COPPER TRANSPORT THROUGH IRON-RICH REGOLITH

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INTRODUCTION

Copper transport through regolith is of interest because its concentration in soil can be due to upward transport from an ore body via dissolution into the groundwater (Gunton 2003). Copper levels in water and/or soil can also reach toxic levels due to contamination from landfills, urban runoff, mining, tailings and industries (Ferrara *et al.* 1984, Drever 1997, Bradl 2004). The manipulation of factors affecting transport of heavy metals is the basis for the design of remediation methodologies (Siegel 2002). Metal transport can be due to a combination of physical, chemical and biological processes. Of particular significance is the influence of groundwater flow and accompanying geochemical reactions, which are dependent on pH, complexation, oxidation and reduction, as well as equilibrium with gas phases, solubility, sorption (Ferrara *et al.* 1984, Drever 1997) and accumulation by vegetation and microorganisms (Drever 1997, Siegel 2002).

The most important control on metal transport in regolith is thought to be sorption. Of the many phases onto which this occurs, iron oxyhydroxides are thought to be the most adsorbent. Goethite and hematite are the most common iron oxyhydroxides (McKenzie 1980, Schwertmann & Cornell 1991, Langmuir 1997) and are common regolith constituents as coatings on silicate minerals and as discrete grains(Drever 1997).

Adsorption of metals by iron oxyhydroxides is affected by many solution properties, including pH, redox potential (Siegel 2002), ionic strength, temperature (Siegel 2002), competition from other cations (Balistrieri & Murray 1982), anions such as chloride (Gunton 2003) and sulfate (Balistrieri & Murray 1982) and polar organic compounds (Christl & Kretzschmar 2001). Sorbent phase characteristics such as composition, surface area, sorption site density and surface charge also have an effect on the amount of sorption (Pabalan *et al.* 1998).

The present study aims to better understand copper transport in groundwater flow through the regolith. More specifically the aims are to understand:
- The effects of pH, salinity and organic acids (acetate) on copper transport;
- The effect of different iron-rich regolith materials on copper transport;
- How copper is trapped within regolith materials, and;
- The length and time scales of copper transport in groundwater and regolith under different conditions.

PREVIOUS STUDIES

Previous work on copper transport has used batch experiments to understand the effect of solution variables (pH, salt content, complexing ligands and competing ions) on sorption to synthetic hematite (McKenzie 1980, Christl & Kretzschmar 2001, Peacock & Sherman 2004) and synthetic goethite (Barrow *et al.* 1981, Balistrieri & Murray 1982, Padmanabham 1983, Ali & Dzombak 1996, Gunton 2003, Peacock & Sherman 2004).

It is well established that at very low pH there is little adsorption. However, as pH rises cations are strongly adsorbed. The transition from zero to full adsorption (the adsorption edge) occurs over a range of pH which is unique for each ion (Barrow *et al.* 1981, Bradl 2004, Peacock & Sherman 2004) and mineral. The adsorption edge for copper onto hematite has been found to occur between pH 3.5 and 6.0, and onto goethite between pH 2.5 and 6.0 (McKenzie 1980). These values were obtained in air at room temperature at a mineral concentration of 20 g/L in 0.2 M potassium nitrate and 0.05 mmol/g of metal. The adsorption edge for copper has also been found to occur between pH 3.0 and 6.0 for hematite and between pH 3.5 and 6.0 onto goethite (Peacock & Sherman 2004). These values were obtained at a metal concentration of 25 ppm in 0.1 mol/L sodium nitrate and 3.33 g/L of mineral. Equilibration was under nitrogen gas at 25°C for 1 week. Copper adsorption to goethite has also been found to occur between pH 3.5 and 6.0 at metal concentration of 0.8 mg/g in 1 mol/kg sodium nitrate, mineral concentration of 9.19 g/L. Equilibration was under nitrogen at 25°C for 2 hours.

