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SPECIATION OF HEAVY METALS AT WATER-SEDIMENT INTERFACE

SPECIATION DES METAUX LOURDS AUX INTERFACES EAU-SEDIMENT

SPECIAZIONE DI METALLI PESANTI ALL'INTERFACCIA ACQUA-SEDIMENTO

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Abstract

The objective of the study was to understand the equilibrium relationship between the heavy metals concentrations in superficial water and pore water. At water-sediment interface, the equilibrium rapidly changed and it is influenced by chemico-physical parameters of aquatic ecosystems. The hydraulic safety of Bologna plain (North Italy) depends on network of artificial canals and they are related with natural rivers of Reno basin (Reno river and its tributaries). The natural and artificial water courses flowed in agricultural, urban and industrial land. The heavy metals concentration in water and sediment discriminated the human pressure on the land and their spatial distribution in sediment could predict the hazard of pollution in aquatic ecosystems. We compared the heavy metals concentrations in pore water and superficial water determined in natural rivers and artificial canals, and more pollution in artificial canals than natural rivers was found. Furthermore, the coefficient of partition (log Kd) between water and sediments was calculated to evaluate the bioavailability of heavy metals adsorbed on the sediments. The heavy metals extracted in deionised water at equilibrium after 16 h showed higher concentrations than those determined directly on water samples.

Keywords: *heavy metal, bioavailability, coefficient of partition, sediment sorption, toxicity*

Résumé

L'objectif de l'étude était de comprendre la relation d'équilibre entre les concentrations de métaux lourds dans des échantillons d'eau de surface et l'eau interstitielle. Interface eau-sédiments, l'équilibre a changé rapidement et il est influencé par les paramètres chimiques et physiques typiques des écosystèmes aquatiques. La sécurité hydraulique de la plaine de Bologne (Italie du Nord) dépend du réseau de canaux et ils sont reliés par des rivières naturelles du bassin du Rhin (le Rhin et ses affluents). Les cours d'eau naturels et artificiels qui coule à travers les terres agricoles, urbains et industriels. La concentration de métaux lourds dans l'eau et les sédiments discriminer la pression humaine sur

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l'environnement et leur distribution spatiale dans les sédiments pourrait prédire le risque de pollution des écosystèmes aquatiques. Nous avons comparé les concentrations de métaux lourds dans l'eau des pores et l'eau de surface de certains cours d'eau naturels et canaux, et une plus grande pollution a été trouvé dans les canaux que ceux d'origine naturelle. En outre, le coefficient de partage (log Kd) entre l'eau et le sédiment a été calculé pour évaluer la biodisponibilité des métaux lourds adsorbés sur les sédiments. Les métaux lourds extraits dans de l'eau déminéralisée à l'équilibre après 16 h ont montré des concentrations élevées de ceux qui sont directement déterminés sur des échantillons d'eau.

Mots-clés: métaux lourds, la biodisponibilité, l'eau de partitionnement, l'absorption des sédiments, la toxicité

Riassunto

L'obiettivo dello studio è stato quello di capire il rapporto di equilibrio tra le concentrazioni di metalli pesanti nei campioni di acqua superficiale e acqua interstiziale. All'interfaccia di acqua-sedimento, l'equilibrio è cambiato rapidamente ed è influenzato dai parametri chimico-fisici tipici degli ecosistemi acquatici. La sicurezza idraulica della pianura bolognese (Nord Italia) dipende dalla rete di canali artificiali ed essi sono collegati con fiumi naturali del bacino del Reno (fiume Reno e i suoi affluenti). I corsi d'acqua naturali e artificiali scorrevano attraversando terreni agricoli, urbani e industriali. La concentrazione dei metalli pesanti in acqua e sedimenti discriminano la pressione umana sull'ambiente e la loro distribuzione spaziale nel sedimento potrebbe predire il rischio di inquinamento degli ecosistemi acquatici. Abbiamo confrontato le concentrazioni di metalli pesanti nelle acque interstiziali e acque superficiali determinati corsi d'acqua naturali e canali artificiali, e un inquinamento maggiore è stato trovato nei canali artificiali rispetto a quelli naturali. Inoltre, il coefficiente di partizione (log Kd) tra acqua e sedimenti è stato calcolato per valutare la biodisponibilità di metalli pesanti adsorbiti sui sedimenti. I metalli pesanti estratti in acqua deionizzata ad equilibrio dopo 16 h hanno evidenziato concentrazioni più elevate di quelle direttamente determinato su campioni di acqua.

