Heavy metals in sediments – monitoring the quality of the marine environment

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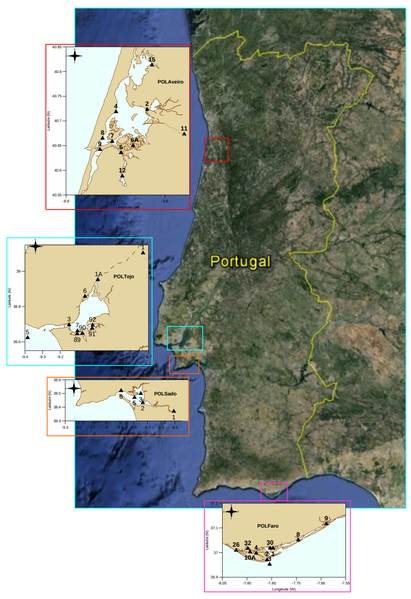
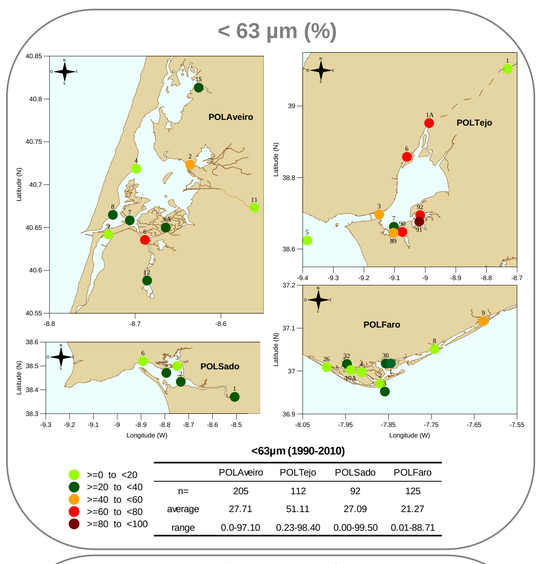
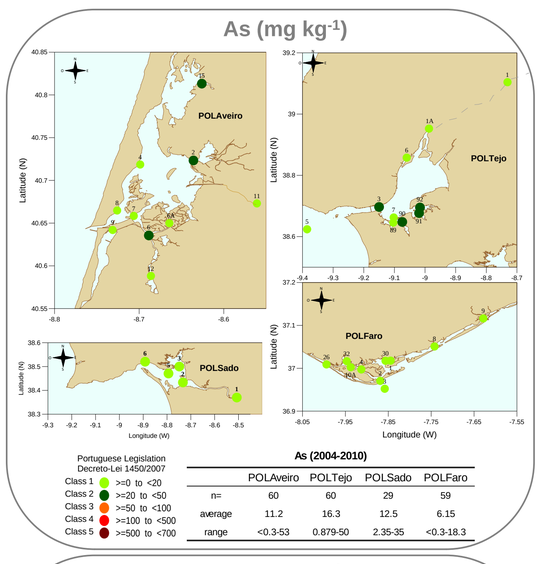


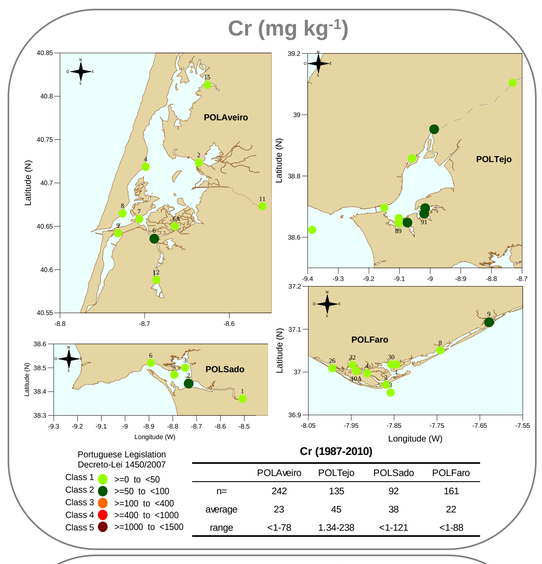
The Hydrographic Institute conducted the Program "Monitoring the Quality of the Marine Environment" during the period 1985-2010. Sediment samples were collected in four different areas, each corresponding to a different estuarine area of relevant economic, social, and ecological importance at Portugal Continental Coastal areas : POLAveiro (mouth of Vouga river and other minor rivers); POLTejo (mouth of Tejo river); POLSado (mouth of Sado river) and POLFaro (Formosa lagoon, complex and extended coastal area of small islets, dunes and bars).

