THE EFFECT OF ORGANIC CARBON ON THE AVAILABILITY OF COBALT IN SEDIMENTS

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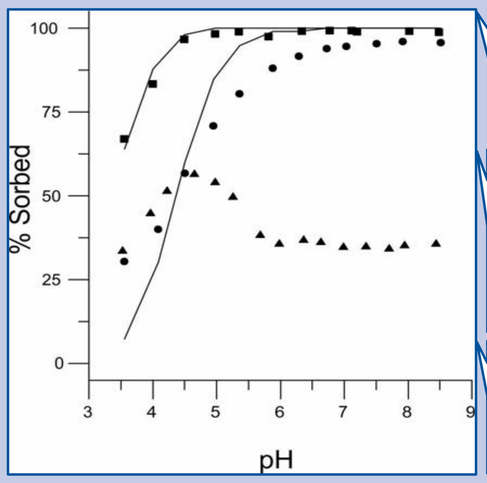
Introduction

Cobalt is a waste product in many industrial processes and emissions have been associated with coal power plants, vehicle exhausts, cement plants, and glassworks. Therefore there is potential for it to be released into the environment, where it can have a number of ill effects. In plants, Co toxicity alters the structure and number of chloroplasts in leaves, and excessive intake of Co in animals can cause heart disease. It is important to understand its mobility in natural environments in order to understand what effect it will have on wildlife if it were to be a cause of contamination. Organic carbon can be present in sediments in varying amounts, so it is important to know how changes in the organic C content affects Co mobility. Co was sorbed to composites of humic acid and ferrihydrite or kaolinite (both common constituents of sediments and soils). EXAFS analysis determined the atomic binding mechanisms and this knowledge was used to model the sorption behaviour. This understanding was then used to try to understand Co sorption to 3 natural sediments with varying organic carbon contents.

Cobalt Sorption to End-Member Phases and Composites



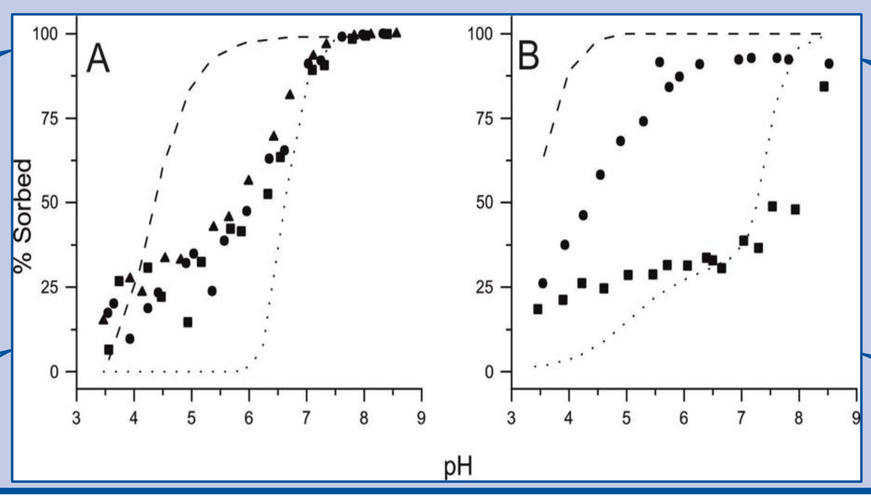
When filtering sorbed Co with 0.22 um filters (▲), Co was bound to colloidal humic acid that was highly mobile and passed through the filters.

Decreasing the filter size to 10 kDa (■ and ●) resulted in ~90% sorption. Increasing the ionic strength from 0.001 M (■) to 0.1 M (●) decreased sorption at low pH, suggesting outer-sphere sorption.

Straight lines show EQLFOR model fits assuming outer-sphere (electrostatic) sorption at low pH, and inner-sphere sorption at high pH

Co sorption to ferrihydrite-humic acid composites (A) showed little change in the sorption edge depending on the carbon content of the composite: ■ 5%; ● 10%, ▲ 17%. Sorption to all the composites was intermediate between end-member ferrihydrite (dotted line) and humic acid (dashed line).

