Absorption and Mobility of Cr and Zn in Soil in the Vicinity of Jordan River

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Abstract. Sediments from the basin of Jordan River are to some extent significantly contaminated by heavy metals. The goal of this study was to examine the nature of the heavy metals, their mobility, and their binding in the soil matrix in order to understand the accumulation mechanism. Exhaustive mineralogical and geochemical study on the heavy metals in the vicinity of the river will allow knowing the dominant forms of emitted metals. The structural local order around Cr and Zn in soil samples were investigated by analyzing XAFS data. Our investigations show that the coordination sphere, around both Cr and Zn, is constituted of oxygen atoms at an interatomic distance of ~2 Å which is close to those in clay minerals. It is also shown that Cr(III) is the most dominating redox state in soil samples. Moreover, the next backscattering neighbors around Zn and Cr are either carbon or sulfur atoms which reveal a multiple and heterogeneous speciation of Cr and Zn with organic matter.

1. Introduction

The Jordan River and its major tributary, flow through the Jordan valley, where many important agricultural activities are located. The study of heavy metal pollutants in the sediments of Jordan River is of interest for two reasons. On one hand the flows through ever-increasingly agricultural and urban areas [1]; on the other hand the flow rate of river has decreased drastically, due to the upstream Dam, the increase of the agricultural surfaces as and the climate changes, thus the potential influence of external sources on the river discharge and chemical composition became significant [2].

Pollution of the natural environment by heavy metals is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration [3]. Heavy metals accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds [4].

The degree of metals bioavailability, and thus metals toxicity, is by large determined by the nature of their complication to sorbent surfaces in soils. Therefore, the objective of this study was to explore the speciation of Cr and Zn in soil system and to investigate the local structure in order to understand

the binding system around these heavy metals in soils. This is an essential step to understand the structural behavior around toxic metals in soil and, for future, in the agricultural product.

2. Material and methods

2.1. Study region

The Jordan valley is a part of the geological fault which extends from Syria down to the Red Sea. The Lower Jordan River stretches between the Sea of Galilee and the Dead Sea (~ 417 m below sea level). The river is about 105 km meandering distance. The investigated area (Figure 1) is occupied by rural settlements on east side of the river (Jordan) and the majority of the land is used for agriculture (e.g., field crops and fruit trees).

Figure 1. Location of the sampling region in the vicinity of the Jordan River showing the exact position of the sampling points.

2.2. Sampling, preparation, characterization and Analysis

Soil samples were collected from 3 different locations using a backhoe sampler from the east bank of the Jordan River (Figure 1). The sampling points were recorded and identified using the latitude and longitude coordinates. In order to consider the representativeness of the samples, we were keen that samples will be collected from different soil types ranging from the sediment at the river bank (JR-0m) to the agricultural zone (JR-200m). For each zone samples were collected at different depths with 5 cm sampling thickness. Therefore, sampling depths were at 0-5 cm, 15-20 cm, 30-35 cm and 45-50 cm from the surface down.

Part of samples were dried in the oven at 100 ˚C and, then, were subject to series of tests in order, to estimate the levels of total organic matter (TOM) using loss on ignition at 555 ˚C, to quantify the elemental content of heavy metals and trace elements using ICP-MS and to identify different crystalline structures forming soil through conventional XRD technique.

Natural samples (non-dried) were subject to X-ray Absorption Fine Structure (XAFS) analysis. Data were collected at Cr (5989 eV) and Zn (9659 eV) edges on XAFS beamline at Elettra [5] and mySpot at BessyII [6]. In both beamlines, XAFS data were collected in fluorescence mode using silicon drift detector. XAFS data processing and analysis were performed using IFEFFIT software package following standard procedures [7]. Using different model compounds, linear combination fitting (LCF) has been applied to the X-ray Absorption Near-Edge Structure (XANES) data to estimate the different species that are forming the samples. After normalizing the short-Extend XAFS spectra, EXAFS signals $\chi(k)$ were k^3-weighted and Fourier Transformed (FT) using a Bessel window function. Theoretical scattering paths, used for modeling experimental EXAFS, were calculated with FEFF [8].

A multi-shell approach was used for data fitting. In order to reduce the number of free parameters, the amplitude reduction factor (S_0^2) was fixed at 0.9. In addition, the shift in the threshold energy (E_0) was linked for all the shells. Floating parameters of further shells were the coordination number (N), bond length (R) and the Debye–Waller factor (σ^2). Furthermore, Continuous Cauchy Wavelet (CCW) analyses were performed on the XAFS data collected at the Cr and Zn K-edges [9]. Although the short

k range of the EXAFS data (k=~ 7 Å^{-1}), combining CCW and EXAFS fitting techniques, lots of information were extracted such as the type of backscattering atoms and their interatomic distances.

