



Full Length Article

Long-Term Effects of Wastewater Irrigation on Soil Heavy Metal Contamination in Peri-urban Areas of Aleppo, Syria

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Abstract

The present study was conducted to assess the heavy metal (Cd, Cr, Cu, Ni, Pb, and Zn) distribution in soils of the area that had been under wastewater irrigation for more than 25 years in peri-urban Aleppo, Syria. Wastewater was highly contaminated with Cr with concentration of 0.3 mg L⁻¹ which is three times higher than the Syrian and World Health Organization's standards. Ultimately soils irrigated with wastewater contained significantly higher concentration of Cr as well as Zn compared to the fields irrigated with fresh groundwater ($p < 0.05$). The soil heavy metal fractionation data showed that most of the heavy metals in wastewater-irrigated soils significantly increased in bound to oxides of Mn and Fe or with soil organic matter fractions as compared to groundwater-irrigated soils, except for Ni ($p < 0.05$). Although these fractions are relatively less bioavailable and less mobile, there would pose the risks of the heavy metal release from these solid phase into liquid phase, when soils would be anaerobic condition for poorly crystalline of Fe oxide or decomposition conditions for soil organic matter. © 2014 Friends Science Publishers

Keywords: Chromium; Manganese and iron oxides; Sequential extraction; Urban and peri-urban agriculture

Introduction

The Middle East and North Africa (MENA) region is one of the driest regions in the world, with one of the most rapidly expanding populations. The use of wastewater (WW) in agriculture is expected to continue to increase in the region (Khoram *et al.*, 2007). Although irrigation with treated WW is by necessity a common practice in the MENA region, large amounts of untreated or inadequately treated WW are currently used by farmers in an uncontrolled manner (Qadir *et al.*, 2010). Untreated or inadequate treated WW irrigation can lead to heavy metal accumulation in soils and eventually contaminate crops (Nawaz *et al.*, 2006). Although the total heavy metal content in a soil is useful for characterizing the distribution of contaminants, the bioavailability and behavior of heavy metals in soils does not always coincide with the total content (Han, 2007). Thus, it is important to determine the chemical forms and speciation of heavy metals when estimating their actual dynamics in the environment (Jalali and

Khanlari, 2008). Sequential extraction procedure has been widely employed to assess chemical forms in soils with long-term wastewater irrigation (Li *et al.*, 2008; Bashir *et al.*, 2009) and with sludge amendment (Wang *et al.*, 2008). Incubation studies using heavy metal-spiked soils revealed that the heavy metal pools were transformed into more stable fractions over time (Jalali and Khanlari, 2008). The slow process of transformation of heavy metal pools is largely controlled by both the redistribution of heavy metals among various solid phase components and the slow distribution of surface sorbed or precipitated heavy metal into particles (Han, 2007). Hence, the solid phase components, such as clay mineral, manganese (Mn) and iron (Fe) oxides would control the actual dynamics of heavy metals in polluted soil under WW irrigation regime (Liang *et al.*, 2012). Though, few long-term investigations of WW irrigation have been conducted in the MENA region, however, information about this practice is completely lacking in some MENA countries, including Syria.

This study was conducted to identify the dominant

heavy metal pools in agricultural soils that have been under a WW irrigation regime for more than 25 years. It was hypothesized that the clay mineral, Mn and Fe oxides would control the soil heavy metals [cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)] fractions under long-term application of WW irrigation regime.

Materials and Methods

Study Area and Irrigation Water

The study area is located in the northwestern part of Syria in the Euphrates–Aleppo Basin near Aleppo city (Fig. 1). The mean annual precipitation of the study area is about 300 mm, while the mean annual evapotranspiration is 2500 mm. The citizens of Aleppo and its surrounding areas discharge treated and untreated WW into the Qweik River. The contaminated river water is pumped out by the surrounding farmers for surface irrigation throughout the year. It is referred as “WW irrigation” in the paper because the river water used for irrigation largely consists of WW. The fields on which farmers used groundwater (GW) as irrigation water are referred to as freshwater irrigation because wells are deeper than 30 m. Generally, farmers consume at least 3000 m³ of irrigation water for wheat cultivation in the study areas.

Soil and Water Sampling Protocol

Irrigation water was sampled from the Qweik River at a depth of 40 cm at two sites near the fields irrigated with WW. Five composite surface soil samples (0–10 cm) were collected from 18 WW-irrigated fields in 2009 and 18 GW-irrigated fields in 2010.

