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Molybdenum pollution and speciation in Nver River sediments impacted with Mo mining activities in western Liaoning, northeast China

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ABSTRACT: The concentrations and speciation of Mo, together with Fe, Cu, and Zn, in Nver River sediments impacted with Mo mining activities in western Liaoning, northeast China, were investigated with geochemical method. Using the X-ray fluorescence and X-Ray diffraction, the characterizations of metals in tailings ponds deposited along the Nver River bank were analyzed. Analysis and comparison of the concentrations and speciation of heavy metals show that the maximum concentrations of Fe, Cu, Zn, and Mo detected in river sediments exceed corresponding reference values (S0, P0) by 6.3, 9.7, 16.1, and 494.0 times, respectively, and that of Mo exceeds the abundance of Mo in earth's crust by 1127.9 times. High I_{POLL} showed that all of these heavy metals might pose an environmental risk. Bioavailable fractions of Fe, Cu, and Zn were not detected in both tailings ponds and sediments, but that of Mo presented in tailings pond and sediments are 16.15-18.73% and 18.61-59.07%, respectively. The alkaline condition in sediments and tailings ponds is a significant factor governing chemical speciation of heavy metals. This study indicates that Mo tailings ponds deposited along the bank may have a closely relationship with the high levels of these metals in sediments and Mo in sediments may pose a high risk to the local environment.

Key words: Molybdenum, Tailings, Sediment, geochemistry, Heavy metal, $I_{POLL,}$ Mobility

INTRODUCTION

Molybdenum (Mo) is an essential trace element for both plants and animals. Mo deficiency has often been reported, but at large Mo concentrations, it may be toxic due to causing secondary Cu deficiency (O'Connoe *et al.,* 2001; Vunkova-Radeva *et al.,* 1988). Tailings and waste rocks produced from Mo mining activities may be the major source of Mo contamination in water body (Morin and Hutt, 1999; Yu *et al.,* 2008). Its pollution will have a serious effect on the security of drinking water, eco-environment, integrated control for pollution, and planned management in local area. Mo polluted sediments have been detected downstream of Knaben Mo mining area in the Knabeåna-Kvina drainage basin (Langedal, 1997). Such sediments may be secondary Mo pollution sources for water, soil, and vegetation, dependent on the speciation of the contaminants and on biological activity.

In western Liaoning, northeast China, at least 300 tailings ponds with 9 million tons of tailings from the Lanjiagou Mo mining activities, which started since 1996, are distributed in the upstream reach of Nver River (Fig. 1). The Nver River is a major source of drinking water for Huludao city and also supports the raising and breeding of aquatic products. A report about water quality of the Nver River (2004-2006) revealed that Mo concentrations were 7-24.4 times higher than the GB 5749-2006 (MHC, 2006) standard (0.07 mg/L) (Guo and Wang, 2007). However, there are relatively few reports addressing the concentrations, chemical speciation, pollution intensity and mobility of Mo in sediments in this district. Moreover, the environmental fate of Fe, Cu and Zn (They are main heavy metal elements in Lanjiagou Mo tailings) in sediments is uncertain.

Therefore, it is necessary to determine distribution of heavy metals, especially Mo, in sediments of the Nver River impacted with Lanjiagou Mo mining activities. The sequential extraction procedure (SEP) is a method widely applied to determine the chemical speciation of heavy metals in soils and sediments

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(Rapin *et al.,* 1986; Tessier and Compbell, 1979), and may estimate the present solubility of the metals and predict delayed releases (Förstner, 1995).The major objectives of the present study are (1) to achieve a detailed understanding of concentrations, speciation and mobility of heavy metals, especially Mo, in sediments and tailings ponds along the Nver River, (2) to investigate the relationship between the metal contaminations in sediments with Mo tailings ponds deposited along the river and (3) to assess the bioavailability or pollution intensity.

MATERIALS & METHODS

Fourteen sampling sites were chosen along the Nver River in August 2008 (Fig. 1, Table 1). according to the following criteria: the distribution of Mo tailing pond sites, slope of the river bank, route of the river, and accessibility for sampling. 24 samples were collected from the surface of tailings ponds and sediments, and 11 bed sediment samples of them were taken with a Kajak gravity corer retained in a PVC tube, of which the diameter was 70 mm. The total 24 samples were stored in sealed plastic bags in an ice-packed cool box. Previously, pH measurement (pH according to (MEND, 1990)) was noted (Table 1). These samples were immediately transported to the laboratory for air drying (<35ºC), and then were stored in sealed plastic bags again for geochemical and mineralogical determinations (Dold and Fontboté, 2002).

