

Bioavailability of metals in soils irrigated by synthetic wastewater: Metal speciation

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Abstract: In Lebanon, Bekaa valley is an agricultural zone; during the dry season, water is withdrawn from Litani River for irrigation which is mostly domestic and industrial waste water. Metal mobility, bioavailability, or potential risks can be anticipated by metal speciation in soil and water. The objective of this study was to investigate the speciation of metals in soil and water of upper Litani basin. Soils samples were subjected to a modified BCR sequential extraction technique that operationally extracts metals as acid soluble, reducible, oxidizing, and residual fraction. Metal content in each fraction and total metal in water were determined by AAS and ICP-MS techniques. Sediment pH, Eh and TOC and macro water parameter were determined. Speciation of metals in water was predicted PHREEQC geochemical computer model. Results indicated in non-residual fraction respectively highest average % of total metal are in reducible and acid soluble (Mn: 27 %, 18; Zn: 18 %, 34%; Cr: 27%, 34%; As: 28% , 20%); in oxidizing and acid soluble (Cu: 25%, 10%; Ni: 24%, 33%; Cd: 16%, 23%, Hg: 23%, 12%). Metal speciation variations among sites were related to the levels of TOC and Eh and water BOD. The ICF values indicate a considerable contamination for As, Cd, Cr, Ni; and GCF indicated 50 % of sites of considerable contamination. Speciation in water predicted existence of the toxic free aqua ion (Mn: 6-97%; Zn: 35-89%; Ni: 60-90%; Cd: 35-82%). These and soil GCF values reflect the high degree of metal bioavailability, toxicity, and potential risk.

Key words: wastewater, soil, metal speciation, bioavailability, Upper Litani basin, Lebanon

1. INTRODUCTION

In Lebanon, the Bekaa is an agricultural zone and best known as the food reservoir of the country (Ammar, 2014). Its soils are mostly irrigated by the Litani River and/or ground water. However, the Litani River watershed receives different pollutant sources such as industrial and domestic waste water (Wazne and Korfali, 2016). During the dry season, water is withdrawn from Litani River for irrigation which is mostly wastewater. Irrigation with wastewater is known to contribute significantly to the heavy metal concentrations of soils (Deshmukh et al., 2015; Farahat and Linderholm, 2015). These metals can bio-accumulate in plants and animals, and eventually passing to humans through the food chain (Gu et al., 2016). Thus the soils of the ULB are potentially subjected to heavy metal disposal resulting from previously mentioned reasons. Nonetheless, the behavior of metals in the environment cannot be reliably predicted on the basis of their total concentration. Whereas, the chemical fractionation, speciation of metals in soils can provide information on metal mobility, bioavailability, or potential risks that it poses to the environment and to human health (Sadec et al., 2016). Sequential extraction methods have been widely applied to characterize the chemical forms of metal elements present in soils. Metals bound in the different geochemical fractions in soils are extracted by different reagents, where several chemicals are used consecutively to extract operationally defined phases from the soil in a set of sequence from the most labile to the most resistant. One of these is the modified BCR sequential extraction technique by Rauret et al. (1999) that extracts metals from different soil fractions, operationally defined as: acid-extractable, reducible, oxidizable, and residual (Wali et al., 2014). The first three fractions are the labile ones affected by environmental conditions, such as pH, redox potential, organic content and can be easily mobilized and be bioavailable. Moreover, the degree of soil contamination can be assessed by the individual contamination factor (ICF) and global

contamination factor (GCF) and these would reflect the overall potential risk caused by the toxic metal to the environment (Naser et al., 2015). In parallel to these the forms of chemical metal species in the water column, the organic and inorganic metal complexes and the free solvated metal ions (toxic metal specie), could be used as a predictor of bioavailability (Korfali and Jurdi, 2011; Ahmad et al., 2014; Magu et al., 2016). The free ion activity model (Morel 1983) states that there is a correlation between the toxicity of a metal to an organism and the thermodynamic activity of the free aqua-metal ion. Few studies have been conducted in Lebanon on metal speciation of bed load river sediments, but no citation to present on metals speciation in Lebanese soils. Previous study tackled total metal content in soils of Upper Litani Basin (Korfali et al., 2014). Hence the objective of this study is to investigate the speciation of metals in soil and water of the upper Litani basin so as to establish the metal potential mobility, bioavailability and predict their potential risks.