This paper aims to present metals concentrations (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn), grain size and total organic carbon in sediments collected in 35 annual stations (POLAveiro–10, POLTejo–10, POLSado–5 and POLFaro–10 stations) during almost 20 years.

The results are analyzed taking into account statistical analysis (average and range values and principal components analysis - PCA), Sediment Quality Guidelines (SQGs), Environmental Assessment Criteria (OSPAR, 2008) and Portuguese legislation for dredging purposes.



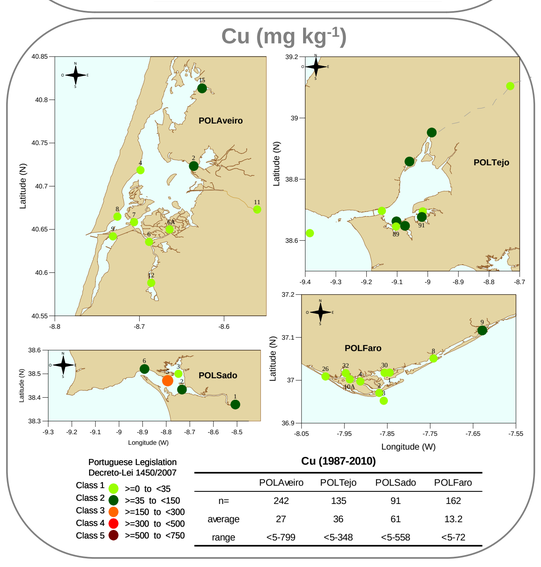


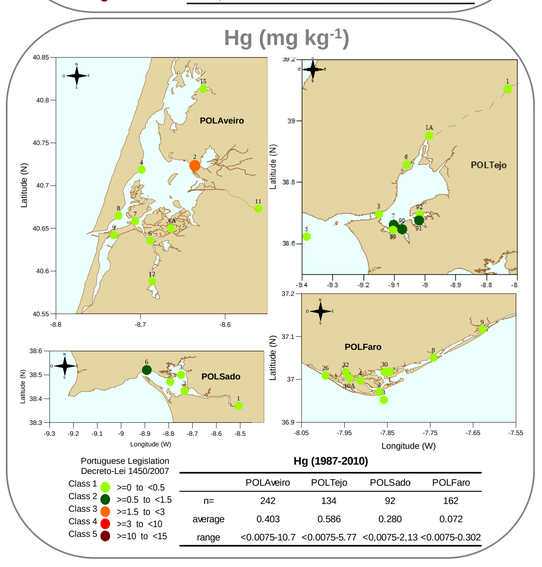


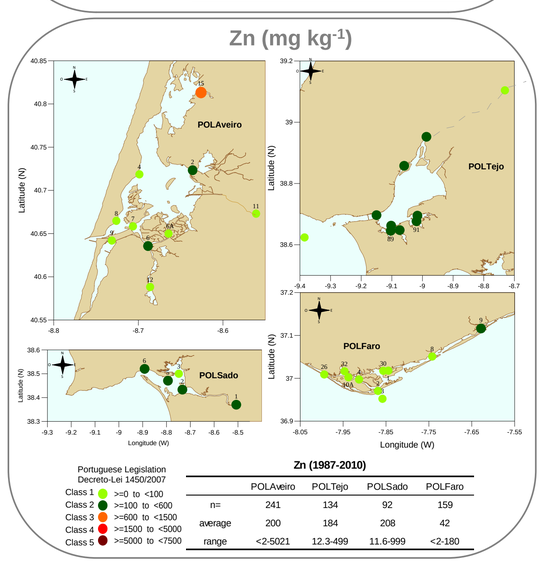
On the side figures are presented the fine fraction (<63 µm) and metals As, Cr, Cu, Hg and Zn distribution maps, with the correspondent sample number; in the lower tables are exposed the respective average and range values. Colored dots are in accordance with the Portuguese legislation of dredged material, with the number of samples analyzed, in tables. Table 1 shows the other analyzed metals and total organic carbon.