The effect of chloride on Cu^{2+} adsorption to synthetic goethite is not well understood. Chloride was found to have no influence at all on copper adsorption (Swallow *et al.* 1980, Balistrieri & Murray 1982, Criscenti & Sverjensky 1999). In other studies chloride was found to enhance copper adsorption (Barrow *et al.* 1981,

Padmanabham 1983). A literature review of empirical data came to the conclusion that as chloride increases, adsorption decreases (Criscenti & Sverjenski 1999), however, a recent study has found that at 1 mol/kg chloride concentration, copper sorption is suppressed, although at 3 mol/kg, sorption is increased at pH <4.5 (Gunton 2003).

The effect of organic acids has also been investigated. Chelidamic and phthalic acids are known to enhance copper adsorption to synthetic goethite at low pH (Ali & Dzombak 1996). Fulvic acid (38 mg/L) is known to enhance Cu (22 µmol/L) adsorption to synthetic hematite (2 g/L) below pH 5.8, but to inhibit adsorption at higher pH (Christl & Kretzschmar 2001).

In competitive experiments, copper (20 µmol/g of mineral) is known to adsorb more strongly than zinc to both synthetic goethite and synthetic hematite at pH 5.5 (McKenzie 1980). It is known that synthetic goethite (20 g/L) adsorbs copper (0.05 mmol/g) more strongly than synthetic hematite at pH 5 (McKenzie 1980).

METHODS

Four different regolith materials were studied. A synthetic goethite-coated sand was prepared by synthesising goethite onto acid-washed quartz sand (Meng & Letterman 1993, Szecsody *et al*. 1994). Natural goethite-coated sand was sourced from a granitic terrain around 80 km west of Southern Cross in the Yilgarn Craton. Hematite-coated sand was collected from a sand plain north of Duketon Well, WA (latitude: 27° 30.460' longitude: 122° 20.080'). A hematite-coated soil was collected from a mineralised area near the hematite-coated sand. The natural sands were washed in ultrapure water 10 times, sieved to between 125 and 1000 µm and cleared of small twigs before analysis and experimentation, but the soil was left untreated otherwise. Table 1 summarises the properties of the prepared regolith materials. Mineral and amorphous component content were estimated from powder X-Ray Diffraction data and interpretation using the SIROQUANT software. Bulk oxide compositions were measured using conventional X-Ray Fluorescence methods (Dr. Ulrike Troitzsch *pers. comm.* 2005). Surface areas were measured using the BET method (Schwertmann & Cornell 1991, Lehmann *et al*. 2001). Copper concentration was measured using LA-ICP-MS.

Table 1: Chemical composition and mineral abundance of regolith materials used in this study.

	Synthetic goethite-rich sand	Natural goethite-rich sand	Hematite-rich sand	Hematite-rich soil
Surface area (m^2/g)	< 0.01	1.4 ± 90%	1.3 ± 90%	15.8 ± 24%
Colour	Light yellow	Brown-yellow	Brown-red	Brown-red
Silicon (oxide wt%)	97.890 ± 0.211	93.455 ± 0.220	92.90 ± 0.21	45.15 ± 0.10
Iron (oxide wt%)	0.175 ± 0.005	0.410 ± 0.006	2.18 ± 0.01	34.15 ± 0.08
Titanium (oxide wt%)	0.010 ± 0.005	0.110 ± 0.005	0.12 ± 0.01	0.83 ± 0.01
Aluminium (oxide wt%)	0.019± 0.005	1.950 ± 0.009	1.96 ± 0.01	11.40 ± 0.03
Potassium (oxide wt%)	0.019 ± 0.005	0.016 ± 0.005	0.08 ± 0.01	0.32 ± 0.01
Amorphous Content (wt%)	-	36.5 ± 0.5	15.0 ± 0.3	31.4 ± 1.2
Copper (µg/g)	-	3.47 ± 20%	4.11 ± 20%	57.22 ± 10%
Quartz (wt%)	>98	56.6 ± 0.3	84.0 ± 0.2	27.3 ± 0.3
Goethite (wt%)	-	-	-	6.7 ± 0.5
Hematite (wt%)	-	-	1.0 ± 0.2	17.7 ± 0.5