Parole chiave: *metalli pesanti, biodisponibilità, il partizionamento acqua, sedimenti assorbimento, tossicità*

Introduction

Human pressure on the environment is an increasing problem throughout the world. Agriculture, industry, transport, domestic activities, etc. produce a high pollution level in the environment with consequent hazard for animals, plants and also for humans (Yi et al, 2011; Uluturhan and Kucuksezgin, 2007). Superficial waters are affected by human pressure, contributing to the diffusion of pollution deriving from erosion, runoff, discharges, atmospheric depositions, etc. (Varol et al, 2012) thus decreasing the quality and safety of the ecosystem. For this reason, the European Water Framework Directive (WFD 2000/60 EC) recommends the monitoring of water quality not only by chemical and microbiological parameters but also by the definition of ecological status concept (Tueros et al, 2009). Contaminants are not necessarily fixed permanently by the sediments and, under changing environmental conditions, they may be released into the water column by various processes of remobilization (Ferronato et al, 2013; Sarmami et al, 1992). Chemical and physical factors (e.g. pH, clay content) influence the mobility of contaminants, e.g. heavy metals, depending on their speciation capacity to dissolve in pore water or their tendency to be adsorbed on sediment colloids (Carlon et al 2004), and face an ongoing process of stabilization and remobilization of contaminants within the water column and the sediment (Lu et al, 2000). These complex interaction processes between water and sediments define the hazard of heavy metals in aquatic environments regulating both their mobility and behaviour (Jung et al, 2005). Today's Bologna plain (Nothern Italy) is the result of extensive reclamation works carried out in the territory at the end of the 19th century with the advent of the steam engine, involving the construction of numerous networks of artificial canals; for this reason water management is a very important issue for both hydraulic safety and irrigation purposes on agricultural land. The ecosystem quality depends on the concentration of contaminants discharged into the superficial waters by human activities (e.g. wastewater from municipal and industrial plants, drainage from agricultural soils, ascent of brackish waters, etc) (Vittori Antisari et al, 2010) and the heavy metal enrichment of sediments. The main objective of this work was the evaluation of the quality of both superficial water and sediments in a natural basin (Reno river and its tributaries) and in a network of artificial reclamation canals in the plain. For these purposes, the heavy metal concentration in the superficial water, pore water and sediments was determined. Furthermore, the heavy metal concentration in superficial water samples were compared with that determined after the deionised water extraction from sediments for 16h in order to establish the most suitable method to define the real heavy metal partitioning in the system (Carlon et al, 2004; Jung et al, 2005).

Materials and Methods

Study area

The study area is in the Bologna district (Emilia Romagna region, Northern Italy) which is one of the most productive districts in the Po Plain. The territory is strictly linked to water management for both hydraulic and productive reasons. The river Reno and its tributaries (Idice, Samoggia, Santerno and Sillaro) flow down from the Apennines and on entering the plain their bodies are adjusted to become artificial, thanks to human manipulation of the territory in order to avoid hydraulic problems. Moreover, in the plain courses, the rivers cross urban, industrial and craft settlements (Vittori Antisari et al., 2010). The natural water bodies, whose morphology and characteristics have been described in Ferronato et al 2013, are characterized by a low level of human pressure in their hilly courses, due to the sparsely inhabited territory and few industrial settlements impacting river waters. The network of artificial canals flows into the plain collecting water from soil

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drainage and rainfall, and in the summer the canal water is used for irrigation. The canals are affected by several critical points of pollution, e.g., wastewater treatment plants, municipal discharge due to new residential neighbourhoods, agricultural land etc. Figure 1 shows the study area and the location of the sampling points. The black squares correspond to the natural river water and sediment, black rounds refer to canal samples. Data presented in this work refers to the sampling survey carried out in summer and winter 2011- 2012.

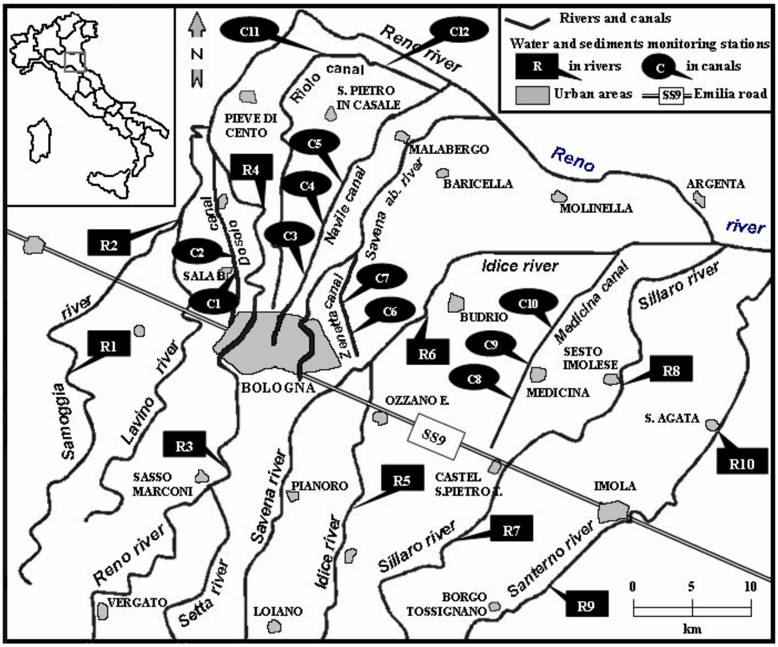


Figure 1
Map of the Reno river basin and location of the sampling stations on rivers and canals.

