Natural background values for heavy metals in the sediments of a contaminated Northern Adriatic lagoon environment: a geochemical perspective

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Introduction and aim of the work

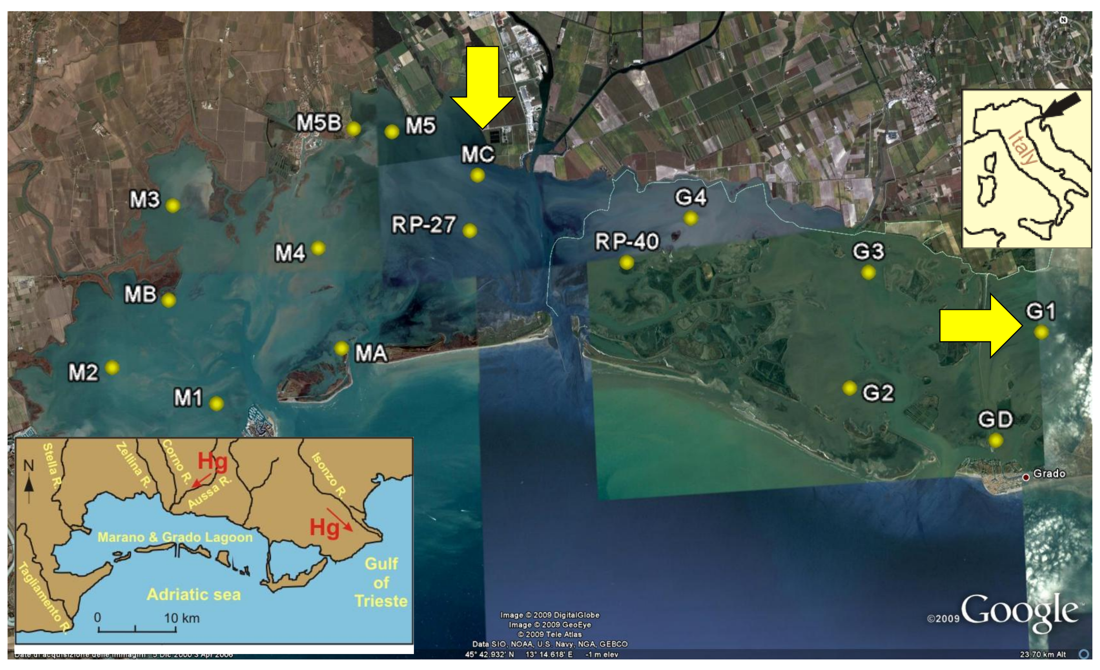


Fig. 1 – Core sampling sites in the Marano and Grado Lagoon

The European Community Water Framework Directive (*WFD 2000/60/EC*) requires achievement of good ecological and chemical status both in waters and sediments of coastal and transitional water bodies by 2015.

To this purpose, it establishes Environmental Quality Standards (EQS) for 33 priority substances, including some heavy metals (As, Cd, Cr, Hg, Ni, and Pb) of well recognized environmental importance and ecotoxicological effects.

False anomalies may then arise because metal values tend to vary with mineralogy and grain-size, higher concentrations being associated with finer-grained sediments. Fine-grained sediments in particular show an ability to accumulate metals from atmospheric deposition, from soil erosion, or directly from wastewater discharge. Several procedures have been proposed for the normalization of geochemical data in river and marine sediments (*Loring,* 1991). Normalization carried out using simple linear regression of metal content versus a grain-size proxy element has been demonstrated to be an useful approach in defining regional metal background values, taken into account local mineralogical characteristics and grain-size variability. On the basis of the geochemical data set of the Marano and Grado Lagoon, regional background values are proposed and compared to the EQS, taking into consideration the sediment grain size variability in the lagoon.

Study area

The Marano and Grado Lagoon (referred to simply as "Lagoon" hereafter) represents one of the best conserved wetlands in the whole Mediterranean area (**Fig. 1**). The area hosts economic, tourism and industrial services, with fishing, clam harvesting and fish-farming. In spite of the level of protection, the Lagoon has also been declared a "polluted site of national interest" (SIN; *Ministerial Decree 468/01*) because of its high level of environmental risk. Among several contaminants, the Lagoon is one of the most Hg contaminated coastal zones in the Mediterranean, due to both industrial processes (chlor-alkali plant) and long-term mining activity.