Metal-bearing solutions were prepared from reagent-grade nitrate salts and chloride solutions were prepared from reagent-grade sodium chloride. All solutions were pH buffered with sodium acetate. Column experiments were used to study the transport of copper under different conditions and through the different regolith materials. The columns were standard chromatography columns (glass tubes) of 16 mm internal diameter and length-adjustable end pieces fitted with 10 µm filters. In each experiment 50 g of regolith material was packed in a length of 16 cm. The tube was filled first with ultrapure water before adding the solid in order to minimise the trapping of air bubbles. Ultrapure water was then pumped upward in the columns using a peristaltic pump set at 1.06 mL/min until a constant electrical conductivity (EC) of the output solution was obtained (approximately 1 hour). The metal-bearing solution was then pumped through

for 24 hours. Experiments were run at room temperature, which was approximately 20 ± 2ºC (Dr Andy Christy *pers. comm.* 2005). Breakthrough and buffer efficacy of solutions were monitored by electrical conductivity and pH of the eluent. Water samples were taken at regular intervals and acidified with concentrated nitric acid before analysis by ICP-AES. Both filtered (0.2 μm) and unfiltered liquid samples were tested. Ultra pure water was flushed through each column for one hour after the metal-bearing solutions, before the columns were taken apart and selective extractions performed on regolith samples taken from the eight 2 cm length intervals. Samples of 1 g were boiled for 6 hours in 0.04 M $NH_2OH.HCl$ in 25% acetic acid before filtration through 0.2 μm syringe filters for ICP-AES analysis. Other extraction techniques tried were agitation in 1 M sodium acetate for one hour, and agitation in 0.31 M magnesium chloride for 20 minutes (Tessier *et al.* 1979). The extraction data from each length fraction were reproducible within 15%, and the amount of copper in each column as a whole was reproducible within 7%. The eluent samples were reproducible within 7%.

RESULTS AND DISCUSSION

Control experiments are discussed first, then results are presented by variable tested: pH; salinity; acetate; competition; then, regolith material. Plots of copper transport with time are shown for each variable, and a plot showing the variation in trapped copper with length in the solid material is shown for the pH experiments.

There was no effect on copper transport between filtering (0.2 μm) and not filtering the eluent from natural goethite-rich sand after 10 mg/L copper in 0.01 M acetate was pumped through over 24 hours. This was observed at both pH 4.0 and 4.5. There was no effect on copper transport through acid-washed quartz sand after 25 mg/L copper in 0.01 M acetate was pumped through over one hour at pH 4.0. There was also no measurable copper eluted from natural goethite-rich sand when flushed with ultra pure water and 0.01 M acetate at pH 4.50. All regolith materials were selectively extracted before experimentation, and the amount of copper in the leachate was well below 3 ppm for the soil and < 1 ppm for the other materials. Different selective extraction techniques were applied to the same soil fractions after a column experiment in which 25 mg/L copper in 0.01 M acetate at pH 4.0 was pumped through for one hour. The magnesium chloride method gave 60% of the input copper, the sodium acetate method gave 2% and the hydroxylamine hydrochloride method gave 90%.