Table 1

		POLAveiro	POLTejo	POLSado	POLFaro	Portuguese legislation. Decreto-Lei 1450/2007
TOC (%) (1990-2010)	n=	138	101	59	116	
	average	1.33	1.05	0.67	0.56	
	range	<0.4-5.65	<0.4-3.89	<0.4-2.19	<0.4-2.80	
Al (%) (1990-2010)	n=	173	114	69	130	
	average	29	45	32	18.9	
	range	1.88-75	3-100	0.51-119	1.62-65	
Fe (%) (1990-2010)	n=	242	135	92	162	
	average	11.4	19.05	16.0	7.82	
	range	0.36-38	0.21-45	0.91-57	<1-33	
Mn (mg kg^{-1}) (1990-2010)	n=	242	135	92	162	
	average	116	280	233	63	
	range	2-644	13-923	11.1-1393	<2-292	
Ni (mg kg^{-1}) (1990-2010)	n=	242	132	89	154	Class 1 <30 mg kg^{-1}
	average	10.4	13.3	17.5	7.86	Class 2 30-75 mg kg^{-1}
	range	<2-73	<2-177	<2-176	<2-65	Class 3 75-125 mg kg^{-1}
						Class 4 125-250 mg kg^{-1}
						Class 5 >250 mg kg^{-1}
Pb (mg kg^{-1}) (1990-2010)	n=	242	135	91	161	Class 1 <50 mg kg^{-1}
	average	31	66	30	15.3	Class 2 50-150 mg kg^{-1}
	range	<2-187	<2-332	<2-113	<2-81	Class 3 150-500 mg kg^{-1}
						Class 4 500-1000 mg kg^{-1}
						Class 5 >1000 mg kg^{-1}
Cd (mg kg^{-1}) (1990-2010)	n=	240	133	91	158	Class 1 <1 mg kg^{-1}
	average	0.764	0.670	0.401	0.390	Class 2 1-3 mg kg^{-1}
	range	<0.3-8.24	<0.3-5.23	<0.3-3.14	<0.3-3.64	Class 3 3-5 mg kg^{-1}
						Class 4 5-10 mg kg^{-1}
						Class 5 >10 mg kg^{-1}





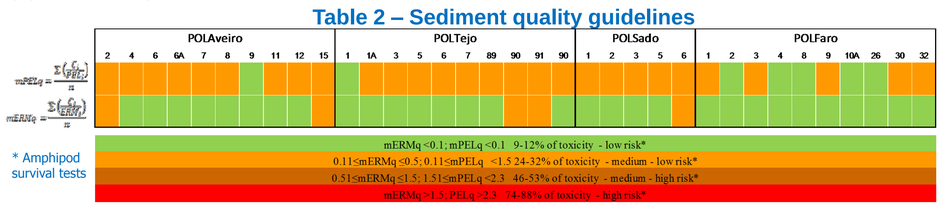


POLFaro presents the metals lower values when comparing to the other locations. By contrary Aveiro, Tejo and Sado shows higher values connected with anthropogenic local contaminations.

According to the Portuguese legislation criteria, the average concentrations of As, Cr, Cu, Hg, Zn and Pb in some of the studied stations fall within class 2 (implying some restrictive rules). POLSado and POLFaro for As, and in all areas for Cd and Ni fall within class 1. POLFARO presents all the average concentrations within class 1, except for station 9 (concentrations within class 2), related with the higher silt+clay fraction (40-60%).