Water Analysis

The pH and electric conductivity (EC) of water were determined by using pH (Orion Model 720A, Thermo Electron Corporation, Massachusetts) and EC meters (CDM 83, Radio Meter A/S, Copenhagen, Denmark), respectively. Total suspended solids (TSS) were determined as oven dried method (APHA, 2005). Both unfiltered water samples and those filtered through Whatman no. 42 filter paper (GE Healthcare UK Ltd, Buckinghamshire, UK) were analyzed for the heavy metal concentrations (Cd, Cr, Cu, Ni, Pb, Zn) by inductively coupled plasma optical emission spectrometry (ICP-OES; Ciroc CCD, Spectro, Kleve, Germany) after nitric- hydrochloric acid digestion (APHA, 2005). Samples digested without filtration are referred to as ‘total-heavy metals’ while samples digested after filtration are termed as ‘soluble heavy metals’.

Soil Analysis

Soil samples were air-dried, ground, and passed through a 2-mm sieve. The pH and EC of saturated soil paste extract (Ryan *et al.*, 2001) were determined with pH and EC meters, respectively. The particle-size distribution, organic carbon, and calcium carbonate contents were determined by the hydrometer method, the Walkley-Black method, and the neutralization method using hydrochloric acid, respectively (Ryan *et al.*, 2001). Total manganese (Mn), iron (Fe) and the heavy metal (Cd, Cr, Cu, Ni, Pb, Zn) contents were determined by nitric-hydrochloric acid digestion (Amacher, 1994). The available heavy metals were extracted with 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.1 M triethanolamine (TEA), 0.1 M calcium chloride solution (Amacher, 1994). Chemical fractions of the soil heavy metals were extracted by Tessier *et al.* (1979) method, with slight modifications (Table 1). The heavy metal concentrations were quantified on ICP-OES. The clay mineral in the study areas mainly distributed as montmorillonite (Ryan *et al.*, 1997).

Statistics Analysis

Statistics analysis, including *t*-test and Tukey’s multiple comparison test and Pearson correlation coefficient was performed using the software EXCEL statistics (ver. 6.05a, Esumi Co., Ltd., Tokyo).

Results

Water quality of river was similar at both sample collection sites (i.e. A and B). Water EC, pH and TSS at site A were 1.3 dS m⁻¹, 7.3 and 324 mg L⁻¹, respectively. Water EC, pH and TSS at site B were 1.3 dS m⁻¹, 7.4 and 448 mg L⁻¹, respectively. Overall, soil of the study area is mainly classified as *Calcixerepts* and general soil properties are shown in Table 2.

Irrigation Water Quality

The heavy metal concentration of irrigation water was similar at both sample collection sites (i.e., A and B), with exception of Cu and Zn concentrations which were higher at site B compared to site A. It was observed that the total Cr concentration was the highest among all the heavy metals (Table 3). It was noted that the major portion of Cr, Cu, and Zn fractions were insoluble, which are associated with adsorption with suspended solid.

Total and Available Heavy Metal Contents in Soil

Results showed that total soil Cr and Zn contents were significantly ($p < 0.05$) higher in fields irrigated with

Table 1: Procedure for the sequential extraction of heavy metals from soil and corresponding phases (with slight modifications from Tessier *et al.*, 1979)

Phase/association	Abbreviation	Extractant	pH	Soil:extractant	Shaking time	Temp.
Exchangeable	Exch	1M MgCl ₂	7.0	1:8	1 h	Room temp.
Bound to carbonate	Carb	1M NaOAc-HOAc	5.0	1:8	5 h	Room temp.
Bound to Mn/Fe oxide	MnO/FeO	0.04M NH ₂ OH-HCl in 25% HOAc (v/v)	2.0	1:25	5 h	95 ± 3 °C
Bound to organic matter	OM	0.02M HNO ₃ , 30% H ₂ O ₂ (v/v)	2.0	1:25	2 h	85 ± 3 °C
Residual	Res	NH ₄ OAc in 20% HNO ₃ (v/v) HNO ₃ -HCl	Non-adjustment		0.5 h	Room temp 170 °C

Table 2: Physico-chemical properties of soils irrigated with wastewater (WW) or groundwater (GW) in the Qweik River Basin

