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

Biogeochemical cycling of contaminants in marine waters

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Introduction

From the 20th century, the increment and intensification of the industrial activities has generated 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 the geochemical processes basically induced to an increment on the concentration of elements (i.e. metals) in many environmental receiving matrices and in the last years the research is growing towards the data collection and the understanding of the problem. This relevance grows in interest when regarding Potentially Toxic Elements (PTEs), which is a class of persistent inorganic pollutants that contains both metals and metalloids, capable to bioaccumulate in the organism tissues, and some (like Hg) to biomagnify along the trophic chain. Pb, Cd and Hg are classified as priority pollutants according to Water Framework Directive, due to their capability to generate toxicity in the receiving organisms even at very low environmental concentration.

PTEs can be used as tracers of different emission sources. In fact, besides the well-known Na, Mg, K and Ca as markers of primary marine aerosol sources, elements like Al, Fe can be employed as valuable indicators of crustal inputs. Moreover, metals like As, Pb, Cd, Cr and Ni are tracers of anthropogenic pollution[1], in particular V and Ni are considered tracers for maritime traffic[2].

The study aims to evaluate (1) the characterization of PTEs and in seawater and surface sediments; (2) the possible influence of atmospheric pollution on the marine biogeochemical cycle of PTEs; (3) the partitioning and the interaction between the different matrices, and (4) the seasonal evolution of the pollutant contents in the different 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

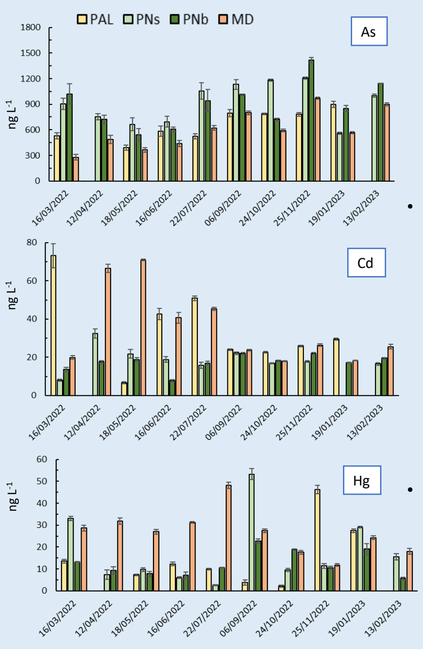
- Differential mass weighing
- Acid microwave digestion ($5HNO_3$:$1H_2O_2$:1HF)
- Atomic Absorption Spectrometry → PTEs (Al, Fe, Mn, Cd, As, Hg, Pb, Ni, V, Co, Cu, Cr, Se)

