An Environmental – Friendly Approach to the Remediation of Dredged Polluted Sediments of the Venice Lagoon, Italy

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Contamination in sediments of coastal areas and harbours is due to a wide range of organic pollutants and trace elements; in these areas sediments may be a significant sink and/or source of those pollutants. Considered the necessity to dredge sediments in order to maintain an optimum navigation, remediation and environmental recovery are foremost aims in harbour areas. The main goal of this project is to assess a novel washing procedure for dredged sediments, environment friendly and suitable for the miscellany of organic and inorganic pollutants, by exploiting the surface-active and complexing properties of natural organic substances commercially available

How to classify sediments in the Venice Lagoon?

Sostanza	Classe A	Classe B	Classe C
Arsenico (As)	15	25	50
Cadmio (Cd)	1	5	20
Cromo (Cr)	2	100	500
Rame (Cu)	40	50	400
Mercurio (Hg)	0,5	2	10
Nichel (Ni)	45	50	150
Piombo (Pb)	45	100	500
Zinco (Zn)	200	400	3.000
Idrocarburi totali	30	500	4.000
PAH totali	1	10	20
PCB totali	0,01	0,2	2
Pesticidi clorurati	0,001	0,02	0,5

In the Venice Lagoon, sediments are classified according the Protocollo Venezia (aka Protocollo Fanghi, aka Protocollo d'intesa '93). In relation to the total concentration of trace metals and the total concentration of organic pollutants, sediments are classified as A, B, C and above C; the sediments C and above C are the most polluted, while the sediments A are the less polluted.

CHARACTERIZATION OF THE DREDGED SEDIMENTS : EXPERIMENTAL DESIGN

In the first phase of the study, GEOSPECIATION of the wet dredged sediments from the industrial area of the Venice lagoon was studied. We modified and optimized a sequential extraction procedure (SEP, from Tessier procedure) in order to evaluate the concentration of the trace elements in the chemical fractions: the exchangeable, the carbonate bound, the Fe and Mn oxides bound, the sulphur and organic matter bound, the residual bound. The first two fractions are considered the most mobile and thus the most bioavailable and those, which may exert toxic effects on biota. Furthermore, dredged sediments were characterized for the total concentrations of several trace elements (such as arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), zinc (Zn), etc.) and or the concentration of persistent organic pollutants (POPs, such as PCBs, PAHs) . All the samples for trace metals were analysed by ICP-MS Agilent, while PCBs and PAHs were analysed by sophisticated extraction procedures and quantification by GC-MS Agilent. All the steps were carried out in order to minimise contamination (e.g. Clean Room Class 100, Trace Select/Suprapur grade reagents for trace elements and Pestanal grade for the POPs.