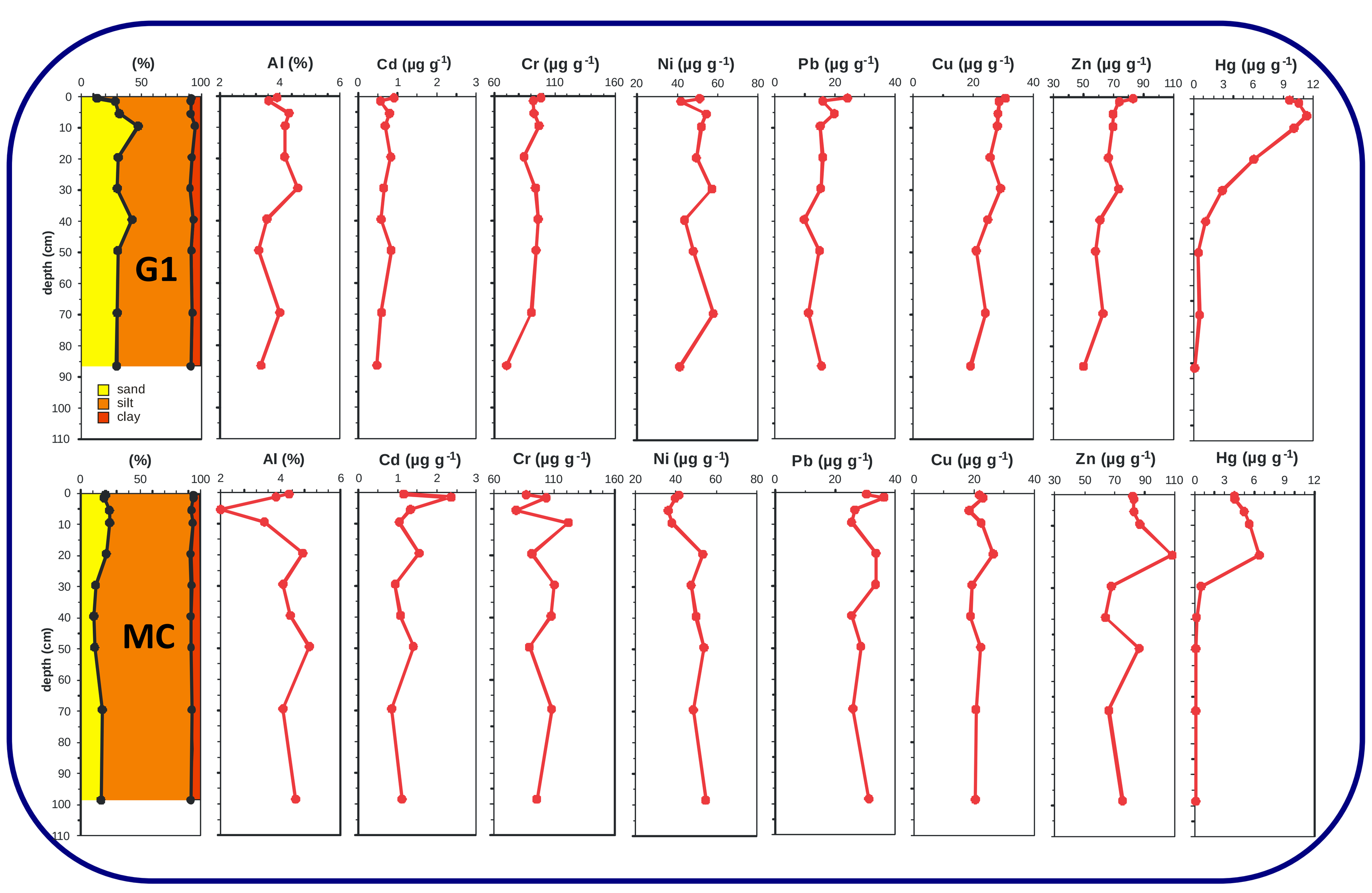
Field and laboratory work

Fig. 2 – Sampling operations

- 14 long cores were manually collected by hand corer
- Grain-size analyses (Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer)
- Total C and N, organic C (CHN Perkin Elmer Elemental Analyzer)
- Total major (Al and Fe) and trace elements (As, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sc, V, Zn) content determined by ICP-OES after total digestion method (HF + *aqua regia*) in a closed microwave system.
- Hg was analyzed through the CVAAS technique (Perkin Elmer AAnalyst 100-FIAS). Quality control was tested using certified reference materials (PACS-2 harbour sediment, NCR-CNR, Canada).
- Sedimentation rate assessments were also performed using ^{210}Pb and ^{137}Cs radiodatings)