Characters	ECe	pHe	SAR	CEC	O.M.	Clay	Silt	Sand	CaCO ₃	Fe _{total}	Mn _{total}
	dS m ⁻¹		(mmolc L ⁻¹) ^{0.5}	cmolc kg ⁻¹	g kg ⁻¹						mg kg ⁻¹
WW	1.3±0.5	8.1±0.2	4.1 ± 1.7	43 ± 6	20 ± 1	612±105	247±25	141±91	213 ± 23	34 ± 5	613 ± 68
GW	1.1 ±0.4	7.8±0.1	1.7 ± 0.7	54 ± 5	16 ± 4	682 ±31	231 ±31	87 ± 35	207 ± 26	37 ± 4	638 ± 55

Values are means ± SD (n = 18)

WW compared to the fields irrigated with fresh GW (Table 4). Available Cd, Cu, Ni, and Zn extracted with DTPA were significantly ($p < 0.05$) higher in WW fields than the fields irrigated with groundwater (Table 5). It was noted that mean available Cu concentration reached 5% of the total content, whereas other DTPA-extractable heavy metals averaged in 3-4% for Pb and Zn and in less than 2% for Cd and Ni.

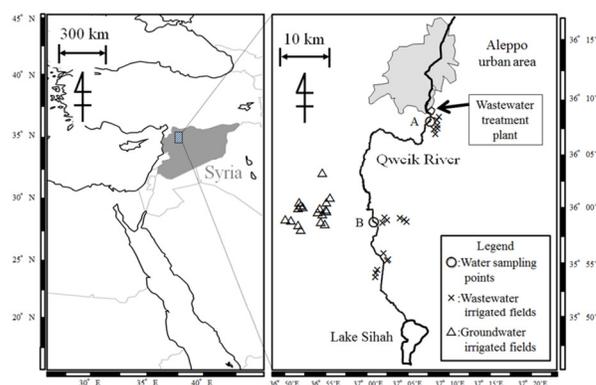
Soil Heavy Metals Fractionation

Chromium, Cu, and Zn fractions predominantly appeared in the residual form; Cd in bound to carbonate fraction (Carb-); Ni in bond to organic matter (OM-) and Residual fractions (Res-); and Pb in the bound to Mn and Fe oxide (MnO/FeO) fraction in the WW soils, and a similar tendency was seen among those of GW soils (Table 6). Statistically, Res-fractions of all heavy metals in WW soils were not significantly larger than those in GW soils ($p > 0.05$). The WW irrigated soils contained significantly greater MnO/FeO fractions than the GW soils for all the heavy metals and OM fractions except Ni ($p < 0.05$).

Discussion

The heavy metal concentrations (Cd, Cr, Cu, Ni, Pb, Zn) of Qweik River were compared with Syrian (SASMO, 2002) and World Health Organization (WHO, 2006) standards, while the soil heavy metal contents were compared with WHO (2006) standard and the proposed standard of European Commission (2008).

As regards contamination in Qweik River, it was observed that, both total and soluble Cd, Cu, Ni, Pb and Zn contents of Qweik river water were within the limits of Syrian and WHO standards. Among the two sites, it was noted that total concentration of the heavy metals

**Fig. 1:** Location of the study area

were higher at Site B. These heavy metals might have originated from urban runoff, including dust and local industries along with the river; Pb from leaded gasoline; and Cu, Zn, and Cd from car components, tire abrasion, lubricants, and industrial and incinerator emissions (Al-Masri *et al.*, 2006). Only total Cr concentration exceeded the Syrian and WHO standards at both locations. However, soluble Cr fractions were within the limits. This high Cr contamination is likely due to the effluents discharged from tanneries (Murugananthan *et al.*, 2004), which comprise the major part of industrial activities in Aleppo. These samples also had high TSS values, which exceeded the SASMO (150 mg L⁻¹) and WHO (100 mg L⁻¹) limits. Chromium, Cu, and Zn in the samples were mainly distributed in insoluble fractions, which are mainly associated with heavy metal precipitation and heavy metals sorbed by river sediments. Removal of suspended solids from the WW at the source of generation or before the field application could be a way to reduce the heavy metal contamination in the irrigated area.

