

Particulate matter as scavenger and carrier of trace metals in simulated mine water

Åsa SJÖBLOM¹, Karsten HÅKANSSON², Bert ALLARD³

¹*Boliden Mineral AB, Aitik, P.O. Box 85, SE-982 21 Gällivare, Sweden, asa.sjoblom@boliden.com*

²*Geoinnova AB, Teknikringen 1C, 583 30 Linköping, Sweden, karsten.hakansson@geoinnova.se*

³*Man-Technology-Environment Research Centre, Örebro University, 701 82 Örebro, Sweden, bert.allard@oru.se*

Abstract The influence of iron (originally as Fe(II), at mg/L-level) on the distribution of trace elements (Cu, Zn, Pb and As) between suspended particulate matter (size above 0.2 µm) and water was investigated in a laboratory study. Scavenging of the trace elements by precipitating iron oxyhydroxides was rapid (reaction within hours) and ranging from 35% to 90% uptake of As, Cu and Pb, in the absence of dissolved organic matter. The presence of a humic acid had a negative influence on the particle growth rate, as well as on the association of the trace elements with the precipitating iron phase.

Key Words Precipitation, particles, iron oxyhydroxides, distribution, humic acids

Introduction

Iron oxyhydroxides that precipitate when ferrous iron in mine drainage is oxidised, are well-known scavengers of trace elements (Johnson, 1986; Kimball et al., 1995; Webster et al., 1998; Paulson and Balistrieri, 1999). This phenomenon may lead to a trace metal transport mechanism that is defined by the mobility of suspended particles serving as carriers rather than by the flux of the water with its load of dissolved species in true solution. This may also represent a natural process for attenuation of contaminants, if the particles are large and dense enough to settle and accumulate in the bottom sediments of draining watercourses. The efficiency of the process is highly pH-dependent, both with respect to the oxidation of ferrous iron (Kirby et al., 1999) and to the distribution of the trace elements between solid phases (adsorption) and the water phase (Johnson, 1986; Webster et al., 1998). The solid/solution distribution is also significantly affected by the presence of organic acids (Düker et al., 1995). Thus, the scavenging of trace metals by naturally occurring or artificially supplied iron oxyhydroxides may serve as the initial step of a complementary method for treatment of metal-rich acid mine drainage. The distribution of trace elements (Cu, Zn, Pb and As) between solid suspended matter and solution when a water with high levels of the elements is mixed with a water with high levels of dissolved iron (mg/L-level) is studied in this project. Emphasis is given to the effects of dissolved organic matter (humic acid) on the formation of solid particles and on the subsequent adsorption of trace elements on the suspended solid matter.

Materials and methods

Experimental setup

Eight waters (denoted G, D, O, S, C, P, H and M), with metal concentrations representative of surface waters and groundwater in a mining area (Kristineberg, Sweden; Sjöblom, 2003) were prepared from a stock solution (1 mM NaHCO₃, 0.1 mM CaSO₄, pH 6) with additives: Iron (Fe²⁺, 2 mg/L), trace elements (Cu, 100 µg/L; Zn, 500 µg/L; Pb, 10 µg/L; As, 5 µg/L), fine-grained (0.063–0.125 mm) gibbsite (0.5 mg/L) and humic acid (TOC 12 mg/L). Milli-Q water and analytical grade chemicals were used, as well as Na-humic acid from Aldrich.

Initial concentrations are given in Table 1. The ferrous iron was allowed to oxidise and precipitate in O and S, however in the presence of the humic acid in S.