Rivers			Canals		
Code station	Water bodies	Coordinate reference system WGS84 – UTM 32	Code station	Water bodies	Coordinate reference system WGS84 – UTM 32
R1	Samoggia	666733 E – 4926826 N	C1	Dosolo	681220 E – 4937559 N
R2	Samoggia	677431 E – 4943376 N	C2	Dosolo	681261 E – 4937772 N
R3	Reno	679718 E – 4918556 N	C3	Navile	687945 E – 4940155 N
R4	Reno	683788 E – 4942528 N	C4	Navile	689910 E – 4942165 N
R5	Idice	696531 E – 4931466 N	C5	Navile	691833 E – 4944913 N
R6	Idice	679185 E – 4913492 N	C6	Zenetta	692640 E – 4932080 N
R7	Sillaro	704445 E – 4914954 N	C7	Zenetta	692125 E – 4933805 N
R8	Sillaro	717635 E – 4926470 N	C8	Medicina	708265 E – 4922593 N
R9	Santerno	710886 E – 4908345 N	C9	Medicina	710380 E – 4929089 N
R10	Santerno	728026 E – 4924617 N	C10	Medicina	710922 E – 4930141 N
			C11	Riolo	692356 E – 4957688 N
			C12	Riolo	693485 E – 4957360 N

Heavy metal analysis in water and sediment samples

The water and sediment samples were collected in July and November 2011 and 2012. Water was sampled from the middle of the water courses. Borosilicate bottles were used for water storage and kept at 4°C until analysis. pH and electrical conductivity (EC) values were measured by Crison electrode (pH-meter, Crison) and Hack Lange Conductimeter, respectively, within 24h from the sampling. Furthermore, 50ml of water was filtered with Whatman 42 and acidified with HNO_3 suprapure (Carlo Erba, at the ratio 1:100 v/v) then stored at 4°C. Heavy metal content (Cd, Cr, Cu, Zn, Mn, Fe, Ni and Pb) was measured using Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP –OES) (Ametek, Spectro). In order to separate pore water, an aliquot of sediment samples was centrifuged at 10000 rpm for 20 min according to Chapman (2002). The pore water was acidified as described above. Detection limits of the instrument (DL) were 0.25, 0.76, 1.2, 0.34, 0.13, 0.70, 1.05, 4.92 µg L^{-1} for Cd, Cr, Cu, Zn, Mn, Fe, Ni, Pb, respectively.

Sediment samples were air dried and sieved at 2mm and fine powder was obtained with agata mill. The pseudo-total concentration of Cd, Cr, Cu, Zn, Fe, Ni and Pb was determined by Aqua Regia extraction: 0.250 g were first digested in a microwave with a mixture of 6ml HCl and 2 ml HNO_3 suprapure (Carlo Erba) and then analyzed by ICP-OES. Analyses were all made in duplicate and both international (BCR) and internal (MO1) standards were determined in every 20 samples, while in every 30 samples a blank sample was determined. The water extraction was carried out on a 2mm sediment fraction using MilliQ Water in a ratio of 1:10 w:v (Sahuquillo et al, 2003). Briefly, 10g dry sediment was shaken for 16h at room tempertaure to reach partition equilibrium (Carlon et al, 2004), then centrifuged at 10000 rpm and the supernatant was filtered with Whatman 42. The water solution was determined by ICP-OES according to Vittori Antisari et al. (2013). The partitioning coefficient water soluble/sediment (Kd) was then calculated from the ratio between the pseudo-total element concentration and those of the water extracts as reported by Jung et al. (2005):

$$Kd = \log [Me(SED)/Me(W)]$$

Where Kd is the coefficient of partition; Me is the element concentration determined in sediments (SED) and water extracts (W), respectively.

