawater

0.45-µm MCE vacuum filtration

- *Dissolved fraction*
  - Colorimetry → Nutrients: PO_4^{3-}, NO_2^-, NO^{3-}, NH_4^+, $Si(OH)_4$
  - Acidification (2%-10% HCl 34% UpA) → AFS - Atomic Fluorescence Spectroscopy → As, Cd, Hg
- *Particulate fraction*
  - Differential mass weighing → Acid microwave digestion ($5HNO_3$:$1H_2O_2$:1HF) → Atomic Absorption Spectroscopy → PTEs (Al, Fe, Mn, Cd, As, Hg, Pb, Ni, V, Co, Cu, Cr, Se)

Ancillary measurements: Depth, S, T, pH, Fluo, turbidity, DO

Surface sediments

Lyophilization and homogenization

- Direct Mercury Analyser → Total Hg
- Acid microwave digestion ($3HNO_3$:1HCl:1HF) → Atomic Absorption Spectrometry → PTEs (Al, Fe, Mn, Cd, As, Hg, Pb, Ni, V, Co, Cu, Cr, Se)
- Loss on Ignition → Organic Matter %

Atmospheric Depositions

0.45-µm MCE vacuum filtration

- *Soluble fraction*
  - Acidification (2%-10% HCl 34% UpA) → AFS - Atomic Fluorescence Spectroscopy → As, Cd, Hg
- *Insoluble fraction*
  - Differential mass weighing → Acid microwave digestion ($5HNO_3$:$1H_2O_2$:1HF) → Atomic Absorption Spectrometry → PTEs (Al, Fe, Mn, Cd, As, Hg, Pb, Ni, V, Co, Cu, Cr, Se)

Ancillary measurements: pH, rain (mm), P (mbar), T, wind speed & direction, RH

Results & Discussion

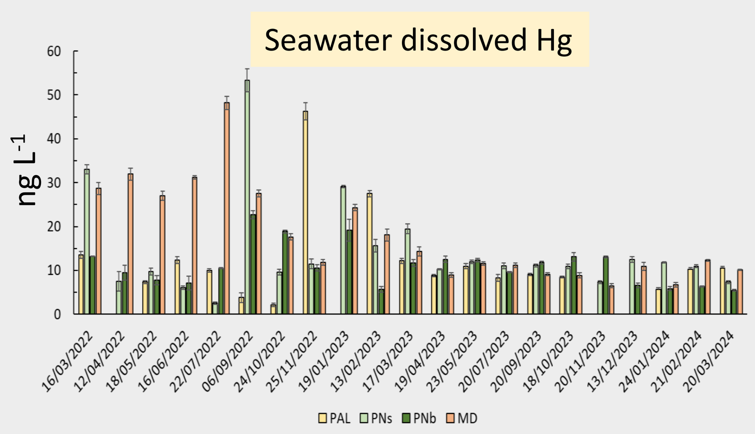
Previously on my PhD:

- 1° year: Methodology validation, bibliographic research, sampling & first results.
- 2° year: Samplings, environmental analysis, first chemometrical setup, intradepartmental collaborations