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

Results & Discussion

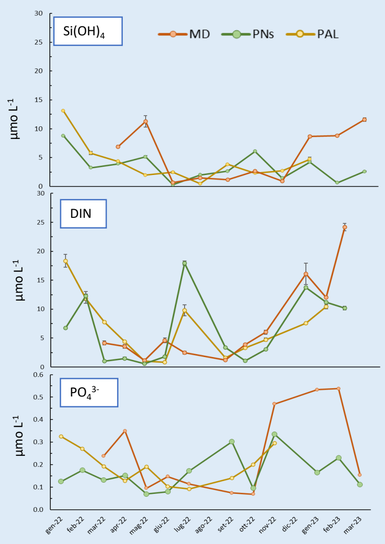
Seawater

Dissolved PTEs



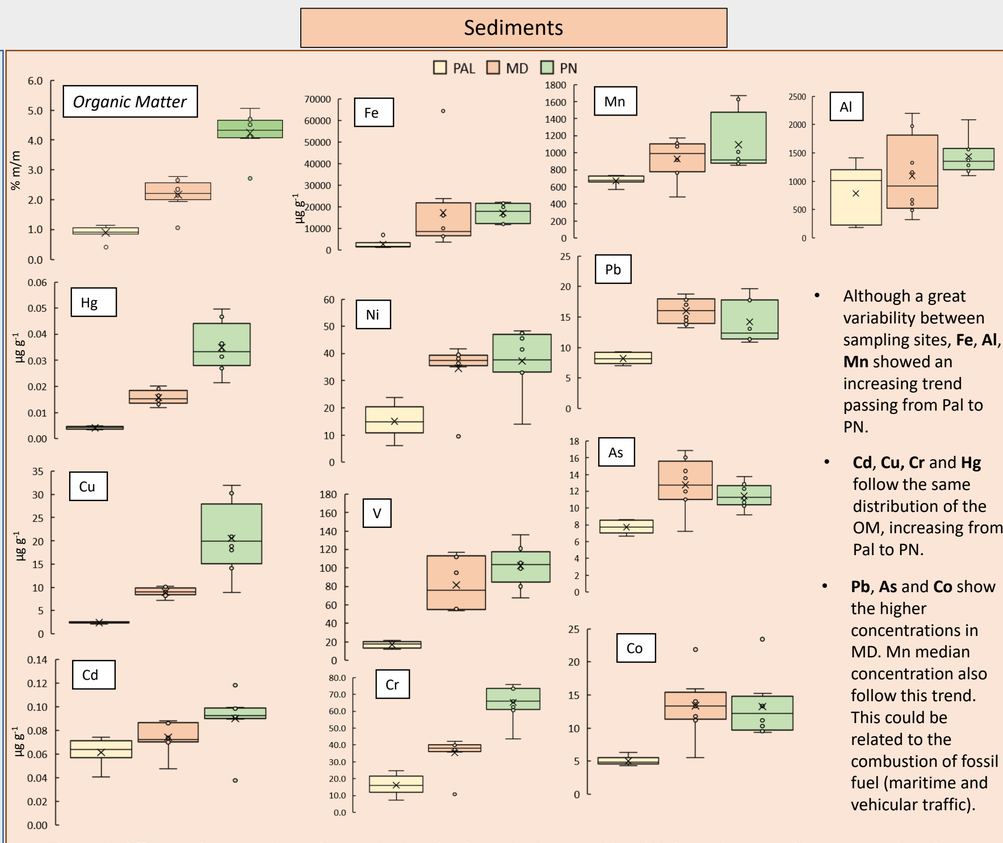
- As_{diss}: PN resulted generally higher than Pal and MD, which can be considered comparable. Concentrations followed a bell-shaped trend, with a maximum in mid-summer. No particular differences between $PN_{surface}$ and PN_{bottom}.
- Cd_{diss}: In the first part of the sampling seasons results were higher for Pal and MD, reaching constant trend at the end of summer. Concentrations are generally high in summer for each site. No particular differences between $PN_{surface}$ and PN_{bottom}.
- Hg_{diss}: MD concentrations are generally higher, especially during the first part of the sampling campaign. No particular seasonal trend was observed in Pal and PN.

Nutrients



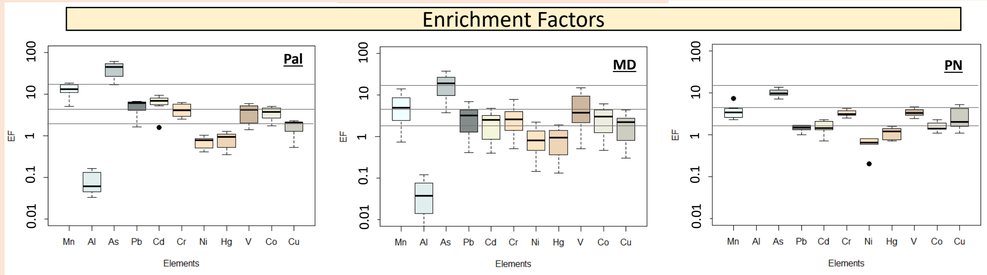
- Dissolved Inorganic Nitrogen (DIN), resulted as the sum of the three N-species (NO_2^-, NO^{3-}, NH_4^+). Nitrates account for ~85% of DIN, while nitrites and ammonia represent ~5-10% respectively.
- MD nutrients, are generally lower in summer and higher in winter with respect to Pal and PN.
- All nutrients showed a seasonal variation, with high concentrations in winter and low values in summer.
- A peak of DIN and Phosphate occurred In July, probably as consequence of rainy events after a long dry period.

Sediments



- Although a great variability between sampling sites, **Fe**, **Al**, **Mn** showed an increasing trend passing from Pal to PN.
- **Cd**, **Cu, Cr** and **Hg** follow the same distribution of the OM, increasing from Pal to PN.
- **Pb**, **As** and **Co** show the higher concentrations in MD. Mn median concentration also follow this trend. This could be related to the combustion of fossil fuel (maritime and vehicular traffic).
- The main difference between the sediments is given by the grain size and Organic Matter content. MD and Pal are coarse, sandy, while PN grain size is fine and rich in OM. This difference, as expected, greatly influences the PTEs adsorption processes[3].
- **Ni** and **V** showed comparable concentrations between PN e MD. V and Ni are usually used as indicator of maritime traffic, which is the main anthropogenic pressure of MD and PN in summer.