Major element analysis of 3 samples (D3, D4, and D5) from the tailings ponds was performed by X-Ray fluorescence (XRF) (SRS3400, Germany). The mineral composition of the same 3 samples was determined by X-Ray diffraction (XRD) (D/MAX-2400, Japan) with CuKα radiation (λ=0.154056 nm) and a monochromator. Scan settings were 5°-90° 2θ, 0.03° step size, 2-S count time per step.

The 24 samples were completely digested with a mixture of HNO_3, HF, $HClO_4$ and HCl. Concentrations of Fe, Zn, Cu and Mo in the solutions were measured by ICP-OES (Varian, Vista MPX, USA) (Dold *et al.,* 1996). Because the concentration of solutions and different metals varied substantially, serial dilution method was needed in some solutions prior to analysis.

To determine the geochemical speciation of Fe, Cu, Zn, and Mo, the 24 samples were sieved to the 0.5 mm fraction for sequential extraction (Table 2) (Langedal, 1997). Since hardly any organic matter is presented in the tailings pond, the oxidizable fraction of heavy metals is probably primary sulfide minerals (Langedal, 1997).

To determine the concentrations of organic matter in samples, the method for determination of soil organic matter from GB 9834-88 (MOAC of China, 1989) was referred in this study.

All chemicals used in the study were analytical grade. Reagent blanks were determined for each new batch of reagent. All reagent stock solutions: 1,000 mg/L of metals (including Fe, Cu, Zn and Mo) used were of analytical reagent grade supplied by National Environmental Bureau (NEB, 2002). Doubly distilled deionized water was used in this study. The sediment and tailings pond samples were respectively analyzed in 4 replicates, for which the relative standard deviations were less than 10% for all metals.

The bioavailability or pollution intensity of metals in sediments is usually evaluated using an Enrichment factor (EF) (Pekey, 2006) and geo-accumulation index (I_{geo}) (Muller, 1979) and Risk Assessment Code (RAC) (Jain, 2004). Karbassi and Monavari (2008) presented a new developed pollution index (I_l) to evaluate the pollution intensity of metals in sediments as follows:

$$I_{poll} = \mathrm{Log}_2^{[B_c/L_p]}$$

Where I_{POLL}, B_c and L_p are indicative of pollution intensity, bulk concentration and lithogenous portion, respectively (Karbassi *et al.,* 2008). In the present investigation, I_{POLL} and RAC were adopted to assess the bioavailability in the Nver river sediments.

RESULTS & DISCUSSION

The river sediments play an important role as both carriers and sinks for contaminants in aquatic environment (Priju and Narayana, 2007; Sundararajan and Natesan, 2010). A comparison of metal concentrations in the river sediments with ones in reference site upstream of mining area is generally taken as a quick and practical method of metal enrichment (Ayodele and Bayero, 2010). The total concentrations of Fe, Cu, Zn, Mo, and organic matter in tailings ponds and sediments are presented in Fig. 2. The concentrations of Fe, Cu, Zn, and Mo detected in sediments at S1-S7 and P1-P7 are considerably higher than the corresponding reference values (S0, P0) (Fig. 1). The maximum concentrations of Fe, Cu, and Zn are observed at P2, and that of Mo is found at S3. These maximum values of Fe, Cu, Zn, and Mo exceed corresponding reference values by 6.3, 9.7, 16.1, and 494.0 times, respectively. When compared to the abundance of Mo in earth's crust, the maximum concentration of Mo exceeds the abundance in earth's crust by 1127.9 times. The high levels of heavy metals observed in the sediments could be caused by the Mo extraction industry activities because most of Mo tailings ponds deposited along the river bank are not managed with AQ 2006-2005 (SAWSC, 2006), which demonstrates again that tailings and waste rocks produced from mining activities are the major source of metal contamination in water body.