1 "Groundwater"	Stock solution + iron; anaerobic (G)
3 "Surface waters"	Stock solution, no additives (D), stock solution + iron; aerated (O); stock solution + humic acid and iron, aerated (S)
4 "River waters"	Stock solution + trace metals (C); stock solution + trace metals and gibbsite (P); stock solution + trace metals and humic acid (H); stock solution + trace metals, gibbsite and humic acid (M)

Table 1 Initial composition of "river waters" (C, P, H and M) and "surface waters" (O and S).
Averages and standard deviations for triplicate samples

	C	P	H	M	O	S
pH	6.2 (0.1)	6.1 (0.1)	6.1 (0.1)	6.1 (0.1)	7.2 (0.1)	7.4 (0.1)
OC ^a mg/l	0.3 (0.2)	<	13.6 (1.5)	13.0 (1.3)	0.8 (0.1)	13.1 (0.3)
IC ^b mg/l	1.8 (0.1)	1.8 (0.0)	1.5 (0.1)	1.4 (0.1)	4.8 (0.1)	5.4 (0.1)
Na mg/l	9.1 (0.1)	10.1 (0.2)	13.2 (0.2)	13.6 (1.0)	9.8 (0.3)	11.8 (0.1)
Ca mg/l	3.8 (0.1)	4.2 (0.1)	4.8 (0.8)	4.5 (1.1)	3.7 (0.1)	3.9 (0.4)
Fe µg/l	<	<	310 (10)	310 (0)	1900 (0)	2200 (0)
Al µg/l	<	<	180 (0)	190 (10)	<	170 (0)
Zn µg/l	510 (20)	540 (10)	550 (50)	580 (50)	3 (2)	3 (0)
Cu µg/l	90 (0)	90 (0)	100 (0)	100 (10)	0.2 (0.0)	0.3 (0.0)
Pb µg/l	10.0 (0.3)	11.1 (0.2)	11.0 (0.0)	11.3 (0.6)	0.1 (0.1)	0.6 (0.0)
As µg/l	4.1 (0.2)	4.2 (0.1)	4.5 (0.1)	4.6 (0.3)	<	<

^a Organic carbon; ^b Inorganic carbon; < = below detection limit

Each "river water" was mixed with an equal volume of each "surface water" and the "groundwater" (250 ml of each one), giving 16 combinations: DC, SC, OC, GC; DP, SP, OP, GP; DH, SP, OH, GH, and DM, SM, OM, GM.

All mixtures of M and P (8) contained an added particle fraction (gibbsite), all mixes with G, O and S (12) contained, with time, a particle fraction of precipitated iron oxyhydroxide, and all mixtures of S, H and M (10) contained humic acid, Table 2.

Sampling and analysis

Samples were taken from the 16 water mixtures after 1, 5, 24 and 48 h. The bottles with the water was shaken, and some 100 ml was withdrawn and split into 3 fractions, each 30 ml: (1) Non-filtered with its load of suspended particles, (2) filtered, through a 1.2 µm-filter, and (3) filtered, through a 0.2 µm- filter (Micro Filtration system, polypropylene equipment; Millipore polycarbonate filters).

TOC (Shimadzu TOC-5000 Total Organic Carbon Analyzer) and pH (Radiometer PHM84 Research pH-meter with a combination electrode) were measured in the three solutions. The samples were acidified (2 drops of supra pure HNO₃ per 20 ml), and metal concentrations were determined (Perkin-Elmer SCIEX Elan 6100 DRC ICP-MS). The concentrations of particulate (>0.2 µm and >1.2 µm) organic carbon and metals were calculated as the differences between total concentrations and the concentration of the corresponding filtrates.

Results and discussion

The total concentrations of all constituents in the various water mixtures reflected the composition of the original waters, however with minor losses of Fe, Cu, Pb and As with time (adsorption on vessel walls?). The average pH was 7.2 (0.1) after 48 h. The partition of iron and the trace elements between the two suspended size fractions and solution were largely established and constant already after 1 h. All distribution results (after 24 h) are summarised in Figure 1.

Large fractions of Cu, Pb and As (above 90%) were recovered in the particulate phase in the presence of iron and absence of humic acid. For zinc, however, less than 15% was associated with particles, reflecting the poor hydrolysis, and poor adsorption to the iron phase, in comparison with copper and lead.