2. MATERIAL AND METHODS

2.1 Study area, sampling sites and sampling

The Litani basin is the largest hydrographic basin in Lebanon flowing longitudinally from the NE to SW, draining over 20% of the countries area. It is in Bekaa valley between two mountainous chains, 170 km in length with 60 km of tributaries, it springs from Nabeh Al Oleik and drains into the Mediterranean Sea (Ammar, 2014). The details of the rocks outcropping in the ULB basin and soil characteristics were discussed in previous work (Korfali et al., 2014). Basically the soils are red Mediterranean rich in iron oxides and high clay content (Darwish and Zurayk, 1997).

The sampling sites for soils (24 sites) paralleled the sites of earlier work of total metal levels in ULB basin (Korfali et al., 2014). It was observed that most industries and domestic wastewater dispose directly effluents into the river flow and soils irrigated by this river water.

Soil sample were collected during the dry season in accordance to method given by EPA (2014). In parallel water samples were collected from river channel adjacent to soil collection and in accordance with APHA, AWWA, WPCF (2012) standard methods.

2.2 Field methods

Temperature, electrical conductivity (EC_w), total dissolved solids (TDS), pH, and Eh for water were measured at site using (Hach Model 44600 Conductivity/TDS meter), and DO by membrane electrode.

2.3 Water treatment and analysis

The collected water samples were immediately filtered through 0.45 µm pore cellulose filters into two polyethylene bottles. One bottle was acidified with nitric acid to pH < 2 and stored at 4 °C for metal analysis (Fe, Mn, Zn, Cu, Cr, Ni, Cr, Pb and Cd) using AAS ("Shimadzu" AA-6300). The concentrations of As and Hg determined by ICP-MS (Agilent ICP-MS 7500-Ce).

The other bottle was used for immediate analysis using: titration for alkalinity, Ca²⁺ and Mg²⁺; spectrophotometry for NO₃⁻, SO₄²⁻ and PO₄³⁻ and procedures followed standard method of analysis of water and waste water; Cl⁻ was determined by ion chromatography (Ion Chromatograph, "Shimadzu" PIA-100).

2.4 Soil treatment and analysis

Soil samples were air dried, homogenized, plastic sieved and the <75 µm fraction was retained for metal analysis.

A modified BCR sequential extraction technique by Rauret et al. (1999) was used on one gram of each soil sample and the four (operationally defined) fractions were derived:

F1: Exchangeable, water and acid soluble (carbonate) by CH_3COOH (0.11 mol/L), pH=2.85

F2: Reducible (Fe and Mn oxides/hydroxides) by 0.1 mol L⁻¹ $\text{NH}_2\text{OH}\cdot\text{HCl}$, pH=2.

F3: Oxidizable (organic substances) by 0.02 mol L⁻¹ HNO_3 / 30% H_2O_2 and heat; followed by: $\text{CH}_3\text{COONH}_4$ (1.0 mol L⁻¹) at pH=2

F4: Residual (native metals) by 10 ml combination (ratio of 4:1) of concentrated HNO_3 and HClO_4

Details of the procedure are given by Naji et al. (2010) and Tokalioğlu (2012).

Metals in solution of each derived fraction on three replicates were determined using AAS and ICP-MS techniques. Analytical quality control was monitored by analysis of certified reference material of NIST (National Institute of Standards and Technology 2586). Eight replicates of SRM 2704 were analyzed; the percentage relative standard deviation (% RSD) was < 10%. The organic carbon content was determined by carbon analyzer (“Shimadzu” V_{CPN}).

2.4 Software used in analysis

Statistical analyses were performed using SigmaStat (version 3). The speciation of each metal in water was predicted using AQUACHEM (™) software applications interfaced with the geochemical modeling program (PHREEQC). The input data to the modeling program were water measured parameter (Table 1), metals as total content, and modeling was done for each site, not as mean values.

