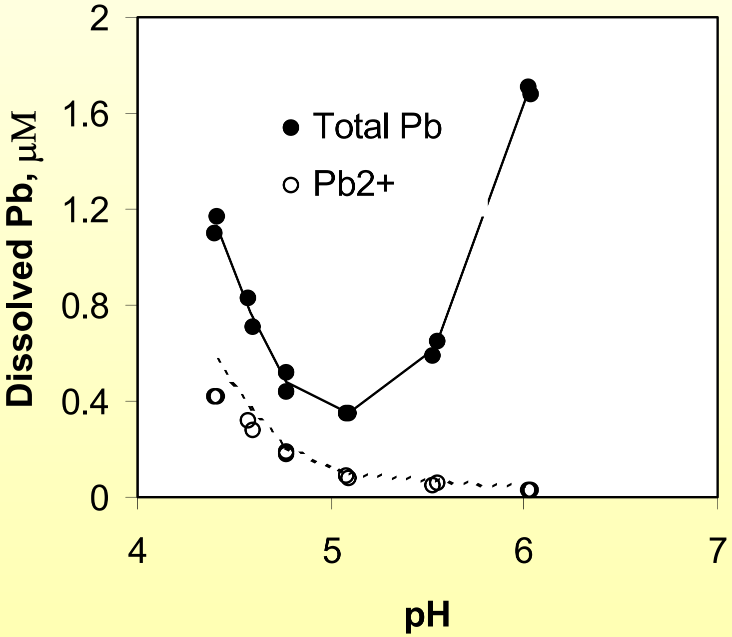
Geochemical modelling – what can it do for you?



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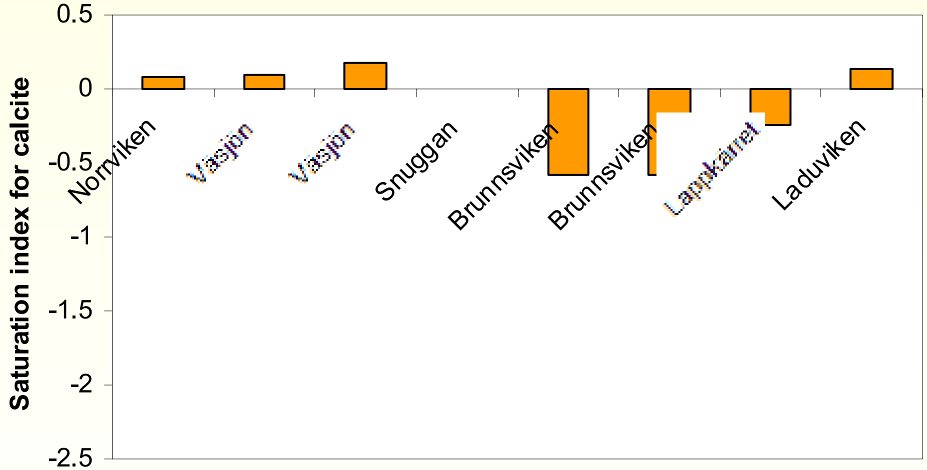
Types of geochemical models

- **Speciation models**
- **Reaction path models**
- **Inverse mass balance models**
- **Coupled mass-transport models**

Increasing complexity

What can we do?

Grupp	Plats	pH	Alk	Ca	Mg	Na	K	Al	Cl	NO3	SO4	DOC	Total P
			ml HCl*	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l
A1	Norrviken	7.86	0.562	49.5	7.74	28.4	6.51	0.03	47.4	7.1	39	12.78	145
A2	Väsjön	7.83	0.617	49.5	7.3	36.3	3.51	0.02	62.4	2.1	11.88	15.21	0
A3	Väsjön	7.97	0.528	50.4	7.25	36	3.45	0.01	64.5	0.2	11.85	15.29	2
A4	Snuggan	5.76	0	4.86	1.02	3.34	0.25	0.51	6.71	0	3.5	33.06	15
A5	Brunnsviken	7.72	0.331	52.1	89.8	1013	92.3	0.03	1453	19	211.5	8.93	49
A6	Brunnsviken	7.71	0.316	52.4	91.9	1009	93.3	0.03	1453	19	211.5	8.96	27
A7	Lappkärret	7.68	0.56	35.5	9.95	79.9	5.08	0.03	107.5	0	2.19	22.43	110
A8	Laduviken	7.9	0.625	51.2	12.85	97.2	11.25	0.03	123.9	3.3	55.2	14.38	26