Table 2 Experimental setup

	<i>Additive</i>	"Surface waters"			"Groundwater"
		---	<i>Fe, HA</i>	<i>Fe</i>	<i>Fe</i>
"River waters"	---	DC	SC	OC	GC
	<i>Al</i>	DP	SP	OP	GP
	<i>HA</i>	DH	SH	OH	GH
	<i>Al, HA</i>	DM	SM	OM	GM

---: No additive; HA: Humic acid added; Fe: Iron added; Al: Gibbsite added

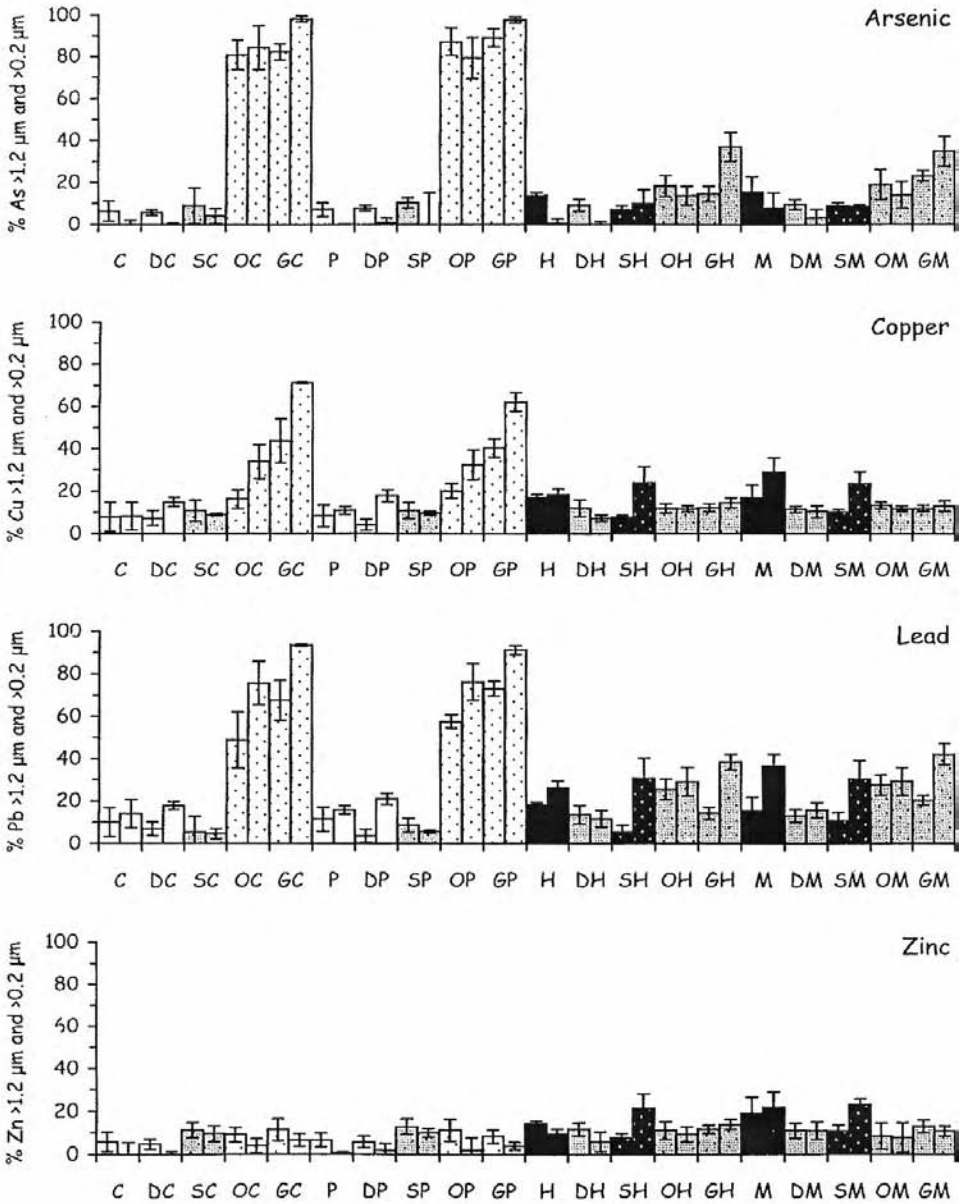


Figure 1 The fraction of the trace element associated with particles >1.2μm (left bar) and >0.2μm (right bar) after 24 h. Average values and standard deviations for triplicate samples. Black and grey bars - systems with humic acid; white bars - systems without humic acid; dotted bars - systems with added iron

The presence of gibbsite had little influence on the distribution in the absence of iron, in contrast to previous observations of trace metal association with fresh precipitates of aluminium hydroxide in AMD (Karlsson, 1987).

The presence of humic acids drastically decreased the fraction of Cu, Pb and As associated with particles (by a factor of 2–3), while the particulate fraction of zinc increased slightly. A large fraction of the humic acid (up to 35%) did not pass the 0.2 µm filter, which indicates the presence of a high-molecular weight fraction. Some of the retention of organic matter on the finest filter may be an artefact – clogging, leading to an overestimation of the particulate fraction (Karlsson et al., 1994).

Conclusions

The study shows that even minor amounts of iron oxyhydroxides can have a decisive influence on the partitioning of Cu, Pb and As (but not Zn) between dissolved and particulate species at near neutral pH. As much as 71% (Cu), 94% (Pb) and 99% (As) were recovered in the particles >0.2 µm already one hour after the addition of an iron-rich water. However, the experimental conditions favoured the iron precipitation, particularly the pH (higher than generally encountered in a non-buffered AMD-system). The presence of consolidated suspended particles in the system (gibbsite) had little influence on the distribution of trace elements – the dominating adsorbing solid phase was the fresh precipitate of iron oxyhydroxides.