CHARACTERIZATION OF THE DREDGED SEDIMENTS : RESULTS

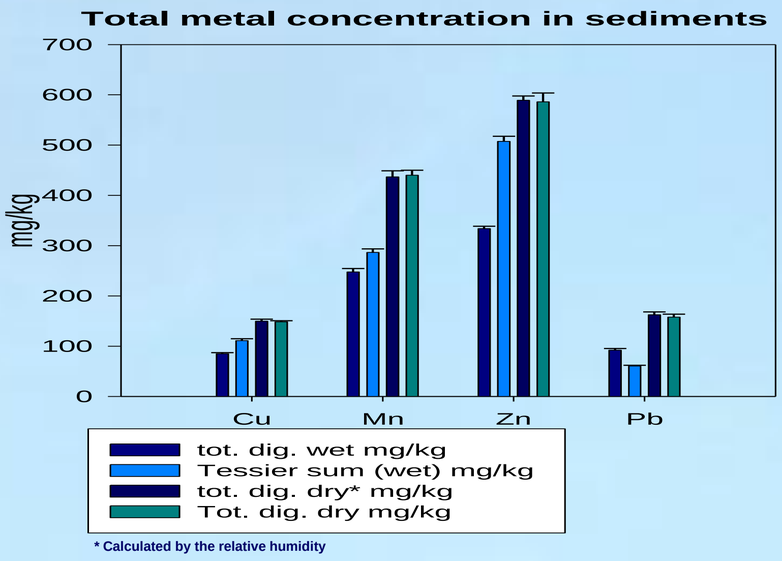
a) Trace elements

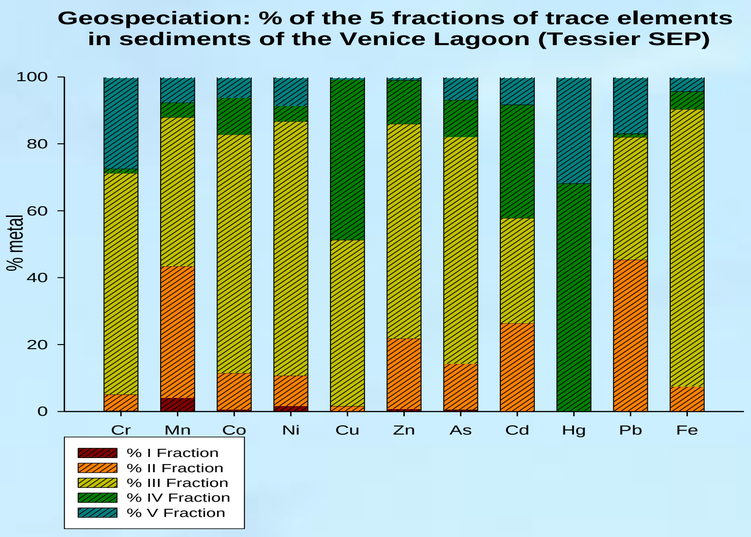
the precision of measurement : RSD ≤ 5% for the elements studied, in the total digestions (wet and dry) and in the 5 phases of Tessier Sequential Extraction Procedure (SEP). Data obtained for the total wet and dry digestion are in good agreement for any element considered (RSD ≤ 10 % or lower). For most of the elements considered the average sum of the 5 phases of Tessier SEP is somewhat higher than the total concentration value observed (average 115% of recovery) , but there are some exceptions. However the results obtained for the total wet concentration and the concentrations of the Tessier SEP (wet) are in good agreement (RSD ≤ 15%).

b) PCBs and PAHs

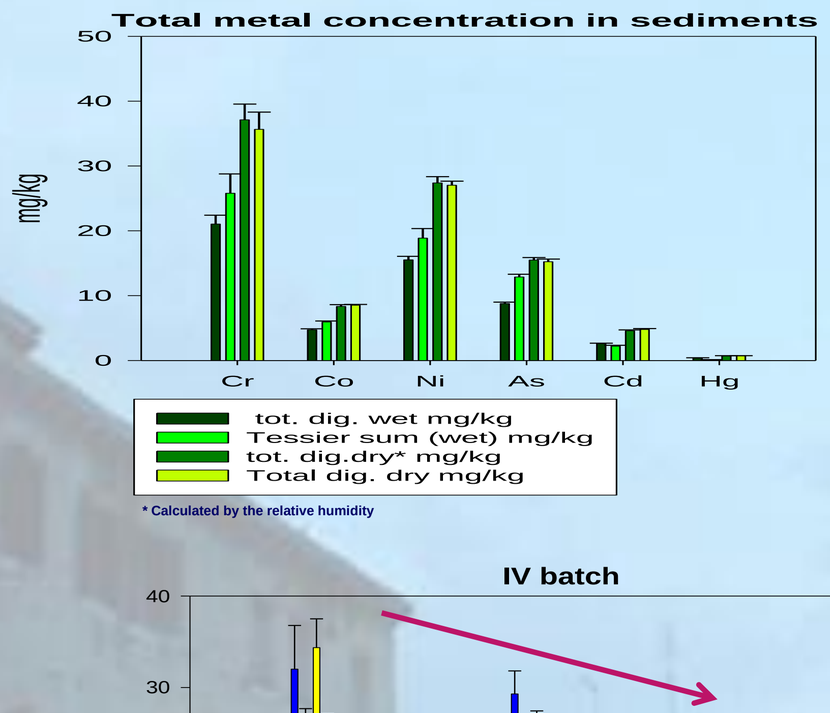
The concentration of the single congenre and the total concentration are reported for PCBs and PAHs. PCBs results are expressed as ng/kg dry weight with a RSD% ≤ 20%, while PAHs results are expressed as µg/kg dry weight with a RSD% ≤ 20%,. The samples analysed were representative of the bulk.