For estuarine and marine sediments the applicability of Sediment Quality Guidelines (SQGs) is a widely used approach to predict adverse biological effects in contaminated sediments: ERL (Effects Range-Low)/ ERM (Effects Range-Median) and TEL (Threshold Effects Levels)/ PEL (Probable Effects Levels) (Long *et al.* (1995) and MacDonald *et al.* (1996). Both approaches derived from statistical analysis of empirical data that associate chemical concentrations of contaminants to biological responses. These two sets of SQGs allow to classify the degree of sediment contamination according to three ranges of concentration that are related to the frequency of occurrence of adverse biological effects on benthic organisms: low range, within which adverse effects occur rarely (<ERL or TEL); middle range, within which adverse effects occur occasionally (ERL-ERM or TEL-PEL) and upper range, within which adverse effects occur frequently (>ERM or >PEL).

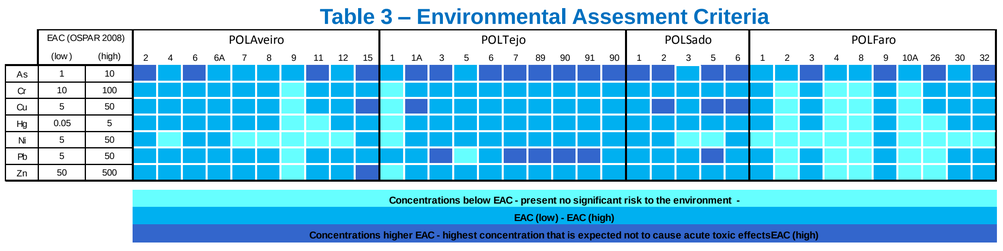
Table 2 – Sediment quality guidelines



* Amphipod survival tests

According to PEL criteria sampling areas are mainly medium – low risk, except POLFaro with half of the stations with low risk of adverse effects on benthic organisms (Table 2). According to ERM criteria sampling areas have low risk of adverse effects on benthic organisms except sampling areas with strong anthropogenic industrial influences (POLAveiro, POLTejo and POLSado (Table 2).

Table 3 – Environmental Assesment Criteria



Environmental Assessment Criteria (EACs) represents the contaminant concentration in the environment below which no chronic effects are expected to occur in marine species, including the most sensitive species. Table 3 shows the EACs for the sampling stations; the values between low and high criteria prevails; POLFaro shows the lower EACs values.

Conclusions:

The spatial pollution status was evaluated in the four different areas:

- POLAveiro - slightly polluted with Cu, Zn, Hg and As (station 2 and 15)
- POLTejo - higher values of As, Hg, Pb and Zn
- POLSado - higher values of Cu, Hg, Pb and Zn
- POLFaro – Lower values of metals

The higher values observed are associated with potential pollution due to anthropogenic industrial discharges and human activities.

PolFaro is the lower contaminated area and without adverse effects to benthic organisms.

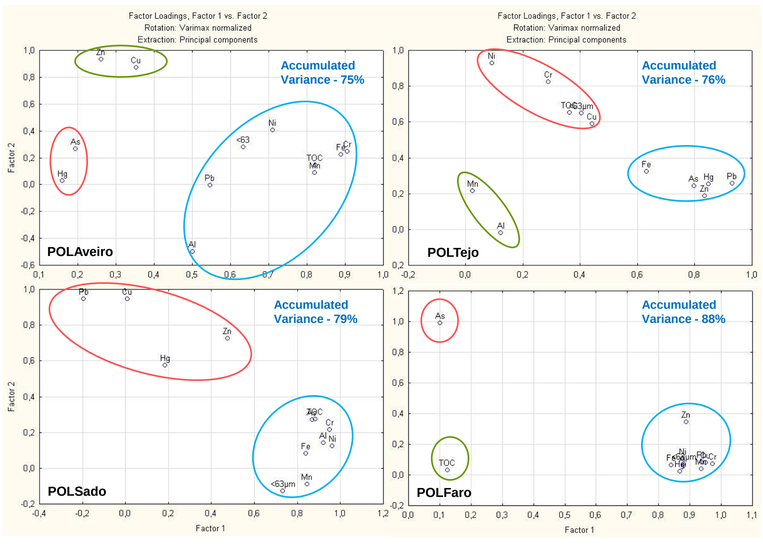
According SGQs, EAC and Portuguese legislation the studied areas present low levels of metal contamination, but with some localized higher values.