Table 1. Average values of measured water parameters

	Average	Min	Max	SD	%CV
pH	7.83	7.3	8.6	0.34	4.3
Temperature (°C)	22	15	29	3.4	15
Eh (mV)	10.5	-80	120	50	480
Cond. (µS/cm)	987	336	2520	707	72
DO (mg/L)	3.6	0.4	8.5	2.7	74
BOD (mg/L)	790	28	2530	697	88
HCO_3 (mmol/L)	3.4	3.0	3.6	0.23	6.8
Cl (mmol/L)	2.7	0.24	9.2	2.5	93
NO^- (mmol/L)	5.8	0.44	21.7	5.97	103
NH_3 (mmol/L)	28.3	0.73	83.2	29	103
PO_4^3 (mmol/L)	0.170	0.002	1.03	0.31	180
SO_4 (mmol/L)	0.168	0.008	0.700	0.150	90
Ca (mmol/L)	43	16	98	23	54
Mg (mmol/L)	4.3	0.00	13	3.2	74
Fe (µmol/L)	55	0.72	269	83	150
Mn (µmol/L)	4.2	0.18	18	5	119
Zn (µmol/L)	0.75	0.05	3.06	0.9	120
Cu (µmol/L)	0.51	0.06	1.58	0.45	87
Cr (µmol/L)	0.47	0.02	1.92	0.56	119
Ni (µmol/L)	0.63	0.03	2.55	0.70	111
Pb (µmol/L)	0.04	0.005	0.145	0.035	97
Cd (µmol/L)	0.042	0.009	0.134	0.032	76
As (µmol/L)	0.176	0.014	0.667	0.217	117
Hg (µmol/L)	0.036	nd	0.250	0.048	135
pH (sediment)	8.0	7.1	8.8	0.4	5
Eh (sediment)	71	-70	160	71	288
% TC (sediment)	40.7	6.1	79	18	45
% OC (sediment)	17.7	1.0	41.8	11.4	65

3. RESULTS AND DISCUSSION

3.1 Speciation of Metals in Soils

Table 2 presents the speciation scheme (metals in the four operationally defined fractions). The

results of the studied twenty four sites were combined for each element, and the data is presented as mean fraction metal content (mg metal kg^{-1}). Figure 1 and Figure 2 present the mean percentage of the metal from total in the different soil fractions.

Table 2. Mean metal content in the different soil fraction

Metal Content (mg kg^{-1})	F1	F2	F3	F4
Fe	2058	8286	3488	18527
Mn	133	167	51	246
Zn	20	16	11	47
Cu	6.0	3.8	12.0	25.0
Cr	54	41	8.0	40
N	35	8.0	24	31
Pb	3.5	2.0	4.3	9.5
Cd	1.67	0.43	0.98	1.62
As	4.12	4.99	1.35	6.90
Hg	0.87	0.31	1.42	2.69

The speciation of Fe and Pb were mainly in the native residual soil fraction. The mean percentage speciation of Fe in residual fraction was 46%, which most probably are due to red Mediterranean soils, rich in iron oxides. While, the mean percentage speciation of Pb in residual fraction was 67%, and low percent (27) at site 13, that exhibited high percentages in F1 (33%) and a high total Pb content 164 ppm. This indicates a site receiving pollutant from the solid waste dump of the asphalt industry at this site (Korfali et al., 2014).

3.2 Speciation of Mn, Zn, Cr, As

Speciation results (mean values) of Mn, Zn, Cr, and As indicated the highest percentages of these metals were in Mn and Fe oxide hydroxide fraction (reducible, F2), and acid soluble (F1) Figure 1. High percentages in these fractions indicate pollutant inputs and metal bioavailability by environmental changes. The mean percentage of Mn in F2 and F1 were respectively 27% and 18%, with a range between 15% and 35%, and 5% and 40%. The association of Mn in Fe oxides / hydroxide has been reported in literature (Jackson, 2015). For Zn, the mean percentage in F2 and F1 were approximately 18%, with a range between 9% and 31%, and 5% and 35% respectively. High percentages in F1 were at sites with low sediment Eh values (site S1 and S17). Similarly As speciation, with higher percentages in F2 than F1. The mean percentage of As in F2 was 27%, with a range between 6% and 40%; F1 it was 21%, with a range between 3% and 40%. The association between Zn and As with Fe and Mn oxide hydroxide fraction arises from the strong binding of Zn and As to Fe oxides that cannot be released except the matrix subjected to reducing conditions (Suda and Makino, 2016). Whereas Cr speciation were higher in F1 than those in F2. The mean percentage of Cr in F2 and in F1 were respectively 27%, and 35%, with a range between 17% and 34%, with a wide range in F1 between 5% and 49% (sites 6 and 8). These sites are in the vicinity of tanneries that discharge their wastes in river and/or on adjacent soils; which may justify the high levels in F1. Our results were in line with Reijonen and Hartikainen (2016) that indicate Cr speciation in Fe and Mn oxides/hydroxides soil fraction. The speciation of Cr in the reducible fraction is mainly influenced by the oxidizing environment of soil that enhance the formation of the insoluble oxides/ hydroxides of Fe and Mn. Whereas, under reducing conditions, these oxides and hydroxides forms are reduced to soluble Fe and Mn types, leaching Cr metals and decreasing the levels of Cr in F2 fraction. This is justified by the lower percentage of Cr at site 17 (17% and Eh = -70 mV).