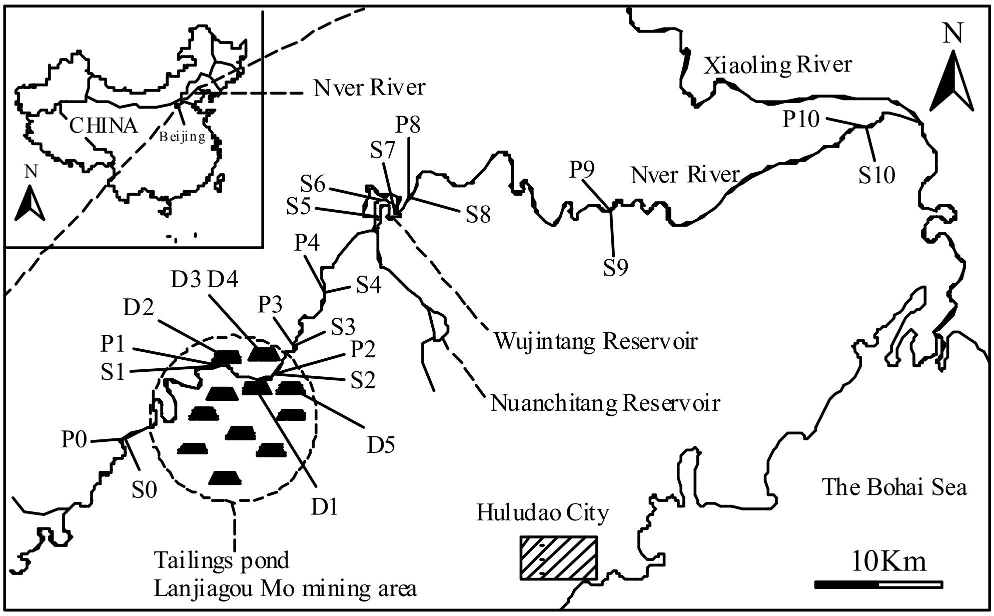

Fig.1. Map over the study area with sampling sites. Samplings media: D = tailings pond, P = overbank sediment, S = bed sediment

Table 1. A list of sampling sites

Sample No.	Sample type	pH	Depth (cm)	Distance from the Mo mining area (km)
D3, D4, D5	Tailings pond	7.41-8.17	20	
D1, D2		7.38, 7.56	20	
S0	Bed sediments	7.81	15-20	2 km upstream of the Mo mining area
S1, S2		8.31, 8.25	15-20	
S3, S4		8.39, 8.28	15-20	1, 7
S5, S6, S7		8.27-8.34	15-20	16, 17.5, 19
S8, S9, S10		7.62-7.85	15-20	21, 55, 78
P0	Overbank sediments	7.88	17	2 km upstream of the Mo mining area
P1, P2		8.27, 8.48	16, 21	
P3, P4		8.11, 8.14	22, 19	1, 7
P8, P9, P10		7.39-7.51	16, 15, 21	21, 55, 78

Table 2. Sequential extraction scheme

Extraction step	Sample weight(g)	Extractant	T (°C)	pH	Incubation time(hours)
1 Bioavailable	5	30 ml 0.01 mol/L $BaCl_2$	20		2 (r = 200) [a]
2 Adsorption/ ion exchangeable	5	30 ml 1 mol/L NH_4OA	20	4.5	2 (r = 200) [a]
3 Oxidisable	5	(a) 10 ml 30% H_2O_2 (b) 40 ml 1 mol/L NH_4OAc	80 20	 4.5	dryness 2 (r = 200) [a]
4 Reducible	2.5	40 ml oxalic acid (535 ml 0.2 mol/L + 700 ml 0.2 mol/L)	20	3	2 (r = 200) [a]
5 Residual	1	2.6 ml HCl + 0.9 ml HNO_3 Addition of 14.25 ml water before analysis	90		1.5