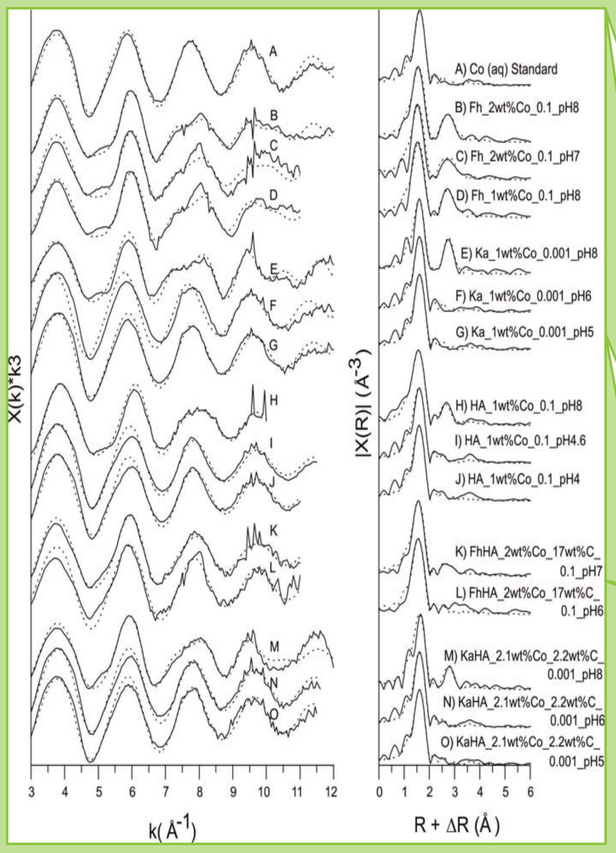
Co mobility remained constant with increases in C content.



Co sorption to kaolinite-humic acid composite are also intermediate to the end-member phases (kaolinite, dotted line; humic acid, dashed line) but the sorption edge of the two composites vary greatly with changes in their carbon content: ■ 1.4%, and ● 2.2%.

Co mobility decreased with increases in C content.

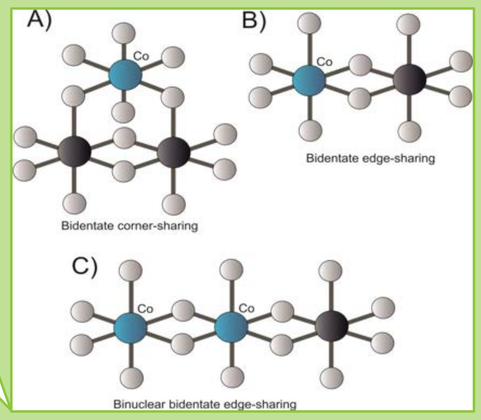
EXAFS (Extended X-ray Absorption Fine Structure Spectroscopy)



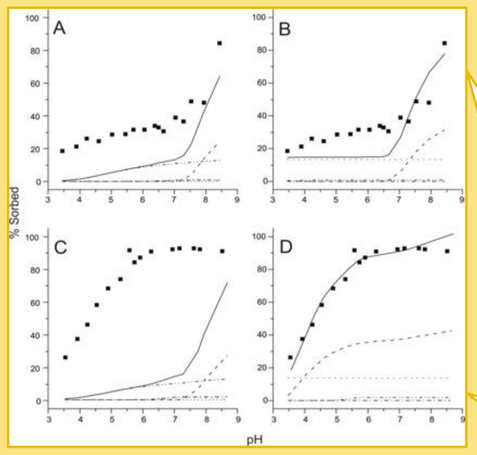
EXAFS analysis of Co sorbed to ferrihydrite, kaolinite, humic acid, and composites of ferrihydrite-humic acid, and kaolinite-humic acid. At low pH (4-6) sorption to kaolinite and humic acid end-member phases is via weak outer-sphere complexes. This is also true of the composites that contain these end-members.