Speciation

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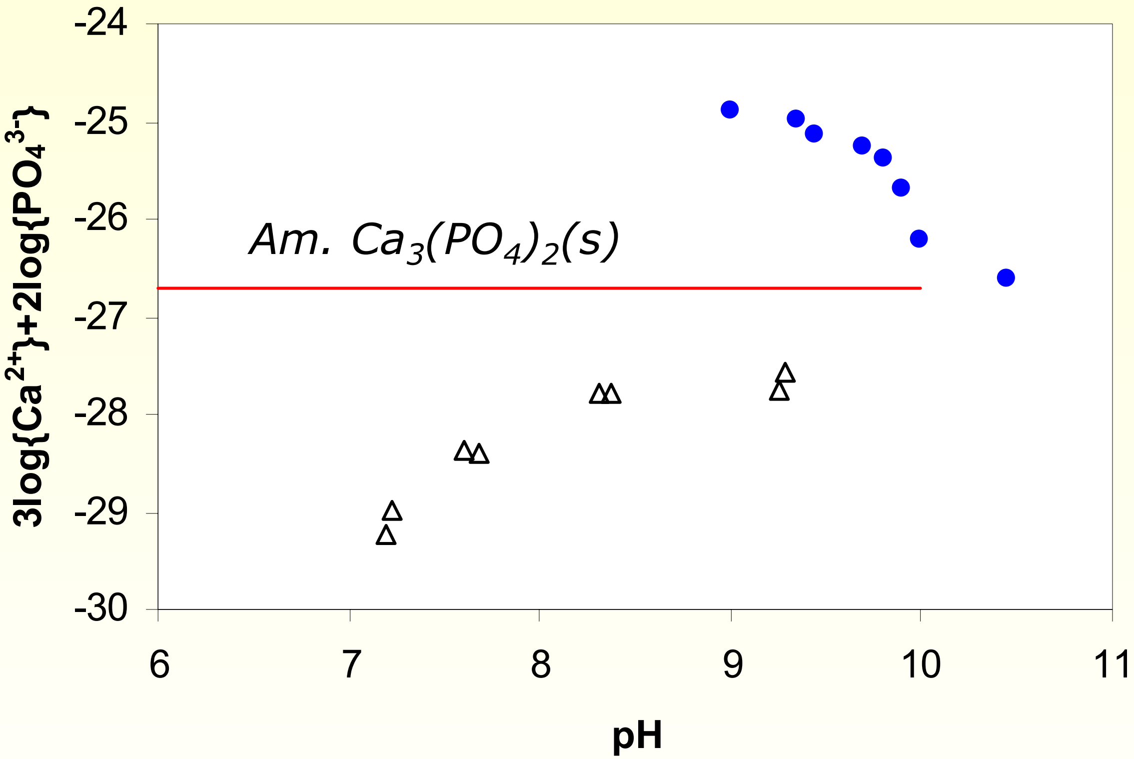
Investigation of mineral equilibria