[a] Mixing speed = 200 rounds per minute

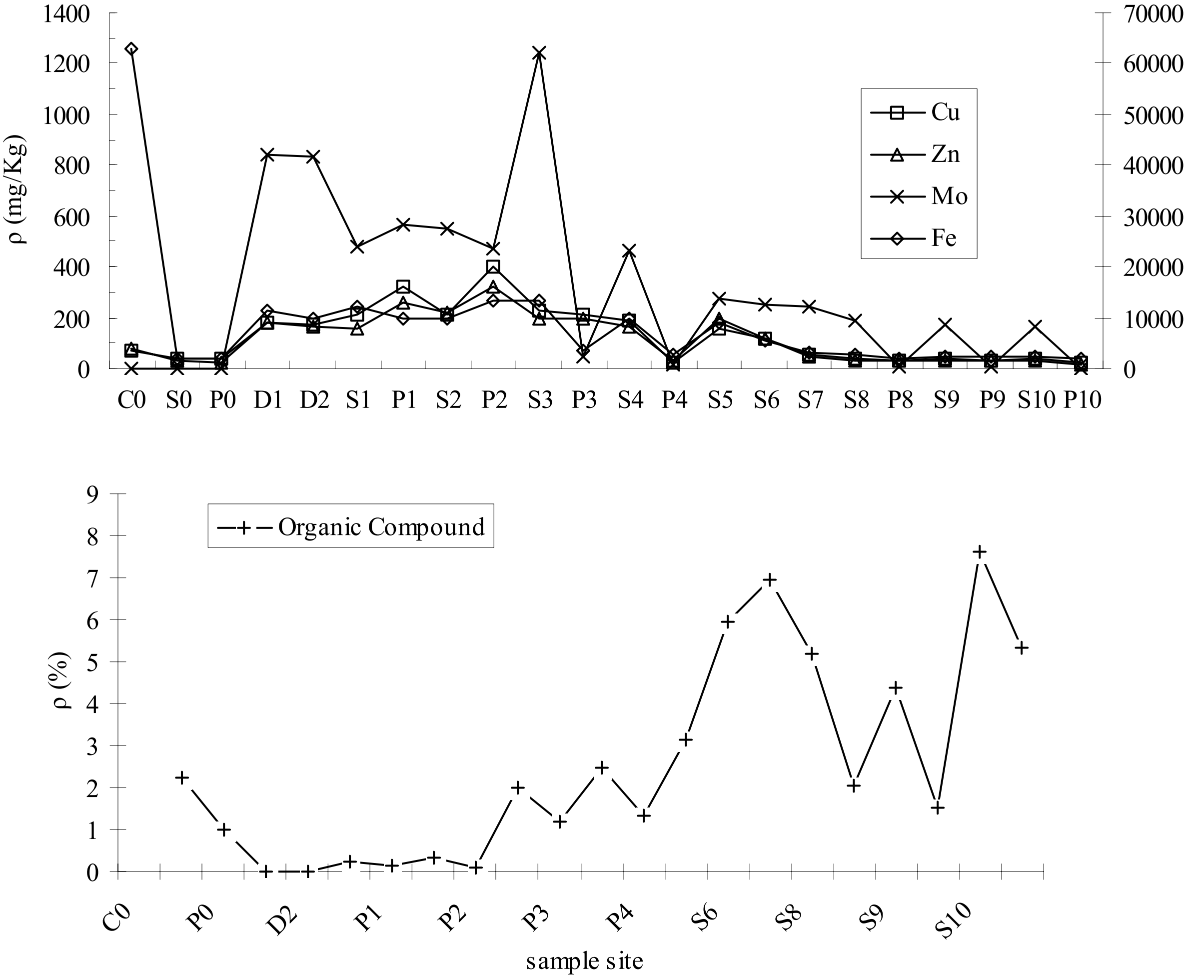

Fig. 2. Variation of concentrations of Fe, Cu, Zn, Mo (a) and Organic compound (b) in Lanjiagou Mo tailings ponds and the Nver River sediments

The concentrations of heavy metals in sediments and tailings ponds do not necessarily reflect their potential for release. Chemical speciation of heavy metals would remarkably influence their releasing and migrating behaviors in the environment as well as pollution intensity (Karbassi *et al.,* 2008) or biotoxicity (Opuene *et al.,* 2008).