Data Analysis

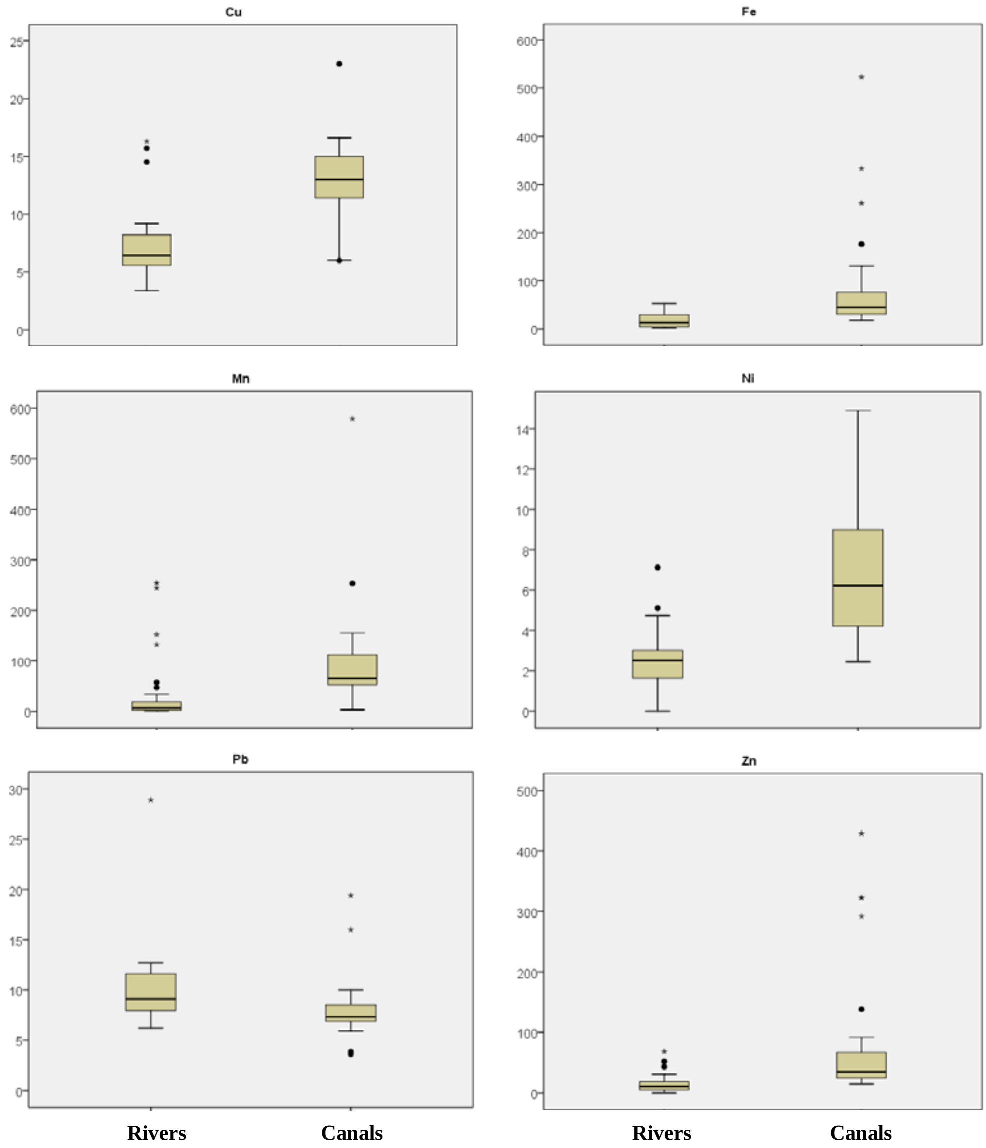
Descriptive statistics (maximum and minimum values, 25th, 50th and 75th quartiles, and outlier values) for total and bioavailable heavy metal content were used to describe heavy metal variability in the water and sediment samples. Outlier values are presented by ● when the values are between 1.5 and 3 times higher than the Interquartile Range (IQR) and with * when the values is 3 times greater than IQR. Mean and Relative Standard Deviation (RSD) was also calculated for each heavy metal concentration in the river and canal populations. Boxplots were realized by SPSS software.

Results and Discussion

Heavy metal concentration variability in water and sediments

The boxplot of the heavy metal concentration in the water samples is shown in Figure 2, in which the population is divided into quartiles and the minimum and maximum values are also reported, while the mean values ± RSD of the populations are presented in Table 1.

Figure 2 - *Boxplot of trace element in water samples of canals and rivers. Data are expressed as µg L^{-1}. Outlier values are also presented. Different scales are presented for the two populations.*



Cd and Cr data were not shown because their concentration was almost always below the Detection Limit (DL) values. Statistical differences ($p<0.05$) were found between the two data sets except for Cu and Pb; high variability within the two populations was indicated by several outlier values, suggesting that water analysis can detect efficiently the status of the system and record any irregular values when they occur during the monitoring survey (Solmini et al, 2006; Borja et al, 2004). These outlier values are very important to evaluate the quality of an ecosystem because they are usually localized at critical sampling points that describe the hotspots of the system.

Table 1
Mean values of heavy metals concentration in canals and rivers water samples ±RSD.
Ns=not significant; *p<0.05; **p<0.01

	Cd		**Cr**		**Cu**		**Fe**	
	µg/l	RSD	µg/l	RSD	µg/l	RSD	µg/l	RSD
Canal	0,3	0,4	0,8	0,4	5,7	0,9	105,2	1,3
River	0,2	0,1	0,6	0,9	5,6	0,7	20,8	1,2
	**		**		Ns		**	

	Mn		**Ni**		**Pb**		**Zn**	
	µg/l	RSD	µg/l	RSD	µg/l	RSD	µg/l	RSD
Canal	121,3	2,5	5,9	1,1	5,5	0,7	59,9	1,5
River	24,5	2,3	2,6	0,8	7,8	1,0	22,6	2,0
	Ns		**		Ns		**	

For instance, the maximum value of Fe (747 $\mu g\ L^{-1}$), Mn (1884 $\mu g\ L^{-1}$) and Ni (29 $\mu g\ L^{-1}$) concentration was localized in one single canal (Dosolo) into which wastewater is discharged from a water treatment plant. The highest Pb concentration (54 $\mu g\ L^{-1}$) was found in rivers in a Reno tributary (River Samoggia) after the confluence of some drainage water courses. Table 2 presents the mean values of total heavy metal concentration in the sediments. Statistically significant differences between river and canal samples were found for all the heavy metals considered ($p<0.001$) except for Fe and Mn ($p=0.08$ and $p=0.37$ respectively). Higher concentrations of contaminants were found in canal sediments than in those of rivers and in many cases the concentration exceeds the threshold set by Italian law (D.lsg. 152/2006), highlighting a very bad environmental status of these water courses.