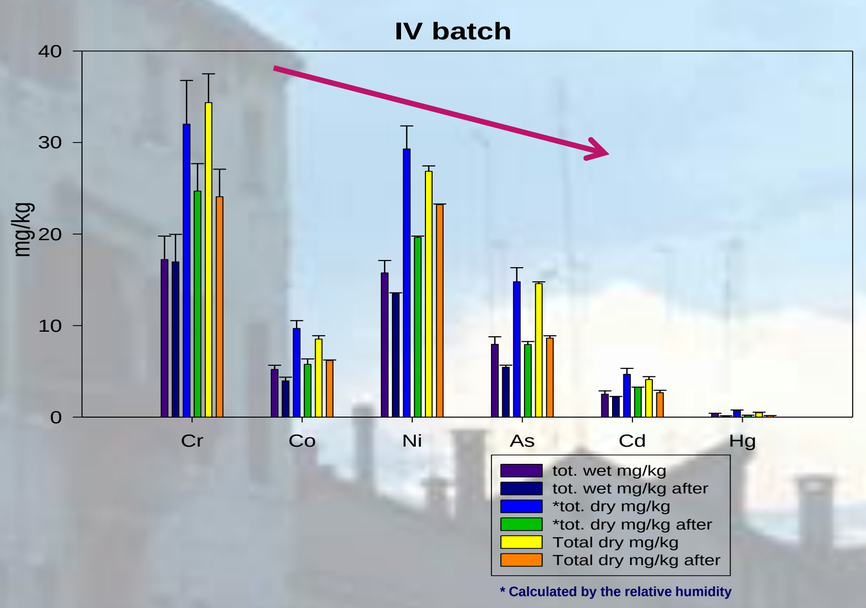
The dredged sediments from the industrial area of the Venice Lagoon belong to C class, which means they were highly polluted.

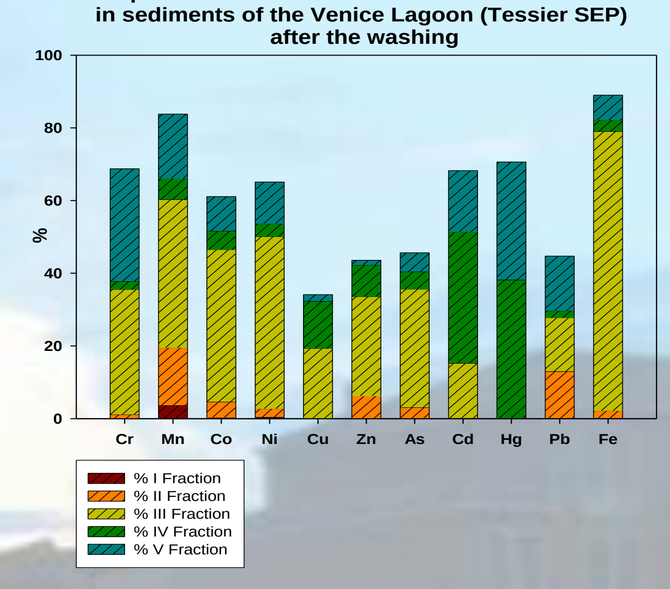




CH_3COONH_4 1 M pH= 7 Extraction stirring for 2h at room temperature
→ Centrifugation → I-exchangeable fraction
→ residue
CH_3COONH_4 1 M pH= 4,8 extraction stirring for 6h at room temperature
→ Centrifugation → II- carbonate-bound fraction
→ residue
$(NH_4)_2C_2O_4 \cdot H_2O$ / $(COOH)_2$ 0,2 M pH = 3 Extraction 3h30 min in MW T= 130 Power= 1500 W
→ Centrifugation → III- Fe /Mn oxides/hydroxides – bound fraction
→ residue
30% H_2O_2 pH= 2 extraction for 1h at room temperature, then in MW 2h e 30 min T= 85 C, Power= 1500 W. Cooling, then CH_3COONH_4 3,2 M pH=2 and overnight stirring at room temperature
→ Centrifugation → IV- organic matter/sulphur bound fraction
→ residue
HNO3/HF, 1,5:1 Digestion in MW 1h50 min , T=200 C, Power=1500W → V- residual fraction







Conclusions

According to the Protocollo Venezia (aka Protocollo Fanghi, aka Protocollo '93), the most toxic sediments, C and above C class, after dredging, must be disposed as harmful toxic waste. The dredging and the disposal costs will deeply affect the Venice Lagoon, environmentally, socially and economically speaking.