The XRF and XRD analyses (D3, D4, and D4) show that the tailings pond material mainly consists of silicates (Table 3 and 4). Only traces of the primary sulphide minerals are detected by XRD. Since hardly any organic matter is present in the tailings pond (Fig. 2). the Fe, Cu, Zn, and Mo in oxidisable fraction are probably pyrite, chalcopyrite, sphalerite, and molybdenite, respectively (Fig. 3). The molybdenite, like as pyrite, can be easily oxidized during weathering (Rankama and Sahama, 1950). After oxidation of these metal sulfide minerals, Fe, Cu and Zn are not significantly mobilized in the alkaline condition prevailing in the tailings pond (pH> 7.38, Table 1) for precipitation/co-precipitation, adsorption, and ion exchange mechanisms. Fe, Cu, and Zn are mainly contained in the ion exchangeable, reducible fractions (Fig. 3). No bioavailable fractions of Fe, Cu, and Zn are detected at D1 and D2, while 16.15-18.73% of Mo is bioavailable fraction. The alkaline condition is helpful for increasing the solubility of molybdate ion (Table 1) and most of which will leach from tailings pond with mine drainage. As a contrast to Mo, the high levels of Fe, Cu, and Zn observed in sediments could be mainly caused not by weathering eluviations, but by rainfall erosion, wind erosion on the surface of tailings pond.

As showed in Fig. 3. from S1 to S4 (Fig. 1). the percent of reducible fractions of Fe, Cu, and Zn is higher than that of oxidisable fractions, probably because particle abrasion during flow transport has exposed fresh these sulfide minerals to the highly oxidized environment in the turbulent river water. The percent of

Table 3. Chemical composition according to XRF analysis of samples from the tailings ponds (%)

Oxide [a]	D3	D4	D5
SiO_2	76.87	76.45	77.52
Al_2O_3	2.04	2.61	1.88
K_2O	3.22	3.89	3.78
Na_2O	3.28	3.05	3.14
Fe_2O_3	2.85	2.01	1.64
CaO	10.2	10.14	10.68
TiO_2	0.11	0.34	0.17
MgO	0.41	0.58	0.47
MnO	0.67	0.61	0.67
P_2O_5	0.05	0.07	0.04
Sum	99.7	99.75	99.99

[a] The oxide composition has been calculated assuming surplus of oxygen

Table 4. Minerals identified by XRD analysis of samples from the tailings ponds

D3	D4	D5
Quartz	Quartz	Quartz
Potassium feldspar	Potassium feldspar	Potassium feldspar
Plagioclase	Plagioclase	Plagioclase
Calcite	Calcite	Calcite
Epidote	Epidote	Epidote
Pyrite	Pyrite	Pyrite
Molybdenite	Molybdenite	Molybdenite
(Chalcopyrite)	(Chalcopyrite)	(Chalcopyrite)
(Sphalerite)	(Sphalerite)	(Sphalerite)

Minerals in parenthesis were only indicated

bioavailable fraction of Mo abruptly increases with distance (31.14-59.07%), because of the alkaline condition in sediments. From S5 to S7, located in Wujintang Reservoir, the percent of oxidisable fractions of Fe, Cu, Zn, and Mo is higher than that of reducible fractions because of the dissolution of Fe or Mn oxides under reduction condition (Karbassi *et al.,* 2006; Lahann, 1976). In such a reduction condition, the bioavailable fraction of Mo (18.61-20.25%) does not account for the high amount of the Mo in the reservoir sediments. This is interpreted as secondary Mo sulfide precipitation under the slightly reducing conditions (Brookins, 1988). Moreover, from S1 to S7, low abrasion strength of some Fe, Cu, Zn, and Mo-bearing minerals may have reduced the residual metal fractions (Langedal, 1997). In sediments downstream of the Wujintang Reservoir, the reducible fractions of Fe, Cu, Zn, and Mo gradually increase, while their oxidisable fractions decrease. The bioavailable fraction of Mo gradually increases from S8-S10. Such an increase is surprising since molybdate solubility increases considerably at oxidizing, slightly alkaline conditions (Lahann, 1976; Langedal, 1997).

The distribution of geochemical speciation of Fe, Cu, Zn, and Mo in overbank sediments is similar with corresponding that of in bed sediments.

Metal fractions obtained from sequential extractions may correlate with concentrations in microorganisms. In the present investigation, bioavailable, adsorption/ion exchangeable, reducible and oxidizable fractions are considered the fractions that are more or less available to aquatic biota (Tack and Verloo, 1995), especially bioavailble fractions (Jain, 2004). In order to assess the bioavailability or pollution intensity in Nver river sediments (from S1/P1 to S10/P10), mean concentrations of metals and chemical fractions were used to provide a measure of the level of pollution in the study area according to I_{POLL} and the RAC (Table 5). High I_{poll} indicates that all of these four heavy metals might pose an environmental risk.