Table 2
Mean values of heavy metals concentration in canals and rivers sediment samples ±RSD.
Ns=not significant; *p<0.05; **p<0.01

	Cd		**Cr**		**Cu**		**Fe**	
	mg/kg	RSD	mg/kg	RSD	mg/kg	RSD	g/kg	RSD
Canal	0,8	0,8	160,5	0,5	205,1	0,7	30,3	0,5
River	0,1	0,4	97,9	0,6	30,6	0,6	39,2	0,6
	**		**		**		Ns	

	Mn		**Ni**		**Pb**		**Zn**	
	mg/kg	RSD	mg/kg	RSD	mg/kg	RSD	mg/kg	RSD
Canal	1219,8	0,6	77,8	0,5	75,2	0,7	705,6	1,2
River	1398,7	0,6	47,6	0,5	26,1	1,3	80,5	0,5
	Ns		**		**		**	

Comparing river and canal samples, it is evident that canal sediments absorb high quantities of elements and this is probably due to a higher transport rate in the canal flow than in that of rivers. Zinc (Zn) and Copper (Cu) are essential microelements for many organisms but high concentrations can be toxic for the environment; indeed Cu is a well known biocide (Borkow and Gabbay 2005).

The Italian law (D. lsg 152/2006) equates the sediments to soils for residential use establishing the threshold of 120 mg/kg and 150 mg/kg for Cu and Zn, respectively. Generally, concentrations below the legislative threshold were found in river sediments, while in canals mean values of 205 mg kg^{-1} for Cu and 705.6 mg kg^{-1} for Zn were found; maximum values of 538.9 mg kg^{-1} of Cu and 3768.5 mg kg^{-1} of Zn were detected in two canals near water treatment plants (Navile and Dosolo). Manganese (Mn) concentration is very high in both artificial canal and river sediments (1219.8 mg kg^{-1}± 0.6 RSD and 1398.7 mg kg^{-1}± 0.6 RSD respectively). Even though high Mn levels in water can be toxic for ecosystems (Kuperman 2004 and Norwood 2007) no limit value is yet present in the Italian legislations. Chromium (Cr) is a very toxic element but its hazard depends on the Cr speciation: the Cr^{6+} form is more dangerous than Cr^{3+}, which is essential in low concentrations; the threshold of total Cr in sediments is 120 mg/kg; this value is exceeded by the mean of the canal concentrations (160 mg kg^{-1}) but generally the main form in the sediment ecosystem is Cr^{3+}. Nickel concentration is below the threshold in both canal and river sediments and in some cases the high background in the plain for Cr and Ni may be due to geochemical anomalies rather than anthropogenic pollution (Bianchini et al., 2012). In the present case, the high amount of Cr in the canal sediments seems to be derived from anthropogenic discharge, since the Po river sediment has a low influence in this territory (Bianchini et al., 2012). Cadmium (Cd) and Pb are typical anthropogenic heavy metals and their concentration in the sediments of both canals and rivers is below the legislative limit (2, 100 mg kg-1, for Cd and Pb respectively). The legislative limits represent a great burden for Environmental protecting and managing agencies: in fact, as they have to guarantee the quality of the system from both environmental and hydraulic points of view, every year tons of sediment have to be dragged for the hydraulic maintenance of the territory. When sediments exceed the threshold of Italian law for some elements, they have to be transported and managed only for commercial use or waste materials, at a high management cost. As reported by many authors (Okoro et al, 2012; Campanella et al, 1995) the total concentration of heavy metals in soil or sediment does not always represent the real environmental risk. Therefore, bioavailability tools should be improved for environmental hazard analysis.

Regarding the total concentration analysis, river ecosystems are less contaminated than those of canals and this may be due to the lower human pressure on the water courses (mainly in their Apennine flow) but also to the presence of riparian vegetation on their benchmarks which can have a positive effect on contaminant mitigation. Increased absorption of heavy metals in canal sediments may be due to their different characteristics as well as the presence of carbonate, the colloidal fraction and the amount of dissolved organic matter. In fact, the presence of suspended organic matter triggering oxidation processes in the water-sediment interface may contribute to heavy metal precipitation (Namiesnik and Rabajczyk, 2010). Since the water samples do not show a hazard level of contamination we can conclude that the contaminants are still capable of being adsorbed in sediments, and the transport of elements through the flow may help to dilute heavy metals in freshwater. Moreover, the transport of contaminants contributes to the accumulation of heavy metals downstream and onto the sediment.

Heavy metal distribution in water phases

The water phase is very important to understand the chemical and physical processes that occur between water and sediment interfaces. The comparison among the heavy metal concentrations in superficial water, pore water and water extraction from sediments for 16 h is shown in Figure 3a,b.