The surface-active, seizing and complexing action of natural organic substances, such as the humic substances, is extremely important for both trace elements and POPs. Organic and inorganic contaminants may be efficiently "grabbed" by these substances.

After the washing, the concentration of both inorganic and organic contaminants in the dredged C sediments showed a consistent depletion; thus, the sediments washed can be labelled as B.

The results shown are very promising, due to the holistic approach for different classes of pollutants and due to the low impact on the environment.

Furthermore, these results are very promising, since dredged sediments are not only harmful toxic waste, but they may be a very important resource for recovering the lagoon landscape.

This study underlines once again the importance of studying speciation, since, according to the most recent frameworks on risk assessment, it is essential to know the bioavailability and bioaccessibility of pollutants in order to plan the most suitable remediation project.

Sediment washing: experimental design

In the second phase of this study, the washing process was assessed; different parameters were considered (such as pH, concentration of the washing solution, sediments/volume of the washing solution ratio, length of washing, etc.). All the batch experiments were run in duplicate, to test the homogeneity and the repeatability of the procedure. The RSD% of all the batch experiments run was ≤ 10%. The concentration of natural organic substances commercially available (humic substances, Sigma Aldrich) was always above the CMC (critical micelle concentration). The concentration of contaminants were analysed before and after the washing, as well as the concentration of contaminants in the washing solution. Furthermore, on two replicate batches GEOSPECIATION was studied after the washing , in order to see whether the five fractions changed (expressed as %, as shown in the graphic).

The results of two different batches are here reported as an example (VI batch for trace elements, IV batch for trace elements and for PAHs, VII batch for PCBs).

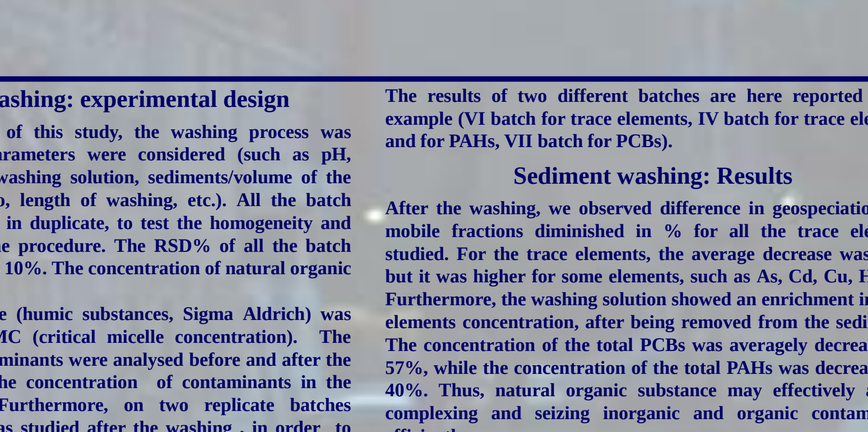
Sediment washing: Results

After the washing, we observed difference in geospeciation; the mobile fractions diminished in % for all the trace elements studied. For the trace elements, the average decrease was 35%, but it was higher for some elements, such as As, Cd, Cu, Hg, Pb. Furthermore, the washing solution showed an enrichment in trace elements concentration, after being removed from the sediments. The concentration of the total PCBs was averagely decreased by 57%, while the concentration of the total PAHs was decreased by 40%. Thus, natural organic substance may effectively act on complexing and seizing inorganic and organic contaminants efficiently.

Before being washed the dredged sediments were "C"; after being treated, the dredged sediments belong to the B class.

PCBs
Before and after

PAHs
Before and after



Aknowledgements

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http://biotech.pd.cnr.it/posters/biotech_3/linea_4.pdf