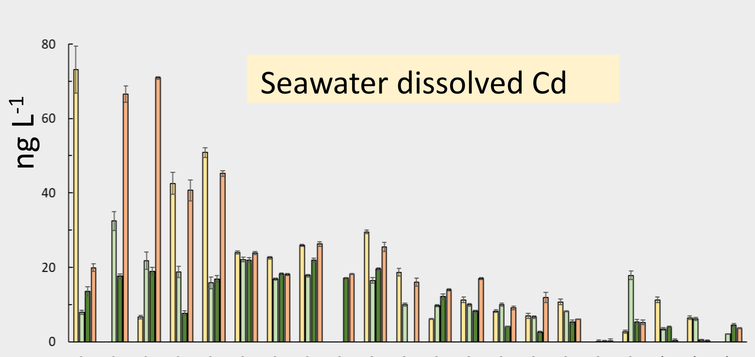
Seawater

Two-year seasonal trends evaluations. Example on dissolved relevant toxic metals

Seawater dissolved Hg

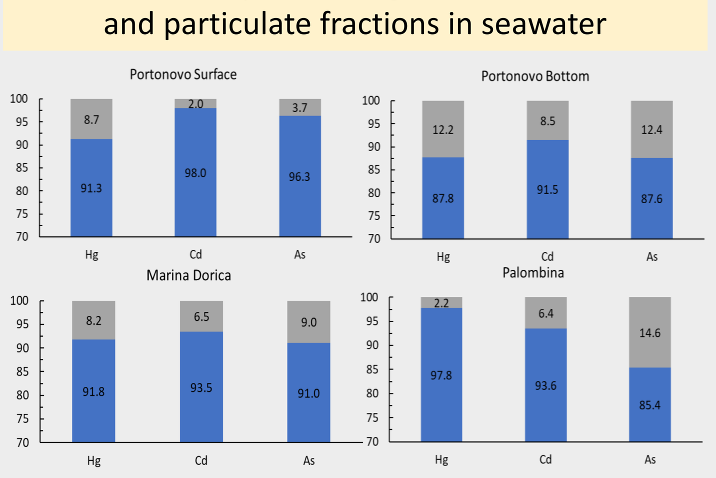


Seawater dissolved Cd



- Both dissolved Hg and Cd levels decreased since about April 2023.
- In the first year, MD showed the highest concentrations of both Cd and Hg.
- No particular differences between Portonovo surface and bottom.

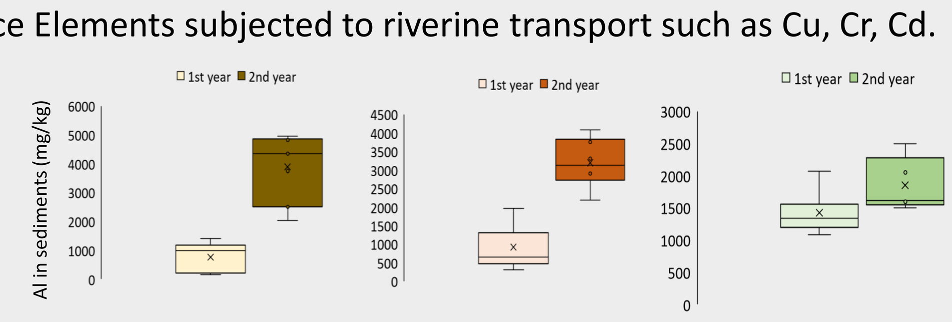
Contaminants partitioning between dissolved and particulate fractions in seawater



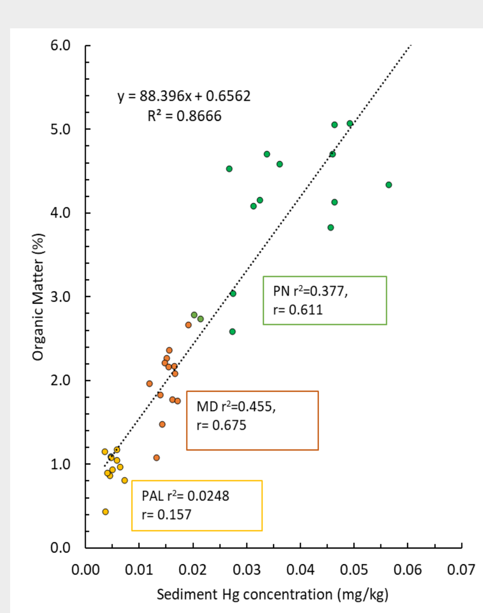
Dissolved fraction is always the predominant one for each ultra-trace element. The lowest particulate contribution was found in PNs site, where resuspension phenomena gain less impact, differently from PAL and MD. In particular, As particulate increase with the bottom proximity.