Each element is presented in a boxplot and its behaviour is compared between river and canal sediment. Pore water describes the weakest bond at the water and sediment interface, representing the part of water that has the closest interaction with the negative charges of the surface sediment, while the water-sediment equilibrium approach describes the heavy metal solubility in controlled conditions by leaching processes (Carlon et al (2004). Generally, higher amounts of heavy metals were determined in pore water than in the other phases.

Figure 3a - *Boxplots present heavy metals (Cu, Fe) variability on water samples, pore water and solubility of heavy metal after water equilibration. Data are expressed in µg kg-1. Different scale are presented for rivers and canals samples.*

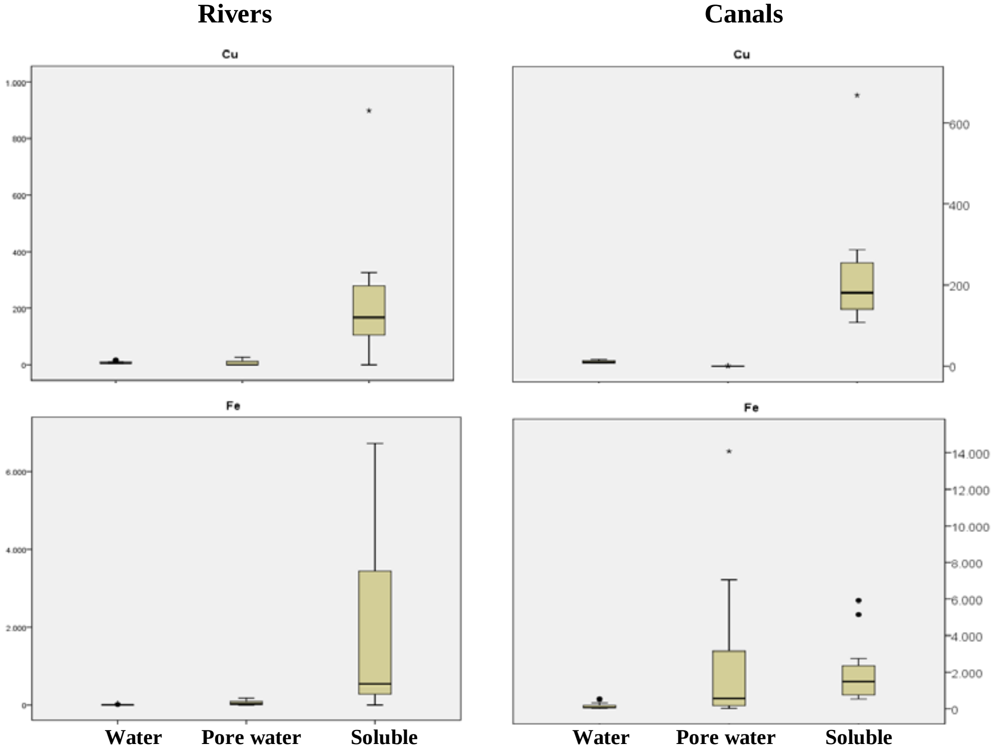
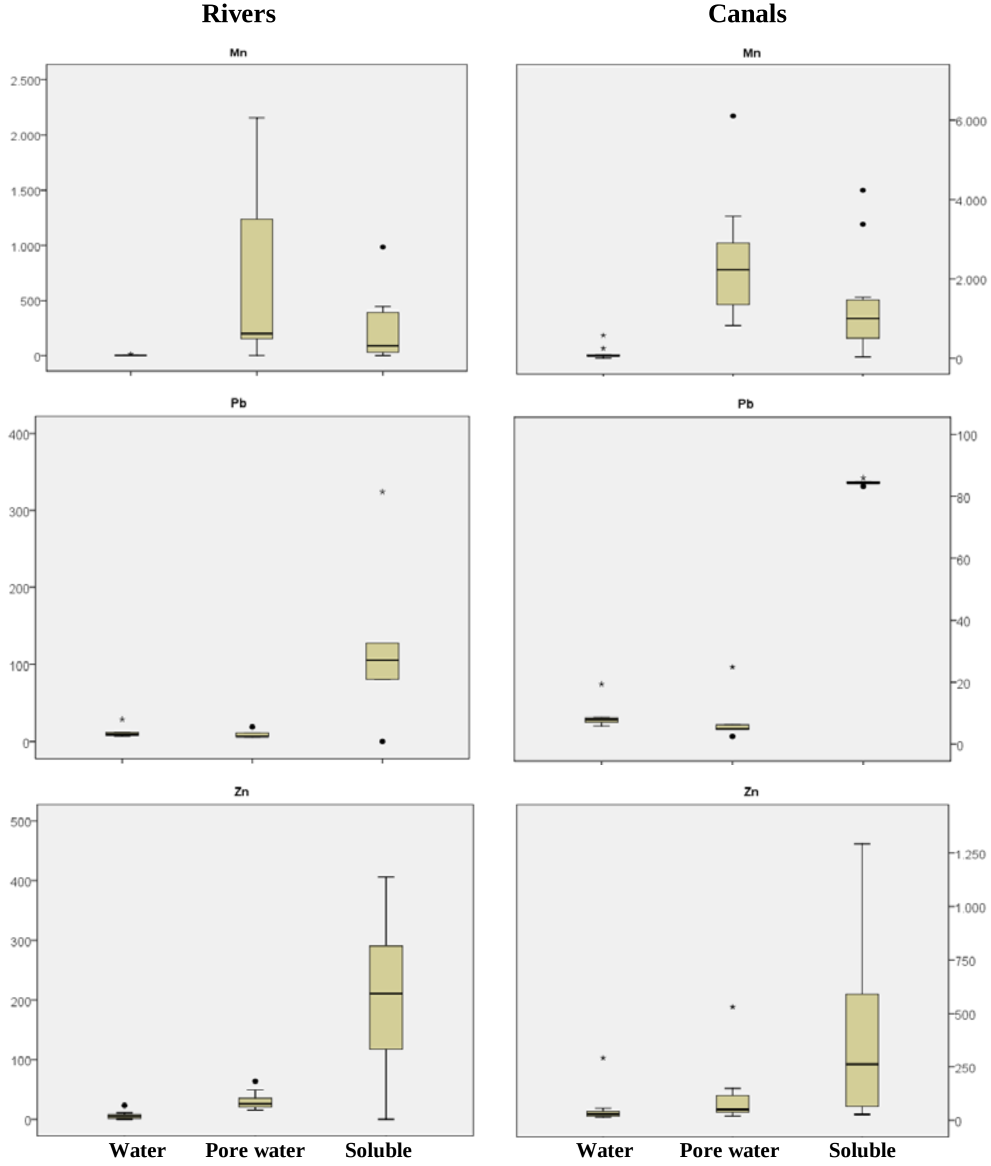