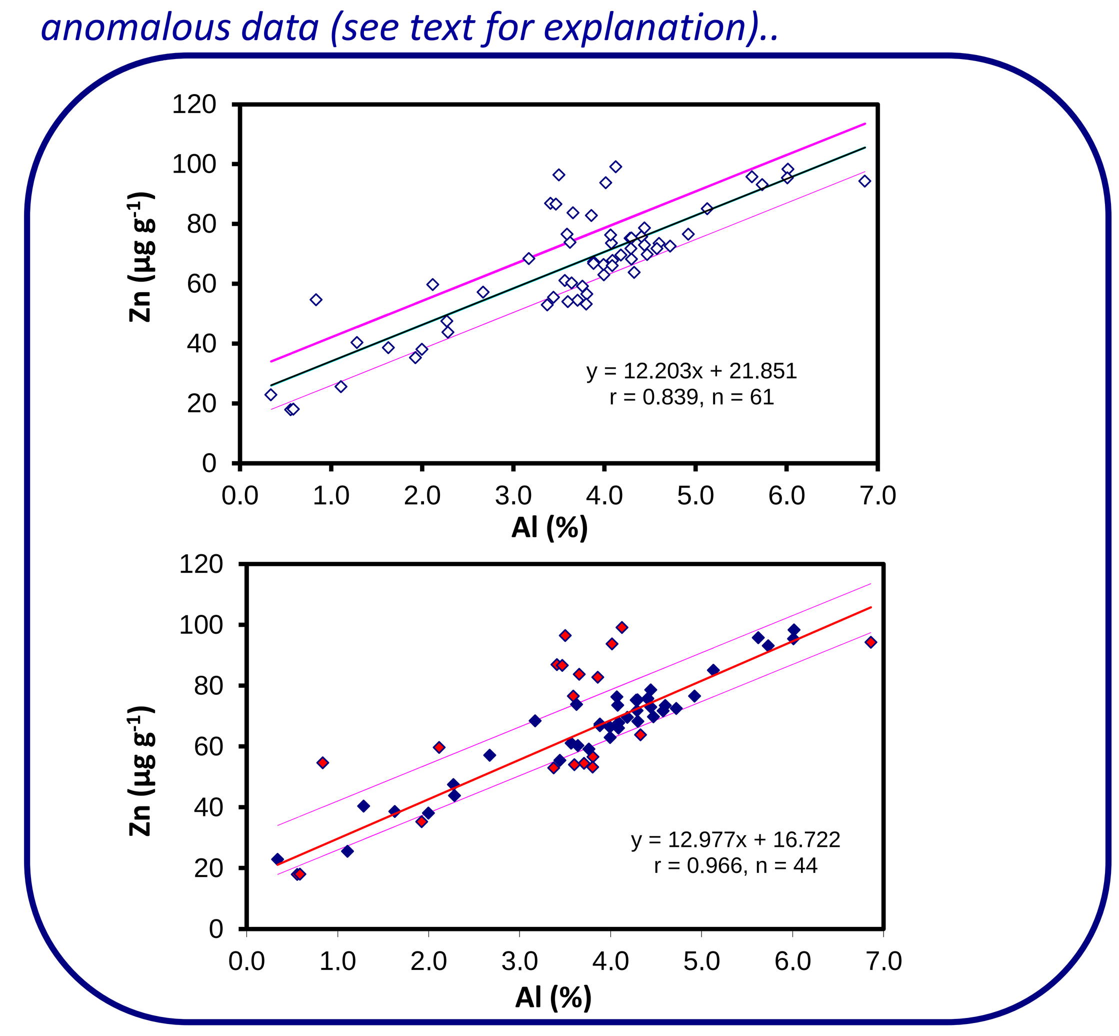
Results and Discussion

Fig. 3 – Examples of vertical variability of grain-size and element concentration in sediment cores (G1 and MC, indicated in Fig. 1).



Only Hg profiles in all cores showed a typical anthropogenic trend of increasing metal concentration from the basal core sections, where local background values (0.13 ± 0.04 µg g^{-1}) were found, to the top core sections. The profiles clearly reflect the massive Hg contamination that has historically altered the study area, which has been well recorded into the lagoon sediments (**Fig. 3**). Geochronological measurements showed that the depositional flux of Hg was influenced by anthropogenic inputs after 1800, when cinnabar mining activity at Idrija (Slovenia) was more intense. After 1950, surface sediments were also affected by the discharge of the Aussa River, which delivers Hg from a chlor-alkali plant (*Covelli et al., 2012*). For other metals, concentration profiles are affected by grain-size variability and the anthropogenic component is not easily discernible by the lithogenic one. Data were then normalized by applying the procedure followed by *Covelli & Fontolan* (1996) and *Covelli et al.* (2006). By means of a data correlation matrix, the relationship between fine-grained fractions, possible grain-size proxy elements (Al, Fe, Li, V and Sc), and trace elements were examined. Aluminum showed the best correlation with the muddy fraction (r=0.806, n=61, p<0.001).

