

The sediment contamination: assessment of heavy metals mobility

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Introduction: Excessive sediment loadings in rivers and canals, due to erosion process, lower the hydraulic safety of the territory, then dredging operations are needed worldwide. Sediments often contain high amount of contaminants, and their dredging constitutes a serious problem for local authorities. Generally the analysis of the total amount of contaminants is sufficient and necessary to assess sediment quality and contaminants hazard and this analysis is required from local authorities and national legislations (e.g. Italian legislation). The total amount of contaminants does not consider their hazard due to speciation of contaminants [1]. Heavy metals are one of the most harmful substances found in freshwater and sediments, because of their persistence and to their toxicity. Heavy metals can have both a natural and anthropic origin and chemical and physical factors (e.g. pH, clay content, redox status) influence their speciation and mobility, influencing their partitioning in pore water, their bioavailability and adsorption on mineral and organic colloids, etc. Therefore the heavy metals risk assessment requires a comprehensive prediction of its potential adverse effects, which involves the study of metal speciation, partitioning, mobility and toxicity. The aim of this study was to assess the heavy metals hazard though partial dissolution techniques and fractionation studies and to demonstrate how these techniques can better predict their environmental hazard in dredged sediments.

Methods: Sediments (1-10cm) of 5 small reclamation canals were collected in the urban area of Bologna District (Northern Italy). Total metal concentration was detected by acid digestion with aqua regia (HNO₃+HCl, 1:3 w:w) while their available percentage was detected using DTPA 1:2 v:w (pH 7.3). A Five-step sequential extraction was performed according to the scheme of [2]. The concentration of Cu, Cr and Zn in the supernatants were detected by ICP-OES (Ametek, Spectro) with different calibration methods.

The *geo-accumulation Index* (*I_{geo}*) was calculated for some metals as follows:

$$I_{geo} = \log_2 (Me_{tot}/1.5Bn)$$

where *Bn* is the mean regional reference background values reported by the Emilia Romagna region soil services and 1.5 is the correction factor (Müller, 1969).

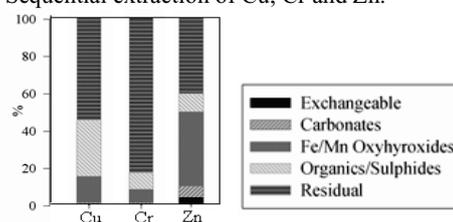
Results: High concentration of Cr, Cu and Zn elements was detected in all total fraction of sediments (Tab.1). According to the qualitative scale given by *I_{geo}*, the hazard of sediments was moderate to strongly polluted of Cu and Zn, while unpolluted of Cr. The DTPA-extr % (Tab 1) showed how Cr availability was always <1 while Cu and Zn was significantly more soluble only in dry extractions.

Tab1. Metals total and available concentration and *I_{geo}*.

	DTPA-ext (%)					TOT (g kg ⁻¹)		<i>I_{geo}</i>
	Wet		Dry		<i>p</i>	Mean	SD	
	Mean	SD	Mean	SD				
Cr	0,16	0,1	nd	nd	nd	162,1	88,5	0,47
Cu	3,72	3,9	15,78	6,4	<0.001	198,05	121,8	1,26
Zn	11,09	10,3	39,43	34,1	<0.05	729,4	881,3	2,68

The five-step sequential extraction of heavy metals is presented in Fig 1 and it showed how the metals were distributed among the different mineralogical phases of sediments.

Fig 1. Sequential extraction of Cu, Cr and Zn.



Discussion: According to the heavy metals total fraction, the sediments are very contaminated from Cr, Cu and Zn. Nevertheless this study demonstrates that a different risk hazard is present for each metal. Cr anthropic enrichment (*I_{geo}*) is null, and Cr is almost immobilized on the residual fraction of sediments (e.g. Cr) and it is non-available, suggesting a geogenic origin and its low environmental hazard [3]. On the contrary, Cu is mostly chelated by organic matter fraction and once sediments are oxidized, high Cu percentage is available because of organic matter mineralization [4]. Similarly Zn availability increases with sediment dredging and this can be linked to the dissolution/formation of Fe oxides and hydroxides during oxidation process [5].

References: [1] Carlon et al (2004), *Env Poll.* **1**:109-115; [2] Hartley and Dickinson (2010), *Env Poll* **3**:649-657; [3] Bianchini et al (2012), *J Soils Sediments* **12** :1145-1153; [4] Prica et al (2010), *Eco. Env. Saf.* **73**: 1370-7; [5] Kazi et al (2005), *Anal. Bioanal. Chem.* **383**:297-304.