Table 3: Total and soluble fractions of heavy metals ($\mu\text{g L}^{-1}$) in Qweik River water

Sites		Cd	Cr	Cu	Ni	Pb	Zn
A	Total	0.9±0.4	328±8	12±0	25±0	20±5	86±8
	Fraction	Trace	82±3	Trace	22±1	19±0	44±2
B	Soluble	3.2±0.0	391±1	101±1	47±0	39±1	286±2
	fraction	0.9±0.1	51±0	Trace	30±0	17±0	35±0
SASMO	10	100	200	200	–	2000	
(2002) limit							
WHO (2006)	10	100	200	200	5000	2000	
limit							

Values are means \pm SD ($n = 2$)

Table 4: Total heavy metal contents (mg kg^{-1}) of soils irrigated with ground water (GW) or wastewater (WW) in the Qweik River Basin

Parameters	Cd	Cr	Cu	Ni	Pb	Zn
WW	1.86±0.34	112±30	46±13	94±16	72±70	74±25
GW	1.78±0.39	96 ± 6	41 ± 4	92 ± 7	50±8	63±6
WHO (2006)	4	–	–	107	84	–
limit						
EC (2008)	1.5	100	100	70	100	200
limit						

Values are mean \pm SD ($n = 18$)

Table 5: Available heavy metal (mg kg^{-1}) contents of soils irrigated with wastewater (WW) or groundwater (GW) in the Qweik River Basin.

Parameters	Cd	Cr	Cu	Ni	Pb	Zn
WW	0.03±0.02	ND	3.1±2.4	1.0±0.4	5.1±13.2	3.1±3.6
GW	0.02±0.01	ND	1.6±0.2	0.6±0.4	0.2±0.1	0.4±0.1

Values are means \pm SD ($n = 18$)

Regardless of the irrigation source, low content of Cd was observed in the exchangeable (Exch-) fraction; most of the Cd content was Carb-fraction. This is likely due to the high calcium carbonate content in the study area (Table 2). Calcium carbonate has a high affinity for Cd due to a similar ionic radius with calcium (Zachara

et al., 1991). The DTPA-extractable soil Cu, Ni, Pb and Zn were higher in WW irrigated areas as compared to the GW irrigated areas (Table 5) which has been reflected in soil fractions as well (Table 6). The total contents of soil Cr and Zn in WW were significantly ($p < 0.05$) higher than those of GW (Table 4). This is likely due to be higher the Cr and Zn concentrations than those of the other heavy metals in the irrigation water (Table 3). The Res-fractions in the most heavy metals were predominant in both WW and GW soils, which would be reflected to geological distribution in the study sites. The Res-fraction is the most stable fractions among soils and it affected by parent material, soil properties and climate condition (Han, 2007). The Res-fractions of all heavy metals in WW soils were not significantly ($p > 0.05$) larger than those in GW soils (Table 6). The long-term WW irrigation had negligible effect on the Res-fraction in the soils, likely due to be slow diffusion process for the transformation of heavy metals from Exch-fraction to Res-fraction (Ahnstrom and Parker, 2001; Jalali and Khanlari, 2008). Long-term WW irrigation led to an increase in the MnO/FeO and OM fractions of all heavy metals (except Ni). The moisture and temperature regimes of soils in the region generally favor the crystallization of ferrihydrite (poorly crystalline) into crystalline of goethite and hematite (Schwertmann, 1985). However, the poorly crystalline Fe oxides are capable sorbing large amounts of heavy metals because their specific surface area (Vodyanitskii, 2010), for example, $600 \text{ m}^2 \text{ g}^{-1}$ (Cornell and Schwertmann, 2003) is much greater than that of their crystalline counterparts, for example, $50\text{--}100 \text{ m}^2 \text{ g}^{-1}$ (Pena and Torrent, 1984). Increase in soil heavy metals in OM fraction was likely due to the increase in soil OM content through long-term WW irrigation (Table 2). Soil OM has high affinity for heavy metal adsorption (Han, 2007). The long-term WW irrigation leads to accumulation of MnO/FeO- and OM-complexes, which are less bioavailable and less mobile

Table 6: Heavy metals fractionations of soils collected from a wastewater (WW) or groundwater (GW) irrigation regime.