Fig. 4 – Scatterplots showing correlation of Zinc vs Aluminum in the sediment core subsamples before and after removing anomalous data (see text for explanation)..



The poor correlations between Al and As, Cd and Hg suggest that their occurrence is not dependent on the muddy and/or aluminosilicate mineral fractions. Simple linear regressions versus Al were initially performed on all core levels and the results were plotted along with the 95% prediction limits (**Fig. 4**). Data points falling outside the two 95% predictions limits, delineating the expected natural range, were considered to be anomalous and removed from the original data set. Metal-Al linear relationships were recalculated for the samples statistically belonging to the natural population of lagoon sediments. These regression lines on a regional scale, along with prediction limits, can be used to assess the expected natural metal value in sediments, on the basis of the analyzed Al content in each sample.

Tab. 1 – Expected element concentrations according to mud content in bottom sediments.

Trace Element	Mud 0-30%	Mud 30-70%	Mud 70-100%	EQS
As (µg g^{-1})	4 - 6	6 - 8	8 – 9	12
Cd (µg g^{-1})	0.5 – 0.6	0.6 – 0.8	0.8 – 0.9	0.3
Cr (µg g^{-1})	37 - 60	60 - 96	96 - 123	50
Ni (µg g^{-1})	0 - 16	16 - 43	43 - 62	30
Pb (µg g^{-1})	11-16	16 - 22	22 - 27	30
Co (µg g^{-1})	0 – 2	2 - 7	7 - 11	n.d.
Cu (µg g^{-1})	2 - 9	9 - 11	21 - 29	n.d.
Zn (µg g^{-1})	15 - 35	35 - 65	65 - 87	n.d

Element	Mud 0-30%	Mud 30-70%	Mud 70-100%
Al (%)	0 - 1	1 - 4	4 - 5
Fe (%)	0.4 - 1	1 - 2	2 - 3
Mn (µg g^{-1})	253- 303	303 - 379	379 - 437
Li (µg g^{-1})	6 - 21	21 - 44	44 - 61
Sc (µg g^{-1})	0.1 - 3	3 - 7	7 - 10
V (µg g^{-1})	7-32	32 - 70	70 - 98

Since Al was well correlated with mud, the following step was to calculate the expected Al content range for the main textural classes (mud <30%, 30-70% and >70%) of sediments. The final step was then to determine the expected metal concentration range for each textural class related to the muddy content (**Tab. 1**). Mercury was the only element excluded from this procedure due to its high level of contamination (up to 12 µg g^{-1}). For this element the background value can be assumed to be 0.13 µg g^{-1} (*Covelli et al.,* 2012) and not dependent on grain-size.

If the expected concentrations of total metals in the Lagoon sediments are compared to the threshold values (EQS) reported in the Italian laws and regulations (*Italian Environmental Ministry Decree no. 56/2009*) for coastal sediments, As and Pb are always lower regardless of the textural class. Conversely, Cr and Ni exceed the threshold values in the Lagoon sediments only where the muddy component is higher than 30%. This means that the Lagoon sediments are naturally "enriched" in Cr and Ni probably due to the sedimentary contribution from rivers which is supplied in terms of clay minerals, such as illite, kaolinite, and chlorite, and of chromite, a Cr-bearing spinel mineral, mainly originated from erosion of flysch outcropping in the surrounding area. On the other hand, Cd is always higher than EQS, regardless of the muddy content. It is hypothesized that other minerals such as sulphides (i.e. ZnS) can be act as metal carriers in bottom sediments.

Final remarks

The approach followed in this study allowed to better define the lithogenic origin of some metals such as Cr, Ni and Cd, whose regional background values are higher than the EQS indicated by the national regulations on the subject, mostly the rules coming from the application of *Water Framework Directive (WFD EC 2000/60)*. Besides, the results suggest that any consideration on sediment quality status on the basis of the total metal content cannot be limited only to the application of simple and general EQS. Regional background values for heavy metals should be determined for each coastal area considering sediment geochemical characteristics (i.e. mineralogical composition and grain-size variability). This approach also provides simple but useful information for studies on sediment quality assessment, also in connection with the management of dredged material in contaminated coastal environments.

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