Co sorption to Fe atoms in ferrihydrite, and at pH 7 and above to Al atoms in kaolinite and C atoms in humic acid, was via multinuclear bidentate inner-sphere complexes. This is also true for the composites that contain these atoms.

Co sorption to the phases in the composites is identical to the individual end-members.



Different types of inner-sphere complexes. We propose that (C) is occurring at high pH.



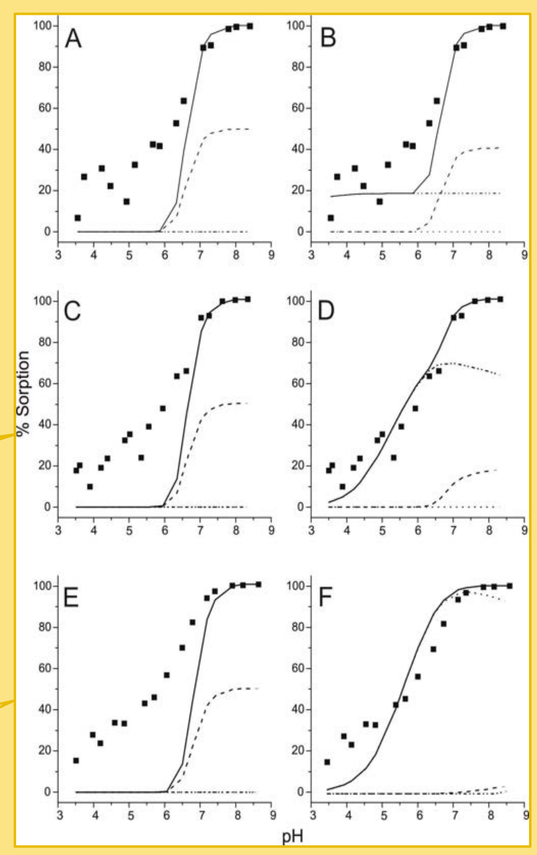
Modelling of Composite Systems

EQLFOR models of Co sorbed to kaolinite-humic acid composites. (A) and (C) show 1.4 and 2.2%C composites with log K's fixed to end-member values, respectively. (B) and (D) show log K's allowed to vary.
——— Total sorption
- ·- ·- ·- Outer-sphere to humic acid
-· ·- · ·- Inner-sphere to humic acid
· · · · · ·Outer-sphere to kaolinite
- - - - - -Inner-sphere to kaolinite

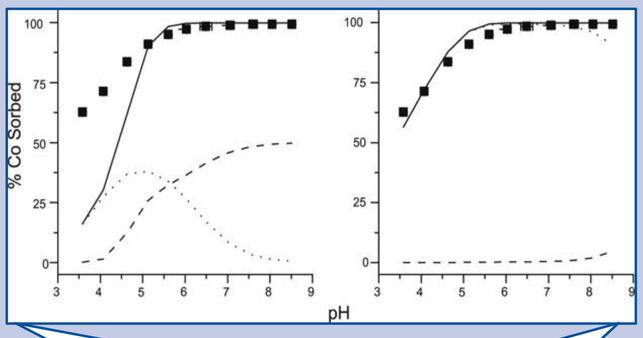
Model predictions of utilized sorption sites contrasts with EXAFS results.

EQLFOR models of Co sorbed to ferrihydrite-humic acid composites. (A), (C), and (E) show 5, 10 and 17%C composites with log K's fixed to end-member values, respectively. (B), (D), and (F) show log K's allowed to vary.
——— Total sorption
· · · · · ·Outer-sphere to humic acid
-· ·- · ·- Inner-sphere to humic acid
- - - - - -Inner-sphere to ferrihydrite

Model predictions of utilized sorption sites disagree with EXAFS results. More research is needed to understand how sorbing phases interact and how this affects sorption.