Surface sediment concentrations

Sediment concentrations varied significantly between the first and the second year. The same pattern showed for Al in the following boxplot was confirmed in other Trace Elements subjected to riverine transport such as Cu, Cr, Cd.



The difference between the years is primarily attributed to the first year being predominantly dry, while the second year was characterized by significant flood events.



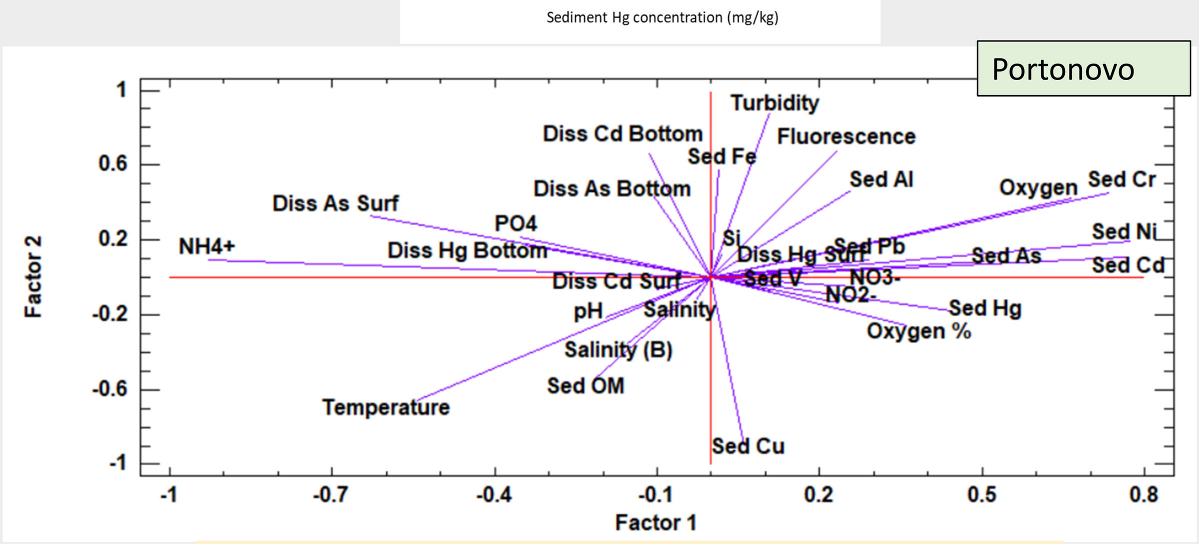
Mercury adsorption on sediment's Organic Matter

Sediment Hg concentration increases with the increment on OM content due to adsorption phenomena.

This correlation is found between the different sites and also in MD and PN. However, it was not observed at the PAL site, probably due to the low OM% content.

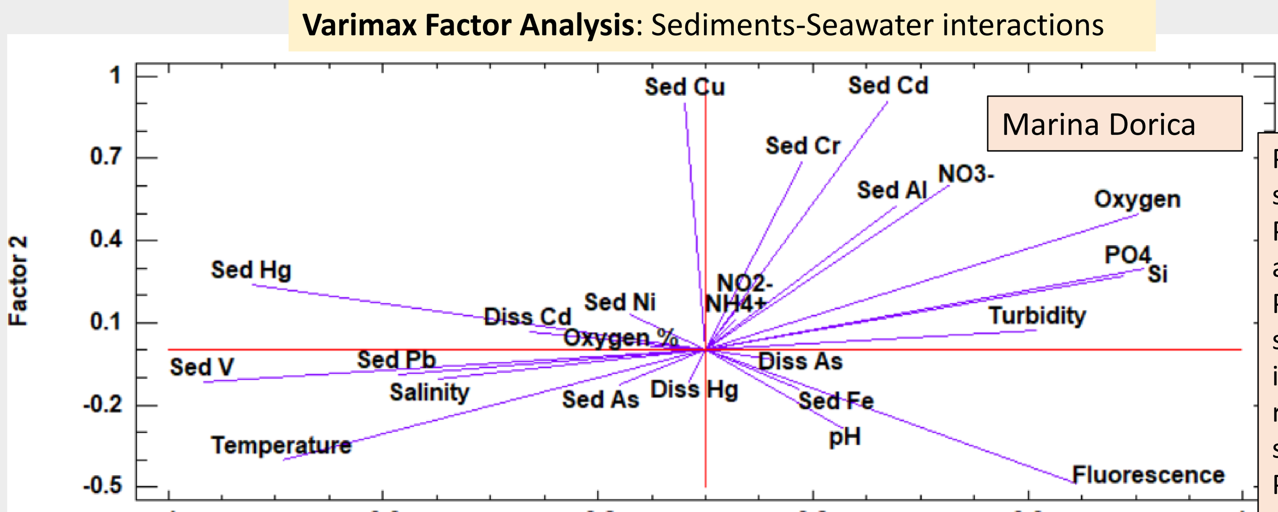
Varimax Factor Analysis: Sediments-Seawater interactions