The I_{POLL} of Fe, Cu and Zn are higher than that of Mo, but the bioavailable Mo fraction is higher than that of the others metals. The RAC reveals that the river and reservoir sediments having 11-30% bioavailable fraction of heavy metals are at medium risk (Jain, 2004) and the bioavailable fraction of these metals can easily enters the food chain. The proportion of bioavailable Mo fraction in the Nver river sediments ranges from 18.61 to 59.07% and mean proportion is 46.5%. Therefore, Mo may pose a higher risk to the local environment in contrast to Fe, Cu and Zn. Bioavailable and ion exchangeable fractions heavy metals reveal the leaching potential in environmental conditions. Heavy metals bound to Fe-Mn oxides, which are absorbed in amorphous or weakly-crystal phases, will be released out with the presence of reducing agents. Heavy metals bound to organic compounds will be migrated into environment by reacting with complexing agents or oxidants. In contrast, heavy metal in residual fraction can not be released out in most cases.Since Fe^{3+}, Cu^{2+}, and Zn^{2+} show low solubility under oxidized, alkaline conditions, massive leaching or release of Fe, Cu, and Zn from tailings pond is an unlikely scenario. Further work on the buffer capacity and acid production capacity of the tailings pond is needed to evaluate this risk. Fe, Cu, and Zn associated with Fe and Mn oxides may show high solubility in the Wujintang Reservoir sediments on account of the dissolution of Fe or Mn oxides under reduction condition. However, these metals may be immediately adsorbed or complexes by organic matter or associated with sulfides in reservoir sediments (Fig. 3). Heavy metals associated with organic matter or sulfides are difficult to release from Wujintang Reservoir sediments under reductive condition.