Hence, the high speciation of Zn, Cr, As in F1 resulted probably either from direct waste discharge into soil and/or to the reducing media of many sites that released these metals from the reducible fraction and consequent association with the most labile fraction F1.

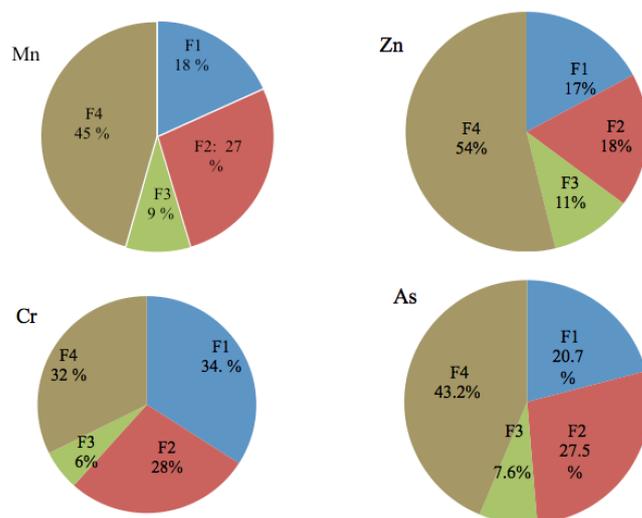


Figure 1. Mean percentage speciation of Mn, Zn, Cr, As in the different soil fractions

3.3 Speciation of Cu, Hg, Ni, Cd

The soil labile fractions, the acid soluble (F1) and organic (F3) were of significance to Cu, Ni, Cd, and Hg speciation (Figure 2). Copper and Hg showed higher speciation in F3 than F1. The mean percentage speciation in F3 were for Cu 25%, and Hg 23%, and respectively with range between 18% and 34%; and between 8% and 36%. Association of Cu and Hg with organic fraction results from the stability of Cu and Hg organic complexes and ease of complexation with humic and fulvic acids (Bavec and Gosar, 2016). While, the mean percentage of Cu in F1 was 10%, with a range between 5% and 15% at site 19 that showed lowest speciation in organic fraction. This site also had very low DO levels in water (DO = 1.06 mg/L), high levels of BOD (1625 mg/L) and low OC % in sediment (0.95%) as indicated in Table 1. Hence the high discharge of waste water at this site, high in organic material was probably accountable to the high oxidation of organic substances releasing metals from organic sediment fraction and association with the most labile fraction F1. Likewise for Hg, the mean % of Hg in F1 was 13%, with a range between 1% and 26% at site 11, that had low speciation in organic fraction (13%), very low levels DO in water (0.38 mg/L), very high levels of BOD (2530 mg/L) and lower organic soil content (Table 1). However, the percentage speciation of Ni and Cd in soil fraction F1 was higher than fraction F3. The mean percentage in F1 were 22% for Cd and 33% for Ni, with a range between 7% and 40%; and between 6% and 48%. Previous studies indicated the high speciation of Cd in carbonate fraction (F1) of Lebanese sediments, the Nahr-Ibrahim River and Qarraoun Reservoir. The strong high association of Cd to carbonate fraction is most probably due to the similarity of the ionic radii of Cd (0.97 Å) and Ca (0.99 Å), where Cd will enter the calcite crystal as a camouflaged element and precipitate with carbonates (Korfali and Davies, 2004; Korfali and Jurdi, 2011). Furthermore, earlier studies exposed the organic fraction (F3) not to be of significance to Cd speciation, explained by Cd smaller organic stability coefficient than other metals (Forghani et al., 2015). The mean percentage of Cd in F3 was 16%, with a range between 3% and 30%. The high association of Cd to organic soil fraction is most probably due to the high % OC in soils, which is reflected at site 10 (% OC was 32, and Cd in F3 was 30%). In regard to Ni, previous studies designated high association of Ni with reducible sediment fraction (Korfali and Jurdi, 2011). Whereas, this study revealed a higher association with acid soluble (F1), mainly carbonate, mostly due to the higher reducing media and alkaline pH values that dissolved Ni and consequent precipitation with carbonate (Zhu et al., 2016). Furthermore, the higher association of Ni with organic fraction (F3), mean percentage 25%, with a range between 7% and 38% than F2 could have resulted from an increase in % OC in soil. This is indicated at site 16 (% OC was 41.8, and Ni in F3 highest 38%).