Copper transport at pH 4.0 was compared with pH 4.5 and 5.0 (See Figures 1 and 2). During the first few hours, copper transport is greatest in the pH 4.0 water, slightly less in the pH 4.5 water, and much less in the pH 5.0 water (See Figure 2). By the 21 hour mark, the copper transport is greatest in the pH 5.0 water and much the same in the pH 4.0 and 4.5 waters. The amount of copper leached from the sand (See Figure 1) showed that 24% of input copper was trapped at pH 5.0, 14% at pH 4.5 and 14% at pH 4.0. At pH 5.0 there is little variation with length, implying that steady state is approaching. At pH 4.0 there is more variation with length.
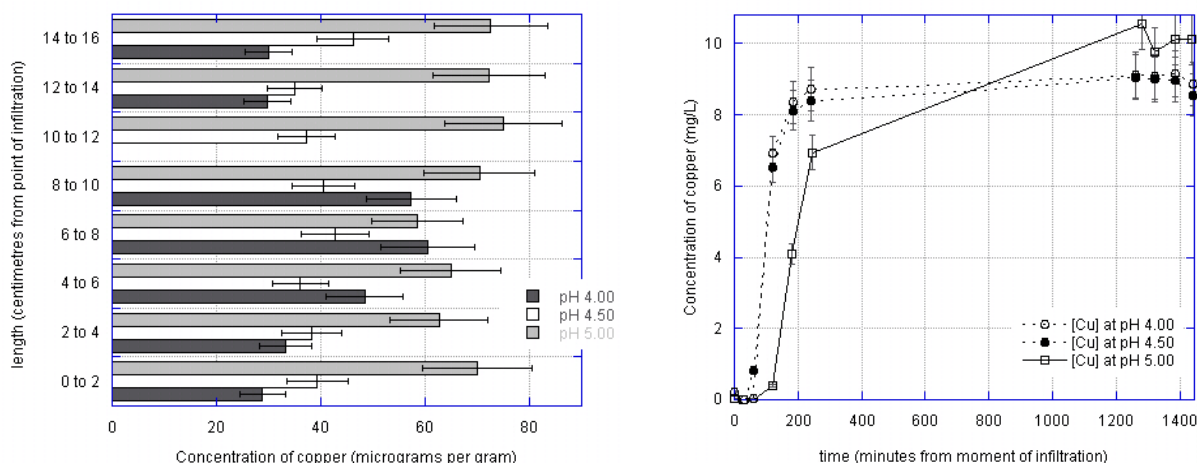

Figure 1 (left): Amount of copper trapped in natural goethite-rich sand after exposure to waters at pH 4.00, 4.50 and 5.00. Solutions of 10 mg/L copper in 0.01 M acetate were pumped through for 24 hours.
Figure 2 (right): Copper transport through natural goethite-rich sand at pH 4.0, 4.5 and 5.0. Solutions of 10 mg/L copper in 0.01 M acetate were pumped through for 24 hours.

Copper transport at 0.5 m chloride was compared with 0.05 m and 0 m (See Figure 3). In the first few hours

much more copper is retained in the more highly saline water than in the less saline water. The amount of copper in the non-saline water sits between the two saline-waters. The result is significant in the first few hours, but after 24 hours there is very little difference. Extraction of the solid material showed that 24% of input copper is trapped in the sand when no chloride is present, 25% is trapped at 0.05 m chloride and 13% at 0.5 m chloride