3. Results and discussion

While XRD patterns didn't reveal more than usual standard soil phases, the elemental content chemical analysis showed that most of heavy metals are in the tolerant contamination range. Exceptionally Cr was found in the moderately contamination range (150 ppm) which can appear to be harmful especially if occurring in its hexavalent form. Knowing the local structure around some of the
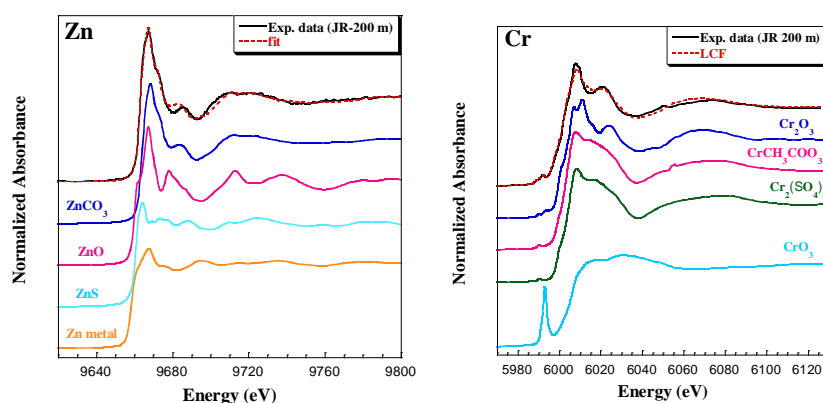
Figure 2. Linear combination fitting of the XANES data collected at Zn (left) and Cr (right) K-edges in soil samples from the vicinity of Jordan River

heavy metals in soil will reveal good information about the soil system in the region.

XANES data collected at the Zn and Cr K-edges were subject to LCF using different experimental model compounds. Results show that Zn is present in a form similar to a smithsonite ($ZnCO_3$-like). Moreover Zn species were not influenced by the agricultural processes (at 200 m from the bank) although the use of fertilizers. This can be an indication that Zn may be present in an organic structure form since it is bind to carbon. It also shows that Zn is not in a sulfurous structure.

In contrast to Zn, the Cr shows a large difference as a function of the distance from the river bank. On the zero distance (at the river bank) Cr occurs in inorganic forms as a chromium (III) oxide (Cr_2O_3) and in chromium sulfate ($CrSO_4$) distributed equally to ~45% for each phase. In the agricultural region (200 m from the bank) Cr is mainly occurring in a chromium (III) acetate form $Cr(C_2H_3O_2)_3$ (~55%). Inorganic phase of Cr still exists in agricultural soil and occurs in sulfate form $[Cr(SO_4)_3]$ but with a smaller content (~30%) compared to the river bank in addition to the oxide phase (Cr_2O_3) which is present with a lower concentration to about 20%.

Results derived from EXAFS data analysis are presented in table 1. Due to the short EXAFS range, the number of backscattering atoms is not accurate and thus is not reported. On the contrary, the interatomic distances are accurate, although we speculate that their accuracy decreases with the increase of the distances.

EXAFS analysis show that Cr as well as Zn are surrounded by light elements at short distances which appeared to be oxygen atoms sitting at the interatomic distance of ~2.0 Å for both structures (Table 1). Further EXAFS results to the next nearest neighbors for semi-quantitative analysis, due to the short range, show presence of carbon backscattering atoms around Zn at an interatomic distance of ~3.2 Å which is in agreement with LCF results. Differences in the local structure around Cr atom in soil samples are dependent on the soil type with respect to the distance from river bank. At a zero distance (river bank), Cr is bound to sulfur at an interatomic distance of ~3.4 Å or in the agricultural soil (200m from the river bank) the S bond disappeared and Cr is bound to carbon atoms at a longer distance (~3.8 Å).
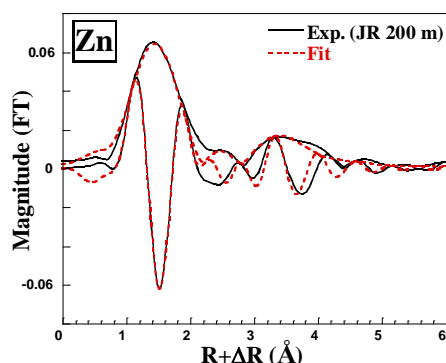
Figure 3. Modelling EXAFS data collected at the Zn edge in soil sample at 200 m from the river bank.
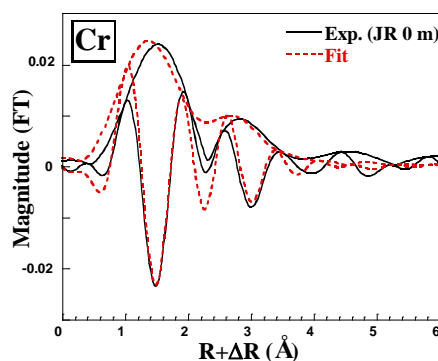
Figure 4. Modelling EXAFS data collected at the Cr edge in soil sample from the river bank.

Table 1. Structural parameters derived from EXAFS data analysis

Sample	Bond	CN	Distance (Å)	σ^2 (Å^2)	ΔE (eV)
<u>Zn</u> in Jordan River 0 m	Zn-O	5.2 ± 2.0	1.99(4)	0. 004(6)	
	Zn-C	-	3.22(4)	0.005(5)	0.57(5)
<u>Zn</u> in Jordan River 200 m	Zn-O	4.6 ± 2.0	1.94(5)	0.002 (6)	
	Zn-C	-	3.21(4)	0.005 (8)	-1.37(6)
<u>Cr</u> in Jordan River 0 m	Cr-O	4.5 ± 2.5	2.02(2)	0.010(6)	
	Cr-S	-	3.41(4)	0.045(7)	-2.12(4)
<u>Cr</u> in Jordan River 200 m	Cr-O	3.7 ± 2.5	1.97(3)	0.01(6)	
	Cr-C	-	3.79(2)	0.08(8)	0.58(5)

4. Conclusion

Soils from the east bank in the vicinity of the Jordan River, in contrast to speculations of pollutions, seem to be in tolerant range from the heavy metals content side except for the Cr case in studied soil samples. Zn occurs in a stable carbonate structure in the region independent of the soil specifications. In the contrary, the local structure around Cr changes between carbonate-like structures, in agricultural soil, to sulphates in non-exploitable regions.

5. Acknowledgment

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