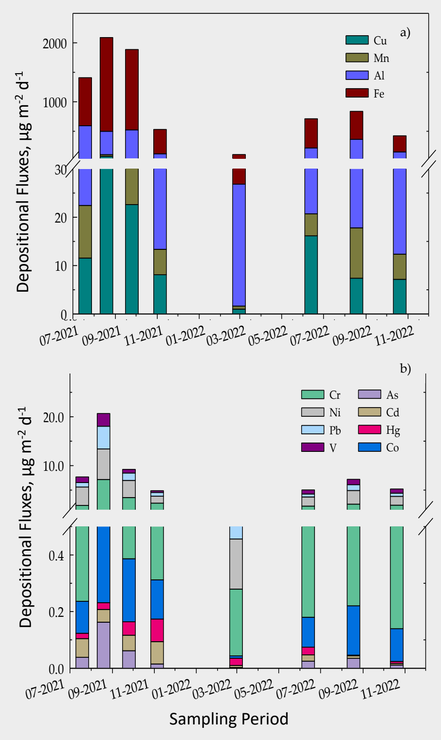
Enrichment Factors



Site / Enrichment	EF < 2 low enrichment	2 < EF < 5 Moderate enrichment	5 < EF < 20 High Enrichment	20 < EF < 40 Very high enrichment	EF>40 Extreme enrichment
Palombina	Cu, Al, Ni, Hg	V, Cr, Co	Mn, Pb, Cd	As	
Marina Dorica	Ni, Hg	Pb, Cd, Cr, Co, Cu	Mn, V, As	As (june, sept, oct)	
Portonovo	Co, Ni, Hg, Cd, Pb	V, Cu, Cr,	As		

$$EF^3 = \frac{X/Fe(sediment)}{X/Fe(Earth's\ crust)}$$

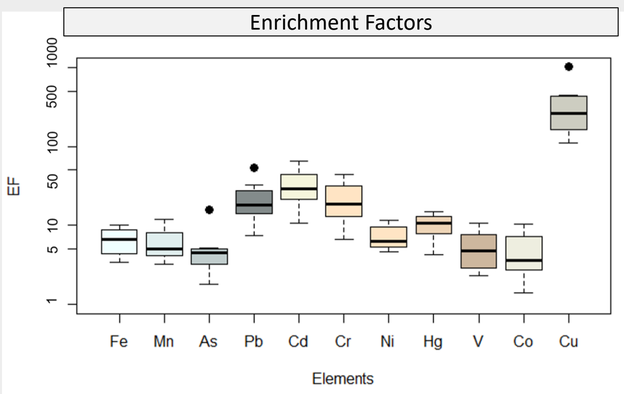
Atmospheric Depositions



Daily depositional flux expressed in µg m^{-2} d^{-1} was calculated for each metal. During the sampling period, the Ancona port area was characterized by a total flux of 8.0±0.4 mg m^{-2} d^{-1}, with values ranging from 0.1 to 2.1 mg m^{-2} d^{-1}. Atmospheric deposition of each element was calculated as the sum of the soluble and insoluble fractions. The daily average fluxes of the determined elements follow the decreasing order: Fe 687±533 > Al 284±196 > Cu 19±24 > Mn 9.8±8.4 > Ni 2.7±1.8 > Cr 2.3±1.8 > Pb 1.3±1.4 > V 0.96±0.75 > As 0.044±0.051 > Cd 0.04±0.03 > Hg 0.029±0.025 µg m^{-2} d^{-1}.

Preliminary results show a seasonal pattern of depositional fluxes with high values during the summer period and low values during the winter season.

Enrichment Factors



Geogenic origin
EFs<10
Fe, Mn, As, Ni, V, Co

Moderately enriched
10<EFs<100
Pb, Cd, Cr, Hg,

Greatly enriched
EFs < 1000
Cu

The enrichment of PTEs in summer, associated with increased daily flows, could be due to high marine traffic, which has intensified since June 2020 as a result of the passage of large cruise ships.

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

Conclusions

- Preliminary results consisted in the sites characterization and seasonal evolution of PTEs, along the coastal area of Ancona.
- Dissolved PTEs concentrations in seawater are always lower than the MAC-EQS for bathing waters (WFD 2008). As mean concentrations are about 5 times lower than the EQS, while Cd about 10 times; Hg ranged from values lower than 10 times to values close to the limit.
- 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.
- First recent data of PTEs depositional fluxes for the Italian coast of the Adriatic sea are showed. Results of depositional fluxes are in agreement with those recorded in the Croatian side of the Adriatic Sea[4], excepting for Cu that show a marked anthropogenic enrichment.
- In the Italian side of the Adriatic Sea and especially near the coast of Ancona, very few studies evaluated the concentration of such elements in the chosen matrices, that's why this study could provide important information on the biogeochemical cycling of these elements and for better understand how the anthropogenic pressure can affect this balance.

Future perspectives

- PTEs seawater particulate fraction determination by GF-AAS.
- Evaluation of transport mechanisms between the different matrices
- Chemometric treatment of data (PCA, correlation matrices, etc…)
- Source apportionment of PTEs.
- Airmass back trajectories model for PTEs sources in the atmospheric depositions.

References

- 1) Wolff, EW. et al., *Quat Sci Rev*, 29 (2010) 285.
- 2) Becagli, S. et al,. (2012). *Atmospheric Chemistry and Physics*, *12*(7), 3479-3492.
- 3) Aprile, F. M., & Bouvy, M. (2008). *Brazilian Journal of Aquatic Science and Technology*, *12*(1), 1-8.
- 4) Penezić, Aet al., (2021). *Chemosphere*, *283*, 131178.