Copper transport at 0.01 M acetate was compared with 0.1 M. More copper was retained in the water at higher acetate, however, the difference between the two was greatest in the short term, becoming less significant towards the end of the experiments (See Figure 4). Extraction of the solid material showed that at 0.1 M acetate 7% of the input copper is trapped in the sand, but at 0.01 M acetate 14% is trapped.
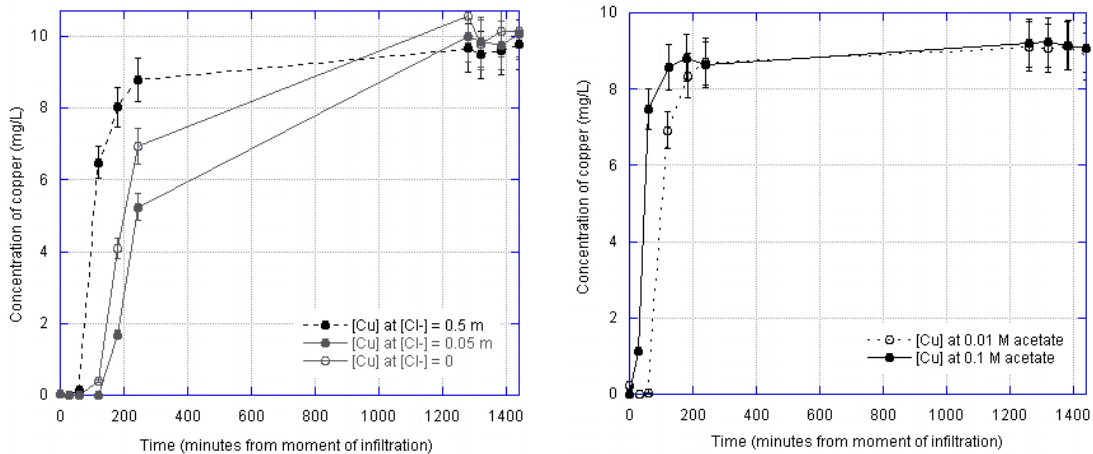

Figure 3 (left): Copper transport through natural goethite-rich sand at chloride concentrations of 0 m, 0.05 m and 0.5 m. Solutions of 10 mg/L copper in 0.01 M acetate at pH 5.0 were pumped through for 24 hours.
Figure 4 (right): Copper transport through natural goethite-rich sand at acetate concentrations of 0.01 M and 0.1 M. Solutions of 10 mg/L copper at pH 4.00 were pumped through for 24 hours.

Copper transport in presence of other metals was tested by comparing transport of Cu and Zn in solitary solutions with transport in a competitive solution (See Figure 5). In the competitive experiment more zinc was retained in the water than copper, and both metals were measured at greater concentrations in the water than in experiments with only one metal ion present. Extraction of the solid material showed that 14% of input copper was trapped when alone, but 11% when in competition with zinc. Amount of zinc extracted was 15% of input when alone, but 8% when in competition with copper.

Copper transport through synthetic goethite-rich sand, natural goethite-rich sand, natural hematite-rich sand and natural hematite-rich soil were compared (See Figure 6). Copper was transported best through the synthetic goethite-coated sand, less through the natural goethite-coated sand, even less through the hematite-sand, and least of all through the hematite-soil. Extractions on the solid materials showed that the soil trapped the most copper at 140% of the input copper. The hematite sand trapped 34%, the goethite sand 14% and the synthetic sand just 1.4% of input copper.

CONCLUSIONS
In the first four hours copper transport was greatest at pH 4.0 and lessened as pH rose, but by 24 hours copper transport was greatest at pH 5.0. Adsorption is known to increase with increasing pH, so this result may indicate that at pH 5.0, the effect of adsorption lowers copper transport initially, but by 24 hours most of the adsorption sites are filled and copper is transported through the regolith. So at higher pH, maximum transport occurs more quickly.

In the first four hours copper transport was greatest at 0.5 m chloride, less at 0 m chloride, and lesser still at 0.05 m chloride. By 24 hours all solutions seemed to have reached maximum transport. Far less copper was found trapped in the sand at 0.5 m chloride, suggesting that in the short term chloride at high enough concentrations could be complexing the copper, inhibiting adsorption processes in the regolith and promoting copper transport, but over longer periods the effect is not much different to low and no chloride.

In the first four hours greater copper transport was observed at 0.1 M acetate than at 0.01 M. In the longer term there was no difference in copper transport, and neither solution had reached transport maximum. This