Portonovo



PC1: water oxygenation and Nitrogen oxydation processes. Anoxya and the production of ammonium seems to be strongly related with sediment Cr, Ni and Cd.
In PC2 the resuspension phenomena and probably related algae blooms seems to play a key role.
The inverse relation between P and some sediment load could confirm the sinking capability given by P-Metal bond[2].
PC1+PC2 accounted for the 52.6% of the explained variance.

Marina Dorica



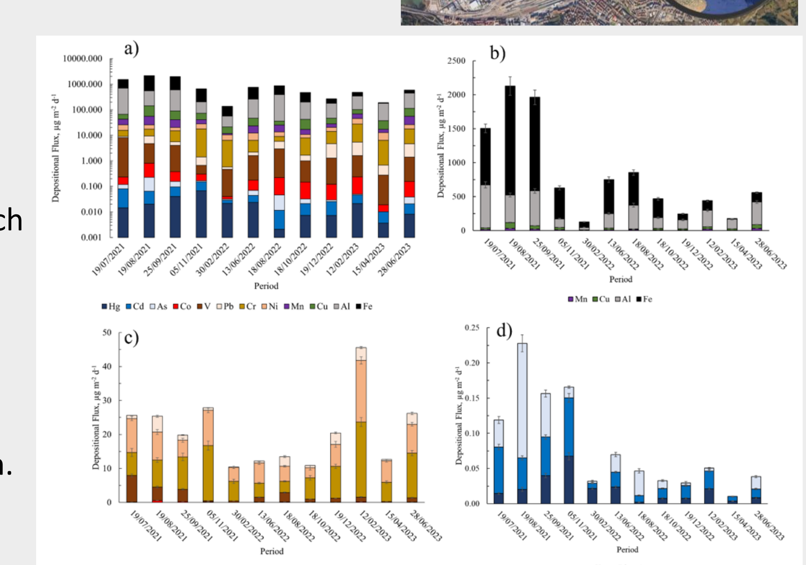
PC1: influenced principally by seasonality, with higher Silicon and Phosphorus in winter periods, aslong as Al, Cd and Cr in sediments.
PC2 is strongly related with sediment Cu content, which increases with pH decrease and his relationship with the fluorescence should be further studied.
PC1+PC2 accounted for the 53.4% of the explained variance.

Atmospheric Depositions

Site characterization, daily depositional metal fluxes evaluation.

Windrose (Rstudio),
Mapping for Saharan Dust events (Panoply)

Metals seasonal evolution:
High dust loads in summer periods, which decreases in winter.
Metal depositional fluxes for minor constituents (b) and ultra trace (d) follows the dust loads pattern.
Trace elements fluxes (c) follows a different pattern.