Figure 3b - *Boxplots present heavy metals (Mn, Pb, Zn) variability on water samples, pore water and solubility of heavy metal after water equilibration. Data are expressed in µg kg-1.*

Different scale are presented for rivers and canals samples.



The canal sediments released higher amounts of heavy metals than those of rivers, and this may be due to a high content of clay and silt in the canal sediment. Iron (Fe) and Mn show high solubility and availability in the pore water of canals. Iron concentration decreases from 2532.2 µg L^{-1} in the canal pore water to 20.42 µg L^{-1} in that of rivers, and the same trend is shown for Mn (from 2410.5 µg L^{-1} to 166.9 in canal and river pore water, respectively). Iron concentration in water extraction at equilibrium for 16h shows high values for both canals and rivers (10231 µg L^{-1}

and 1955.8 µg L^{-1}, respectively), while the Mn amount released from the canal sediments is higher than that from rivers.

The redox condition of the water-sediment interface affects the solubility of Fe and Mn; indeed Fe and Mn released from the sulphide oxidation can be re-precipitated and deposited as insoluble oxid/hydroxides (Hartley et al 2010).

As a consequence, anoxic conditions, more evident in canal sediments, can contribute to a higher Fe and Mn release in both pore water and soluble fraction than in river sediments. Iron mobility in river samples is detected only in the water equilibrium phase and this could be also due to the lack of organic matter and weak bond. The boxplot of Zn, Cu and Pb amount show a higher availability in canals than in rivers, and this could be due to the sediment texture and to a low affinity with the adsorbent phase. The superficial water is very metal-poor (Cu<Pb<Zn), but in pore water and in leaching experiments their concentration increases and different availability (Pb<Cu<Zn) is found. The mean of available fraction obtained by water extraction is 78.8 and 66.3 µg L^{-1} for Pb, 195.8 and 167.8 µg L^{-1} for Cu and 587.6 and115.7 µg L^{-1} for Zn in canals and rivers, respectively. The Ni and Cr partition in the water is very low (data not shown) as the sediments do not release these elements in the water-soluble phase (Bianchini et al 2012). The ratio between total and soluble fraction was used to describe the tendency of the element to be retained by the sediment or to remain in the water and consequently to be available for transport and biological uptake (Anderson and Christen 1998, Jung et at, 2005) and the coefficient of partition (log Kd) is shown in Figure 4.

A high value of Kd (log Kd>2.9) underlines that the element has low solubility and is preferentially sediment-associated while a low value (log Kd<2.9) means that the element has high solubility and is less sediment-associated. (Jung et al, 2005). This partition coefficient depends on the main chemico-physical properties of the sediments, e.g. pH and different texture.

The increased variability of the data in rivers could be due to the variability of the composition of the sediment, where upstream stations are more gravelly and sandy while downstream stations are characterized by silt-clay sediments. Iron solubility in both canal and river sediments is low, showing a high affinity with the sediment (log Kd>4), and the same trend was determined for Mn (log Kd 3.2 and 3.9 for rivers and canals, respectively).

The partition coefficient (log Kd) is higher in canal sediments than in those of rivers, showing that in canal sediments a high stabilization of metals is found even if the total metal concentration in these is higher than in rivers. In canal sediments the log Kd for Zn, Cu and Pb is lower than 2.8 and for Cu and Zn stabilization the high amount of aggregates and organic matter could explain their higher sediment-affinity in canal sediments. The weak bond of river sediments may be due to less organic matter and coarse texture. The log Kd value for Pb decreases from rivers (logKd 1.9±0.9) to canals (logKd 2.9±0.3) showing that Pb is a quite soluble element that could be absorbed by stable bond by organic matter and sulphides, as in the case of canals, otherwise it can be a high soluble element in the environment, as in the case of sandy rivers.