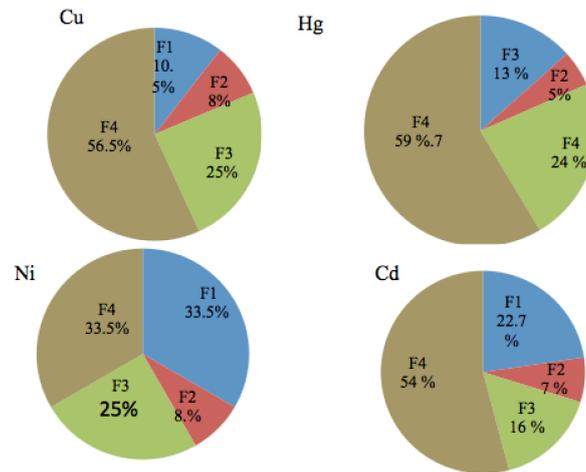


Figure 2 Mean percentage speciation of Cu, Hg, Ni, Cd in the different soil fractions

Hence, what affected speciation of Cu, and Hg is water dissolved oxygen and BOD expelling these from organic fraction and association with acid soluble. For Cd and Ni, the reducing media and % organic carbon in sediment affected the speciation.

3.4 Individual and global contamination factor

The individual and global contamination factors were calculated to evaluate the metal contamination and their bioavailability in soils of ULB. The ICF for the various sampling sites were calculated from the result of the speciation study by dividing the sum of the first three extractions (acid-reducible, oxidisable and organic forms) by the residual fraction for each sampling station. The GCF for each sampling station was computed by summing the ICF. The ICF and GCF classifications are: $ICF < 1$ & $GCF < 6$ –indicates low, $1 < ICF < 3$ & $6 < GCF < 12$ – moderate, $3 < ICF < 6$ & $12 < GC < 24$ –considerable and $ICF > 6$ & $GCF > 24$ –high contamination (Benson et al., 2016).

Results indicated considerable contamination for the metals Cr, Ni, Cd and As, their ICF values were between $3 < ICF < 6$; with metal order $Cr > Ni > Cd \approx As$. While moderate contamination ($1 < ICF < 3$) for metals in corresponding order $Mn > Zn > Hg > Cu$. These indicate the mobility and bioavailability and risks to plant uptake specially Cr, Ni, Cd, and As. Whereas, the GCF that elucidate the overall contamination among sites is presented in Figure 3, and it is explicit that 50% of sites were of moderate contamination ($6 < GCF < 12$) and 50 % of considerable contamination ($12 < GC < 24$). These sites receive excessive domestic and industrial waste, beside agricultural runoffs.

3.5 Speciation of metals in water

The speciation of metal in water is critical to understand metal behavior in aquatic system as that of metal speciation in soil. The forms of the chemical species of toxic metals in water column: the organic and inorganic metal complexes and the free solvated metal ion could be used as a predictor of bioavailability to particular aquatic organism. The free ion activity model states that there is a correlation between the toxicity of a metal to an organism and the thermodynamic activity of the free aqua metal ion in solution (Morel, 1983). The speciation of each metal in Litani River was predicted using computational approach, the geochemical modeling program PHREEQC. The application computes and reports the speciation of metals in terms of their free aqua ion and inorganic complexes. The organic metal species were not tackled based on the assumption that the organic metal complexes would be reduced in basic aqueous media with high alkalinity content

(Korfali and Jurdi, 2011). The measured values (Table 1) were the input data for the metal speciation calculation. Table 3 presents percentage range within the sampling sites of the speciated forms of studied metals in water.