Metals		Exchangeable	Bound carbonate	to Bound oxide	Mn/Fe Bound matter	to organic Residual	Sum	Recovery rate ^a					
		mg kg^{-1}											
Cd	WW	0.11	Ac	0.58	Aa	0.54	Aa	0.24	Ac	0.31	Bb	1.78	99.1%
	GW	0.04	Bc	0.70	Aa	0.45	Ba	0.16	Bc	0.37	Ab	1.72	
Cr	WW	0.1	Ad	0.9	Ad	18.2	Ac	29.0	Ab	75.3	Ba	123.5	108.9%
	GW	Trace	Bd	0.8	Ad	4.9	Bc	16.0	Bb	80.7	Aa	102.4	
Cu	WW	0.10	Ad	0.5	Ad	12.7	Ab	7.2	Ac	25.1	Aa	45.6	102.8%
	GW	0.01	Bd	0.5	Ad	11.6	Bb	4.3	Bc	24.7	Aa	41.1	
Ni	WW	0.2	Ad	2.9	Ac	23.4	Ab	30.5	Aa	29.4	Aa	86.4	91.3%
	GW	Trace	Bd	3.0	Ac	20.6	Bb	29.3	Aa	29.8	Aa	82.7	
Pb	WW	4.7	Ab	6.9	Ab	62.7	Aa	1.6	Ab	5.9	Ab	81.8	104.3%
	GW	4.0	Ab	7.7	Ab	26.3	Ba	0.8	Bc	6.7	Ab	45.5	
Zn	WW	0.03	Ac	2.9	Ac	13.9	Ab	14.6	Ab	42.2	Aa	73.6	97.3%
	GW	Trace	Ad	0.5	Acd	4.3	Ac	9.1	Bb	45.0	Aa	58.9	

Capital letters followed in each column show differences between WW and GW, while small letters in each row show differences among fractions of either WW or GW regime, at $p < 0.05$

^a Recovery rate (%) = Sum of fractions/ Total ($\text{HNO}_3\text{-HCl extract}$) $\times 100$

(Salbu *et al.*, 1998). This is likely why the DTPA-extractable fraction was generally low (Table 5). Although OM and MnO/FeO fractions are relatively less bioavailable and less mobile (Salbu *et al.* 1998), there would pose the risks of heavy metals release from these solid phase into liquid phase, when soils would be anaerobic condition for poorly crystalline of Fe oxide or decomposition conditions for soil organic matter (Han, 2007).

In conclusion, the WW flow in the Qweik River was highly contaminated with Cr, which is likely due to the insufficient Cr removal from industrial WW, such as tannery effluents. The fields under WW irrigation for more than 25 years had significantly higher total Cr and Zn contents and available Cd, Cu, Ni, and Zn contents than those of GW fields. Results of sequential extraction showed that Cd was mainly in the Carb-fraction; Pb in the MnO/FeO fraction; Ni in the OM and residual fractions; and Cr, Cu, and Zn in the residual fraction. The predominance of Cd in the Carb fraction would contribute to its mobility in the soil. No significant difference was observed in the Res- fractions of any metals between the WW and GW fields, whereas most of the heavy metals in WW soils were mainly bonded with MnO/FeO, and OM fractions. The WW irrigation for over 25 years in Aleppo peri-urban areas caused transformation of the soil heavy metals pool into OM and MnO/FeO fraction rather than Res- fraction, which is the most stable fraction in soil and mainly transformation into clay minerals by slow diffusion. Although OM and MnO/FeO fractions are relatively less bioavailable and less mobile, there would pose the risks of the heavy metals release from these solid phase into liquid phase, when soils would be anaerobic condition for poorly crystalline of Fe oxide or decomposition conditions for soil organic matter. Therefore, the risk mitigation under WW irrigation regime in the present study site is a need to minimize heavy metal contamination from car products and untreated WW effluent in factories.