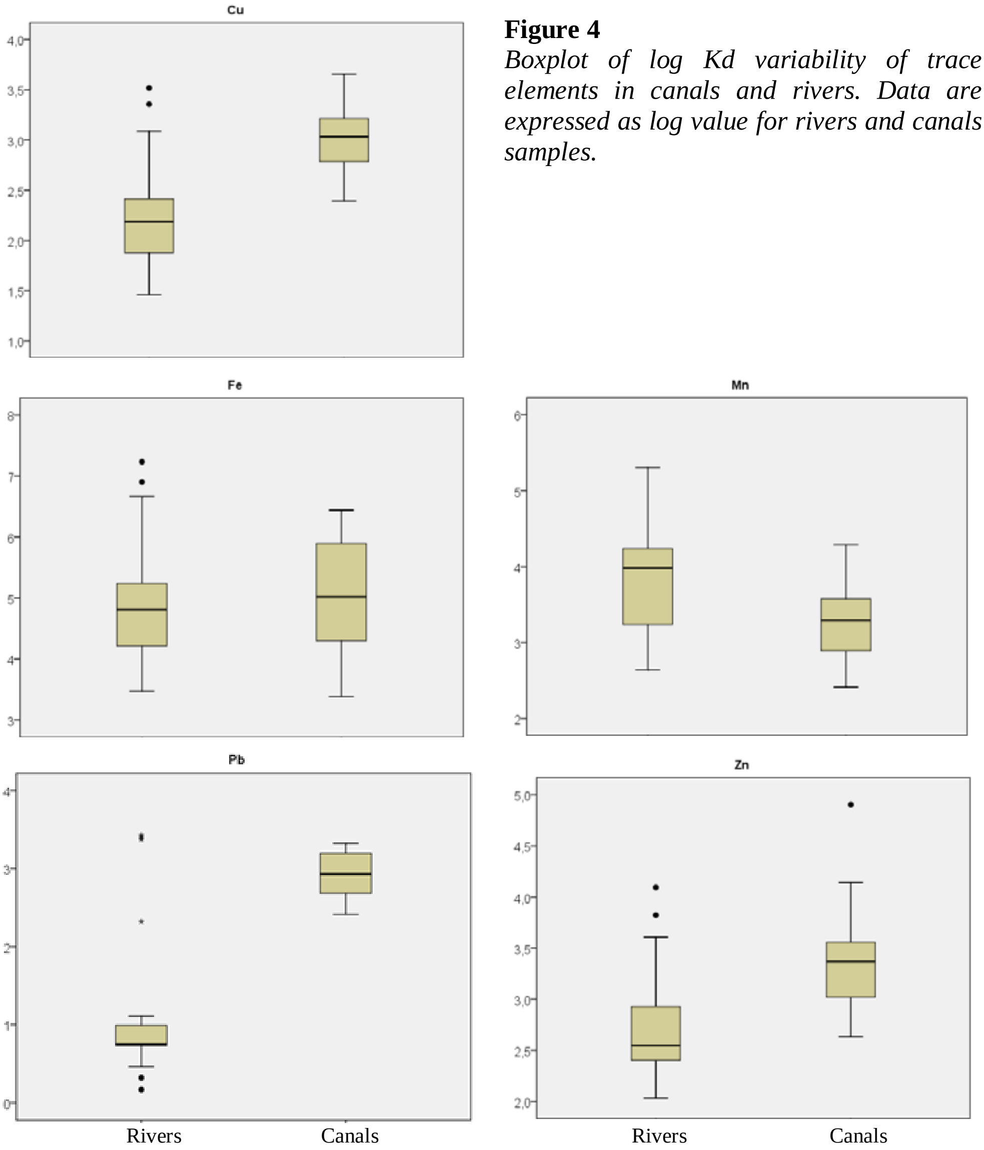


Figure 4
Boxplot of log Kd variability of trace elements in canals and rivers. Data are expressed as log value for rivers and canals samples.

Conclusions

In a fluvial system water analysis can record each irregular discharge in water but cannot predict or describe a tendency of the system quality. Water monitoring should be carried out with a greater frequency in order to monitor any variation in the quality of the system. However, as the monitoring work can be very long and difficult, sediment analysis could prove a better approach to describe the quality of the system. Sediment equilibrium changes more slowly than water equilibrium and can better record the interface relationship between heavy metals in a water/sediment system.

The analysis of pore water and the equilibrium approach describe the real mobility of elements by considering the status of the system, according to its physical characteristics and its redox conditions. In this system we demonstrated that sediment can absorb a great deal of heavy metals and can function as a "pollutant sink" according to its carbonate and organic matter amount. In rivers, the system was found to be weaker in holding heavy metals and the environmental risk is therefore greater even though the human pressure is lower.

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