Presence of metal complexing organic matter (humic acid) had a negative influence on the formation of a particulate iron fraction, as well as on the trace element uptake on this fraction. However, as much as 45% (Cu), 41% (Pb) and 38% (As) were recovered in the particles (maximum values), also in the presence of humic acid.

Acknowledgements

This study was part of a follow-up of the Swedish research program Mitigation of the Environmental Impact from Mining Waste (MiMi), originally financed by the Foundation for Strategic Environmental Research (MISTRA) and in the present analysis part of the Bergskraft Bergslagen program.

References

- Düker A, Ledin A, Karlsson S, Allard B (1995). Adsorption of zinc on colloidal (hydr)oxides of Si, Al and Fe in the presence of a fulvic acid. *Applied Geochemistry* 10:197–205
- Johnson CA (1986). The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage. The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochim. Cosmochim. Acta* 50:2433–2438
- Karlsson S (1987). Influence of hydrochemical parameters on the mobility and redistribution of metals from a mine waste deposit. Linköping Univ. (Dissertation)
- Karlsson S, Peterson A, Håkansson K, Ledin A (1994). Fractionation of trace metals in surface water with screen filters. *Science of the Total Environment* 149:215–223
- Kimball BA, Callender E, Axtmann EV (1995). Effects of colloids on metal transport in a river receiving acid mine drainage, upper Arkansas River, Colorado, U.S.A. *Applied Geochemistry* 10:285–306
- Kirby CS, Thomas HM, Southam G, Donald R (1999). Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. *Applied Geochemistry* 14:511–530
- Paulson AJ, Balistrieri L (1999). Modeling removal of Cd, Cu, Pb and Zn in acidic groundwater during neutralization by ambient surface waters and groundwaters. *Environmental Science and Technology*. 33:3850–3856
- Sjöblom Å (2003). Wetlands as a means to reduce the environmental impact of mine drainage waters. Linköping Univ. (Dissertation)
- Webster JG, Swedlund P J, Webster KS (1998). Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate. *Environmental Science and Technology* 32:1361–1368