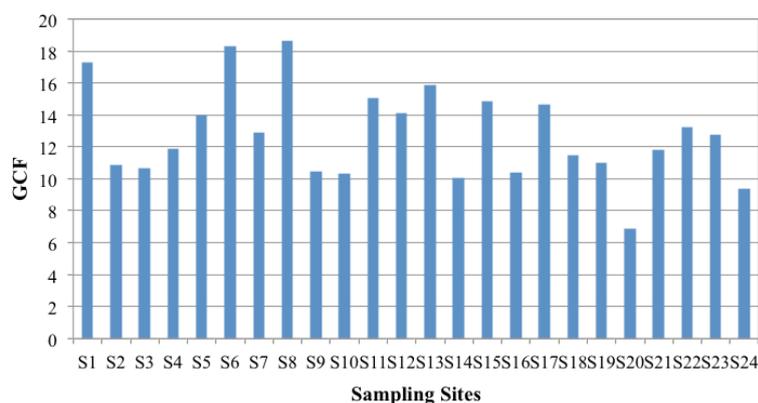


Figure 2. Variation of GCF among sampling sites

Table 3. Range of Highest % of speciated metal forms in Litani River water

Element	Speciated forms	% Range
Mn	Mn ²⁺	60-97
	MnCO ₃ ⁰	2-25
Zn	Zn ²⁺	35-89
	ZnCO ₃ ⁰	4-50
	ZnOH ⁺	1-12
Cu	CuCO ₃ ⁰	50-79
	Cu(OH) ₂ ⁰	20-49
	Cu ²⁺	<1
Cr	CrO ₄ ²⁻	20-94
	HCrO ₄ ⁻	1-18
	CrOH ²⁺	1-10
Ni	Ni ²⁺	60-90
	NiCO ₃ ⁰	8-35
	NiOH ⁺	2-5
Pb	PbCO ₃ ⁰	70-96
	Pb ²⁺	3-26
	PbOH ⁺	1-4
Cd	Cd ²⁺	35-82
	CdCO ₃ ⁰	10-40
	CdCl ⁺	6-18
	CdSO ₄ ⁰	2-7
AS	HAsO ₄ ²⁻	40-98
	HASO ₄ ⁻	2-50
	HAsO ₃ ⁰	2-15

Speciation as free aqua ion were high for Mn, Zn, Ni and Cd. Manganese occurred as free ion due to the low stability of Mn complexes (Stum and Morgan, 1996), and Mn speciation were in accordance with other works for wastewater (Magu et al., 2016). Whereas, Zn, Ni and Cd speciated to a lower extent as carbonate ion pair complexes (ZnCO₃⁰, NiCO₃⁰, CdCO₃⁰) and higher as free ion when compared to previous works on Lebanese water resources (Korfali and Davies, 2004, Korfali and Jurdi, 2011). But in previous studies, the water media had high levels of dissolved oxygen, high Eh values and organic content was low. While speciation of Cu was highly as the ion pair carbonate complex CuCO₃⁰ and nil occurrence as free toxic ion. These were in accordance with previous work of Cu association with carbonate due to the high formation constant (Korfali and Davies, 2004). Cr and As existed as anion oxygen forms (CrO₄²⁻ and HAsO₄²⁻) when media was oxidizing and limited occurrence as reduced species in reduced condition (Cr(OH)²⁺, H₃AsO₃⁰); and these coincide with other reported speciation works (Magu et al., 2016).

4. CONCLUSION

This study has assessed the mobility, bioavailability, and toxicity of heavy metals through determining the metal speciation in the different soil fraction irrigated by contaminated wastewater, and metal speciation in water. Results indicated due to high organic content, reducing environmental media, high levels of BOD in water, metals in soils existed highly in labile bioavailable soil fractions. High percentages of free toxic metal ion also prevailed in water. These results imply an immediate action plan for the construction of excessive wastewater treatment plant and prohibiting discharges of wastewater into rivers that are used for irrigation.

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