could indicate that at least in the short term, copper complexation by acetate inhibits adsorption to the regolith and promotes transportation.
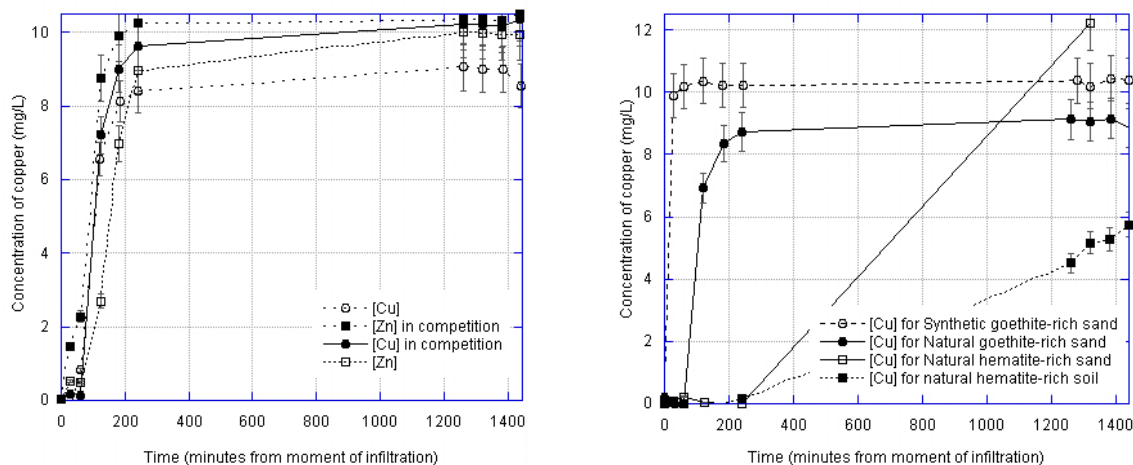

Figure 5 (left): Cu and Zn transport through natural goethite-rich sand in 10 mg/L solitary solutions and in competition at 10 mg/L each. Solutions of 0.01 M acetate at pH 4.50 were pumped through for 24 hours.
Figure 6 (right): Copper transport through different regolith materials. Solution of 10 mg/L copper in 0.01 M acetate at pH 4 was pumped through for 24 hours.

Over 24 hours, the synthetic goethite-rich sand appeared to reach the copper transport maximum. The natural goethite-rich sand transported less, and the hematite-rich soil far less. The hematite-rich sand behaved like the hematite-soil in the first four hours, but by 21 hours had gone beyond the expected transport maximum, perhaps indicating that adsorption was very fast onto this material, but had reached capacity before 21 hours, allowing maximum copper transport. The soil by contrast, adsorbed the copper quickly but did not reach adsorption capacity within 24 hours, resulting in a low level of transport over longer time periods. The goethite-rich sand appeared to adsorb the copper to a lesser extent, but did not reach capacity within 24 hours, resulting in consistent copper transport, but not at a maximum level. The amount of copper trapped in the sand appeared to be in correlation with both the surface area and the iron content of the materials, indicating that the greatest copper transport is to be expected in regolith materials with low iron content and large grain sizes. It is also evident that results can be quite different from synthetic to natural materials, highlighting the importance of studying natural regolith samples.

The use of different selective extraction methods on separate aliquots from the same column gives insight into how the copper is trapped in the regolith. The hydroxylamine hydrochloride method leached off almost all copper associated with the regolith, whereas the magnesium chloride took off 60% compared with 2% from sodium acetate. Each selective extraction presumably targets copper bound in a particular way to the regolith, so the copper leached by each method can be presumed to be trapped differently. It is possible that the copper leached after experiments may not really be 'adsorbed' as presumed, but trapped in some other way.

The effects of pH, chloride and regolith material on copper transport during the first 4 hours were often completely different from those seen over 24 hours. This highlights the significance of the time scale in adsorption reactions, and the importance of doing long-term experiments. The importance of measuring both trapped copper and transported copper is highlighted, as the role of adsorption in the sometimes complicated effects on copper transport can be more clearly defined. My experiments detected little correlation between length and copper concentration in the regolith at pH 5.0. This could be because the regolith became close to copper saturation, indicating that in nature copper can travel quite far through regolith given a steady supply of copper bearing water and enough time that the sorption sites reach capacity.

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