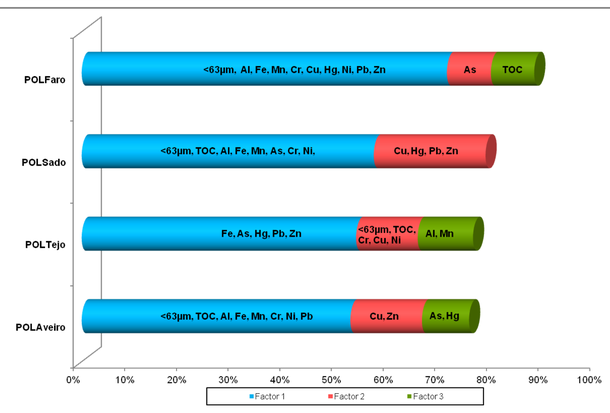
Data in Table 4 with mean, maximum and minimum values shows the concentrations of heavy metals in sediments from other sites. Concentrations of some metals are higher in POLAveiro and POLTejo, than those found in POLFaro

Table 4 – Heavy metals concentrations

Area	As (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Hg (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})	Reference
POLAveiro	<0.3-53	<1-78	<5-799	<0.0075-10.7	<2-5021	<2-187	This study
POLTejo	0.879-50	1.34-238	<5-348	<0.0075-5.77	12.3-499	<2-332	This study
POLSado	2.35-35	<1-121	<5-558	<0.0075-2.13	11.6-999	<2-113	This study
POLFaro	<0.3-18.3	<1-88	<5-72	<0.0075-0.302	<2-180	<2-81	This study
Sado estuary	1.1-50	0.6-63	1-150	0.02-0.7	2.1-507	2-69	Caeiro. S. et al. 2005
Ria Aveiro	–	–	3.0-45.6	–	51-589	6.0-26.4	Monterroso. P. et al 2003
Douro estuary	–	64-142	6.21-120	0.083-0.353	107-336	21-105	Oliveira et al 2011
Mondego estuary	–	52-70	8.92-29	0.027-0.28	79-139	12.4-43	Oliveira et al 2011
Tejo estuary	–	40-116	25-77	0.367-2.46	160-495	27-169	Oliveira et al 2011
Ria Vigo - sandy /muddy	19.09/37.2	11.72/52.58*	7.93/42.44*	–	30.68/158.38*	23.23/89.09*	Rubio. B. et al 2000

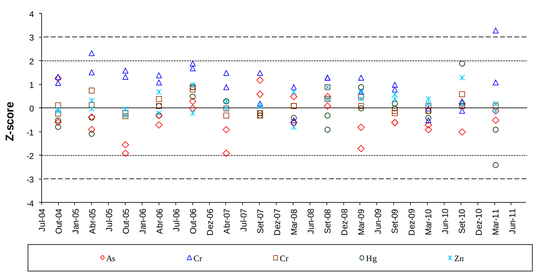
*Average values





PCA is a useful tool to determine the relationships between elements and properties of the sediments. This tool was applied separately for each sample areas. The data points are plotted along the first two components together with each variable contribution to the principal components, that explain most of the variations.

Factor 1 relates fine fraction with different metals in POLFaro, POLSado and POLAveiro, but in POLTejo Factor 1 only shows the principal anthropogenic contamination of metals and the fine fraction is in Factor 2 related with Cr, Cu, Ni and TOC.



The Quality assurance of the results was achieved by the participation in the Quasimeme (Quality Assurance of Information from Marine Environmental Monitoring in Europe) since the first round. Statistical evaluation of the analytical results is made using the Z-score statistical indicator established for each parameter.

|Z|<2 satisfactory
2<|Z|<3 Questionable;
|Z|>3 unsatisfactory

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