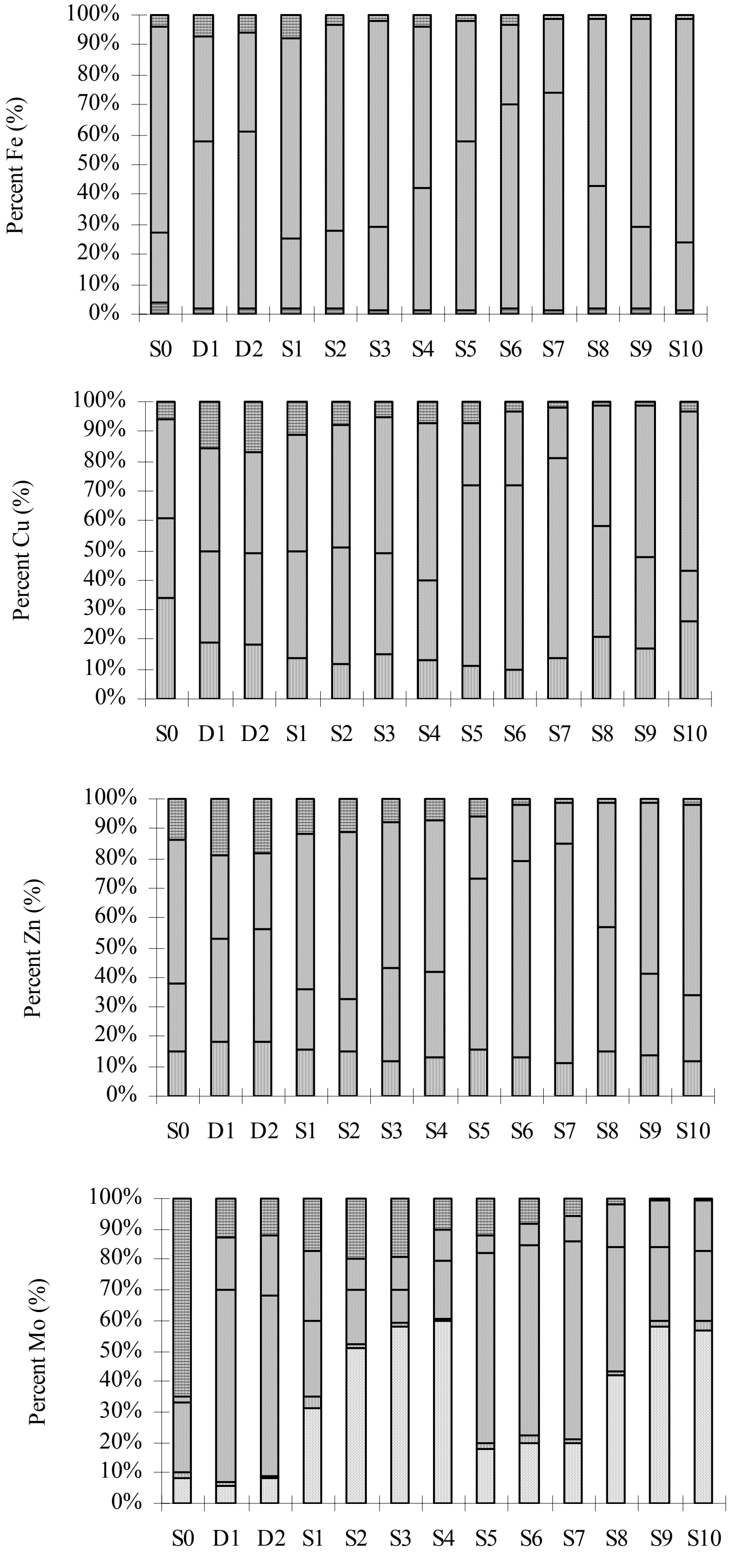

Fig. 3. Distribution of speciation proportions of Fe, Cu, Zn, and Mo in tailings and bed sediments of Nver River. Samplings media: D = tailings pond, S = bed sediment

Table 5. Pollution intensity of metals in Nver river sediments

Metal	Mean concentration (B_c) (mg/Kg)	Mean L_p (mg/Kg)	I_{poll}	Mean proportion of bioavailable fraction
Fe	6257.01	281.57	4.47	Nd
Cu	136.61	7.24	4.27	Nd
Zn	122.06	6.61	4.21	Nd
Mo	302.52	23.60	3.68	46.5%

Nd: Not detected

The retention of heavy metals in the environment is probably dependent, to a large extent, on adsorption/complex reactions with some oxides and organic matters. Iron, aluminum, to some extent, titanium oxides may be important sorbent for Mo, as they may acquire positive charge at low pH (Bibak and Borggaard, 1994; Rietra *et al.,* 1999; Xu *et al.,* 2006). According to the sequential extraction results, in Lanjiagou Mo tailings ponds, Mo will release from the tailings ponds under oxidized, alkaline conditions (Table 1) during weathering. The tailings ponds become the major Mo contamination source of the Nver River. More attention should be attached to the problems of leaching and release of Mo from tailings pond. A wide range pH of complexes with organic matters has been reported in solution (Cruywagen *et al.,* 1995), but this studies show that, except for in Wujintang Reservoir sediments, only partial Mo is adsorbed or complexes with organic matter (Fig. 3). A slow release of Mo adhered to organic matter in the sediments may be expected as the organic matter is oxidized. Bioavailable fraction of Mo presents high leaching potential so that special attentions should be given on the effective techniques preventing the migration of Mo in sediments. However, the risk of acute Mo poisoning of grazing animals is probably low since grass from the floodplains only constitutes a part of their diet.

CONCLUSION

1) Lanjiagou Mo tailings contain the major heavy metals identified in the sediment of the Nver River and Wujintang Reservoir. The average concentrations of Mo in the sediment samples of the Nver River are higher than the corresponding values of the abundance in earth's crust and the reference values (S0, P0). The mean concentrations of Fe, Cu, and Zn in sediment samples upstream of Wujintang Reservoir are also higher than the reference values (S0, P0).

2) High I_{POLL} indicates that all of these four heavy metals might pose an environmental risk. 18.61-58.26% of Mo in the sediments samples is bioavailable, which may pose a high risk to the local environment according to RAC. Special attentions should be given on the effective techniques preventing the migration of Mo in sediments.

3) Based on the comparison analysis of concentrations and speciation of Fe, Cu, Zn, and Mo from the samples in Mo tailings ponds deposited along the bank and sediments in the Nver River, it is indicated that Mo tailings ponds deposited along the river bank may have a closely relationship with the high levels of these heavy metals in sediments.

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