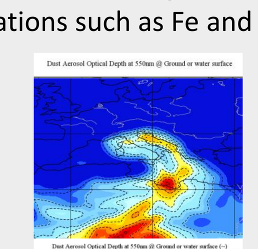
Source apportionment

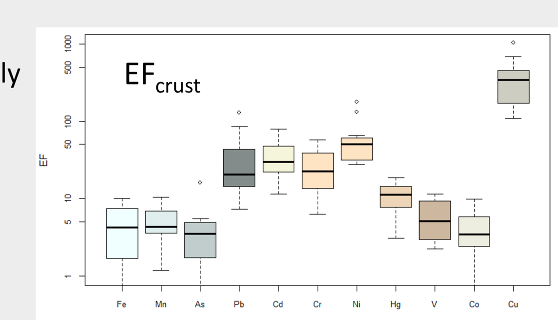
Source apportion allowed to distinguish 2 major in-situ emission sources:

- Vehicle emissions (road and naval)
- Shipyard activities

High enrichment for Cu,
Moderate enrichment for Pb, Cd, Cr, and Ni.

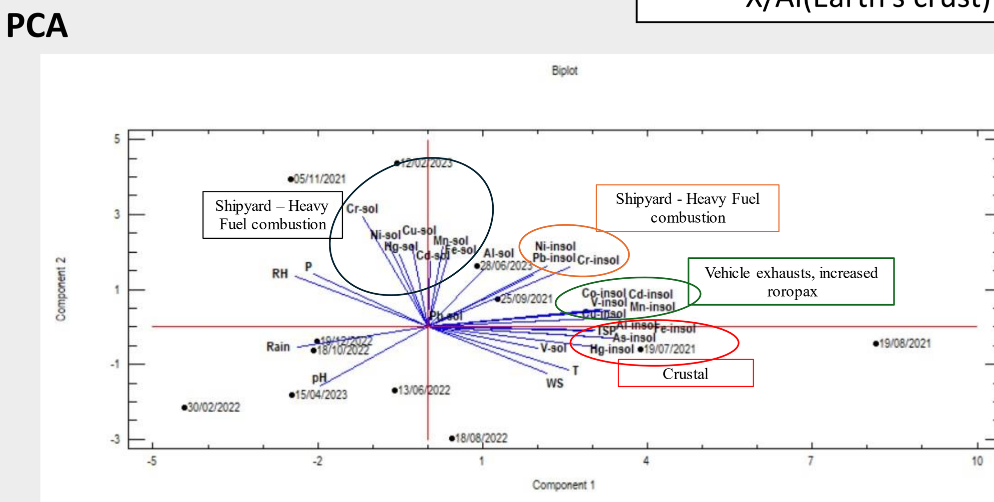
Crustal sources such as Saharan Dusts clearly increase dust and lithogenic elements concentrations such as Fe and Al.





$$EF = \frac{X/Al(deposition)}{X/Al(Earth's\ crust)}$$ [3]

PCA



Paper in progress!

Conclusions

- The sites differences consistently affect the relationships between the variables.
- An interannual difference is observable in both dissolved metals and sediment metal contents. This difference is primarily attributed to significant meteorological differences between the two years: a dry first year and a rainy second year characterized by many flood events and substantial sedimentary deposition on our coasts.
- Dissolved fraction of Hg, As, and Cd is always predominant compared with the particulate fraction.
- Organic Matter plays a key role in some contaminant adsorption, particularly for Hg and Pb.
- Dissolved PTEs concentrations in seawater are always lower than the MAC-EQS for bathing waters (WFD 2008).
- Sediments PTEs content was well-below the Environmental Quality standard for Cd, Hg and Pb; Cr showed values next or above the EQS only for Portonovo site.

Future perspectives

- Biota analysis (in progress).
- Completion of marine particulate analyses and further statistical and chemometric analyses to evaluate the relationships between the different matrices and variables.
- Fluxes evaluation
- Paper publication: Atmospheric deposition in the port area of Ancona.
- Thesis redaption

References:
1) Wolff, EW. et al., *Quat Sci Rev*, 29 (2010) 285. 2) Paytan, A., & McLaughlin, K. (2007), Chemical reviews, 107(2), 563-576. 3) Vagnoni, F. et al., (2021). Atmosphere, 12(8), 1030.