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References

- Al-Masri, M.S., K. Al-Kharfan and K. A-Shamali, 2006. Speciation of Pb, Cu and Zn determined by sequential extraction for identification of air pollution sources in Syria. *Atmosphere Environ.*, 40: 753–761
- Amacher, M.C., 1994. Nickel, cadmium, and lead. In: *Method of soil analysis. Part 3, Chemical methods*, pp: 739–68. Sparks, D.L., A.L. Page, P.A. Helmke and R.H. Loeppert (eds.). American Society of Agronomy/Soil Science Society of America, Wisconsin DC, USA
- American Public Health Association (APHA), 2005. *Standard methods for the examination of water and wastewater*. APHA/American Water Works Association/Water Environmental Federation, Washington, DC, USA
- Ahnstrom, Z.A. and D.R. Parker, 2001. Cadmium reactivity in metal-contaminated soils using a coupled stable isotope dilution-sequential extraction procedure. *Environ. Sci. Technol.*, 35: 121–126
- Cornell, R. and U. Schwertmann, 2003. *The Iron Oxides*. 2nd Edition. Wiley-VCH, Weinheim, Germany
- Bashir, F., M.A. Kashmiri, T. Shafiq and M. Tariq, 2009. Heavy metals uptake by vegetables growing in sewage irrigated soil: relationship with heavy metal fraction in soil. *Chem. Spec. Bioavailab.*, 21: 199–209
- European Commission, 2008. *Environmental, economic and social impacts of the use of sewage sludge on land*. Final report, Part II: Report on options and impacts. http://ec.europa.eu/environment/waste/sludge/pdf/part_ii_report.pdf. Accessed on 30 December 2012
- Han, F.X., 2007. Biogeochemistry of trace elements in arid environments. In: *Environmental Pollution 13*. Springer, Dordrecht, The Netherlands
- Jalali, M., and Z.V. Khanlari, 2008. Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. *Geoderma*, 143: 26–40
- Khoram, R.M., M. Shariat, A. Azar, N. Moharamnejad and H. Mahjub, 2007. Prioritizing the strategies and methods of treated wastewater reusing by Fuzzy Analytic Hierarchy Process (FAHP): a case study. *Int. J. Agric. Biol.*, 9: 319–323
- Li, P., X., Wang, G., Allinson, X., Li and X., Xiong, 2008. Risk assessment of heavy metals in soil previously irrigated with industrial wastewater in Shenyang, China. *J. Hazard Mater.*, 161: 516–521
- Liang, J., Z. Yang, L. Tang, Y. Xu, S. Wang and F. Chen, 2012. Growth performance and tolerance responses of jatropha (*Jatropha curcas*) seedling subjected to isolated or combined cadmium and lead stresses. *Int. J. Agric. Biol.*, 14: 861–869
- Murugananthan, M., R.G. Bhaskar and S. Prbhakar, 2004. Separation of pollutants from tannery effluents by electro flotation. *Sep. Purif. Technol.*, 40: 69–75
- Nawaz, A., K. Khurshid, M.S. Arif and A.M., Ranjha, 2006. Accumulation of heavy metals in soil and rice plant (*Oryza sativa* L.) irrigated with industrial effluents. *Int. J. Agric. Biol.*, 8: 391–393
- Pena, F. and J. Torrent, 1984. Relationships between phosphate sorption and iron oxides in Alfisols from a river terrace sequence of Mediterranean Spain. *Geoderma*, 33: 283–296

- Qadir, M., A. Bahri, T. Sato, and E. Al-Karadsheh, 2010. Wastewater production, treatment, and irrigation in Middle East and North Africa. *Irrigat. Drain. Syst.*, 24: 37–51
- Ryan, J., S. Masri, S. Garabet, J. Diekmann and H. Habib, 1997. *Soils of ICARDA's agricultural experiment stations and sites: climate classification, physical and chemical properties, and land use*. Technical Bulletin, International Center for Agricultural Research in the Dry Areas, Aleppo, Syria
- Ryan, J., G. Estefan and A. Rashid, 2001. *Soil and plant analysis laboratory manual*. International Center for Agricultural Research in the Dry Areas, Aleppo, Syria
- Salbu, B., T. Krekling and D.H. Oughton, 1998. Characterisation on radioactive particles in the environment. *Analyst*, 123: 843–849
- Schwertmann, U. 1985. The effect of pedogenic environments on iron oxide minerals. *Adv. Soil Sci.* 1: 171–200
- Syrian Arab Standards and Metrology Organization (SASMO). 2002. *Sasmo 2752: standard for wastewater reuse for agriculture*. Syrian Arab Standards and Metrology Organization, Damascus, Syria
- Tessier, A., P.G.C. Campbell and M. Bisson, 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51: 844–855
- Wang, X., L., Chen, S., Xia and J. Zhao, 2008. Changes of Cu, Zn, and Ni chemical speciation in sewage sludge co-composted with sodium sulfide and lime. *J. Environ. Sci.* 20: 156–160
- Vodyanitskii, Y.N., 2010. The role of iron in the fixation of heavy metals and metalloids in soils: a review of publications. *Eurasian Soil Sci.*, 43: 519–532
- World Health Organization (WHO), 2006. *Guidelines for safe use of wastewater, excreta and grey water: wastewater use in agriculture*. Vol. 2. WHO, Rome, Italy
- Zachara, J.M., C.E. Cowan and C.T. Resch, 1991. Sorption of divalent metals on calcite. *Geochim. Cosmochim. Acta*, 55: 1549–1562

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