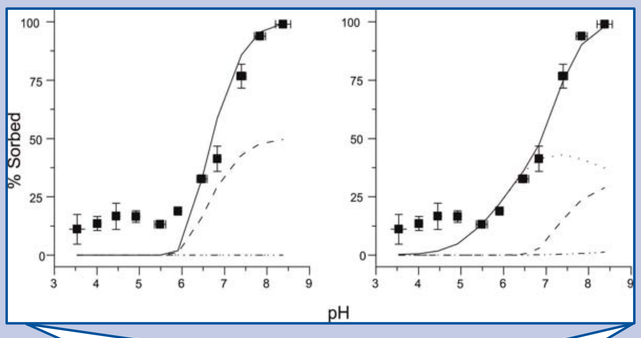


Cobalt Sorption to Natural Sediments



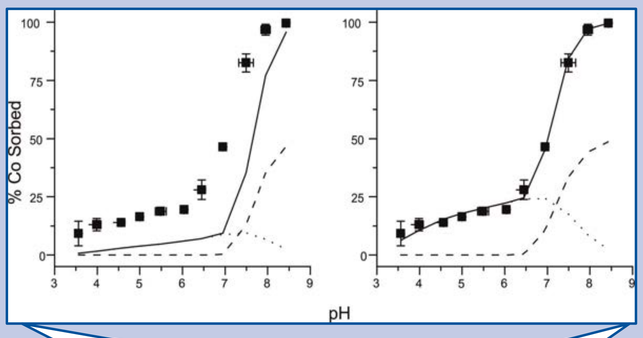
Co sorption to a natural sediment with high C content (49%). Modelled with EQLFOR humic acid model. Left panel shows EQLFOR model with log K's fixed to end-member values, right panel shows log K's iterated.
——— Total sorption
· · · · · · Outer-sphere sorption to humic acid
- - - - - - Inner-sphere sorption to humic acid

Models did not agree with EXAFS results. Must be more than humic acid providing sorption sites.



Co sorption to a naturally occurring sediment that contained 4.45% C. It was modelled with the ferrihydrite-humic acid composite EQLFOR model. Left panel shows EQLFOR model with log K's fixed to end-member values, right panel shows log K's iterated.
——— Total sorption
· · · · · ·Outer-sphere sorption to humic acid
-· ·- · ·- Inner-sphere sorption to humic acid
- - - - - -Inner-sphere sorption to ferrihydrite

Does not agree with EXAFS analysis as no invocation of inner-sphere sorption to humic acid. C present may not have been humic acid.



Co sorbed to a no carbon sediment (<0.5%) that primarily consisted of clays. This system was modelled using an EQLFOR model for kaolinite that was developed. Left panel shows EQLFOR model with log K's fixed to end-member values, right panel shows log K's iterated.
——— Total sorption
· · · · · · Outer-sphere sorption to kaolinite
- - - - - - Inner-sphere sorption to kaolinite

Using a single clay to model a majority clay sediment is not a bad approximation.

Conclusions

- At low pH, Co sorbs to kaolinite and humic acid via outer-sphere complexation.
- Co sorbs to ferrihydrite, and to kaolinite and humic acid at high pH, via binuclear bidentate edge-sharing inner-sphere complexes.
- More C in a composite phase results in higher sorption at low pH.
- Co sorption to composite systems cannot be modelled assuming linear additivity.
- Co sorption to natural sediments cannot be modelled using just the three most common sorbing phases
- Need to understand how the sorbing phases interact that changes the ability of them to sorb Co.

EQLFOR REFERENCES

SHERMAN D. M., PEACOCK C. L. AND HUBBARD C. G. (2008) SURFACE COMPLEXATION OF U(VI) ON GOETHITE (A-FEOOH). GEOCHIM. COSMOCHIM. ACTA 72, 298–310.
SHERMAN D. M. (2009) SURFACE COMPLEXATION MODELING: MINERAL FLUID EQUILBRIA AT THE MOLECULAR SCALE. REV. MINERAL. GEOCHEMISTRY 70, 181–205.

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