PO_4 removal by wollastonite



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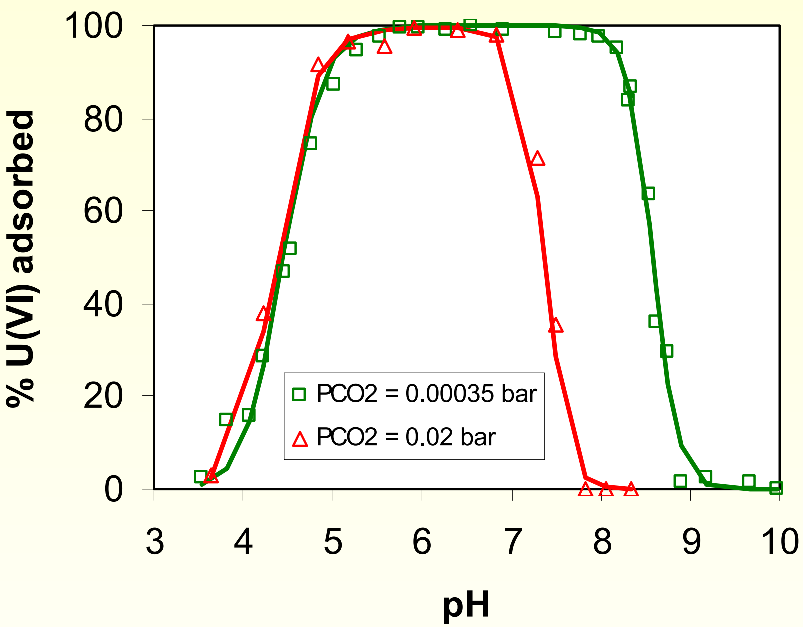
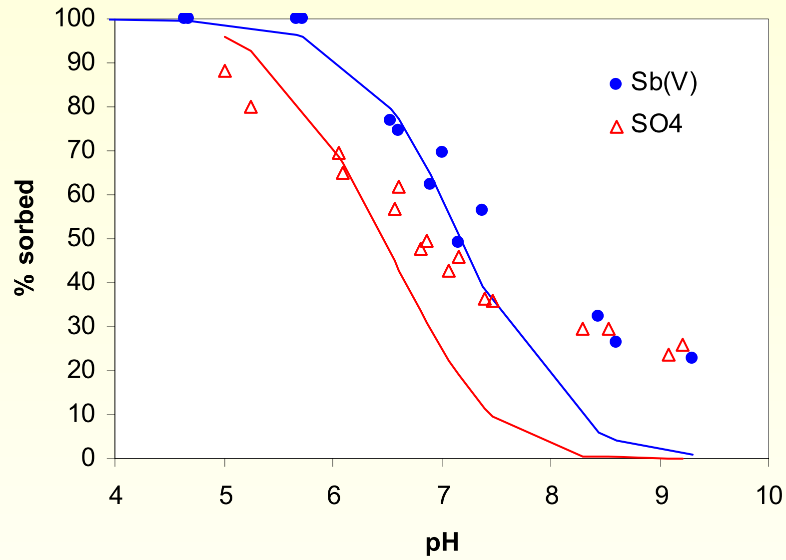
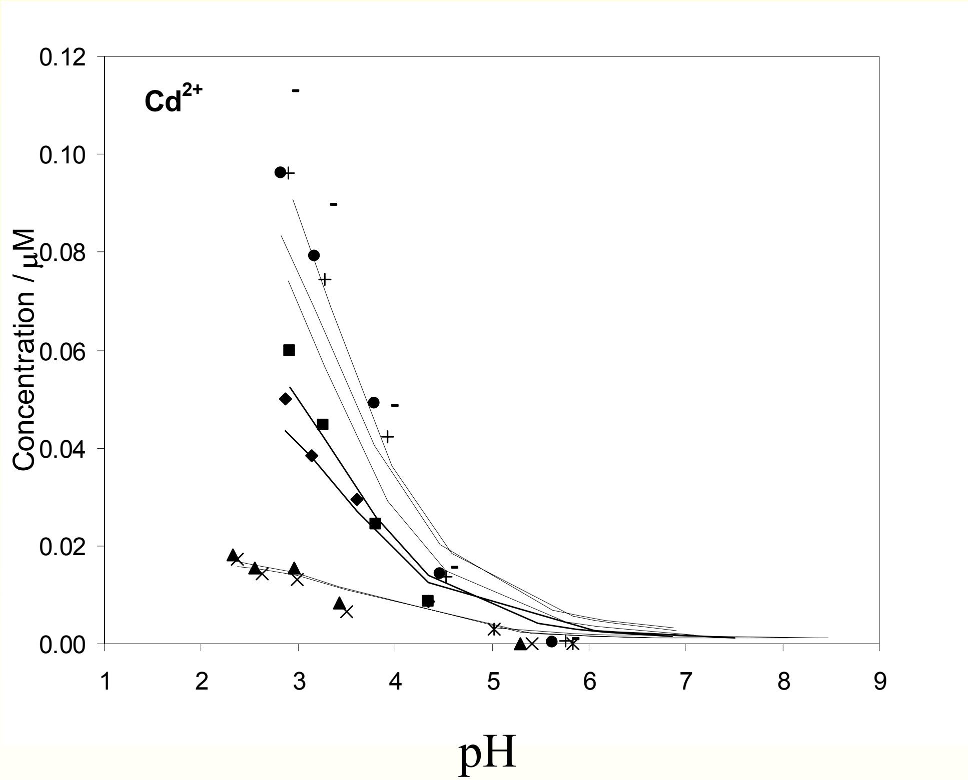
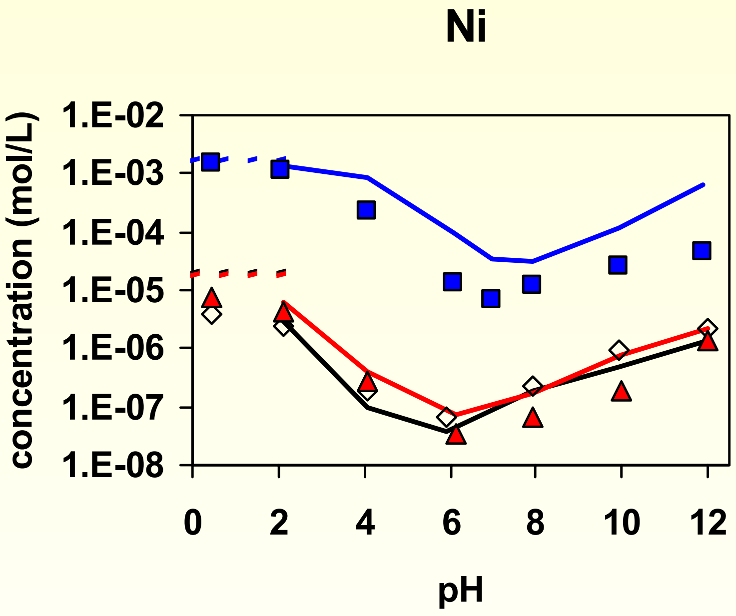
Simulation of metal adsorption to oxides





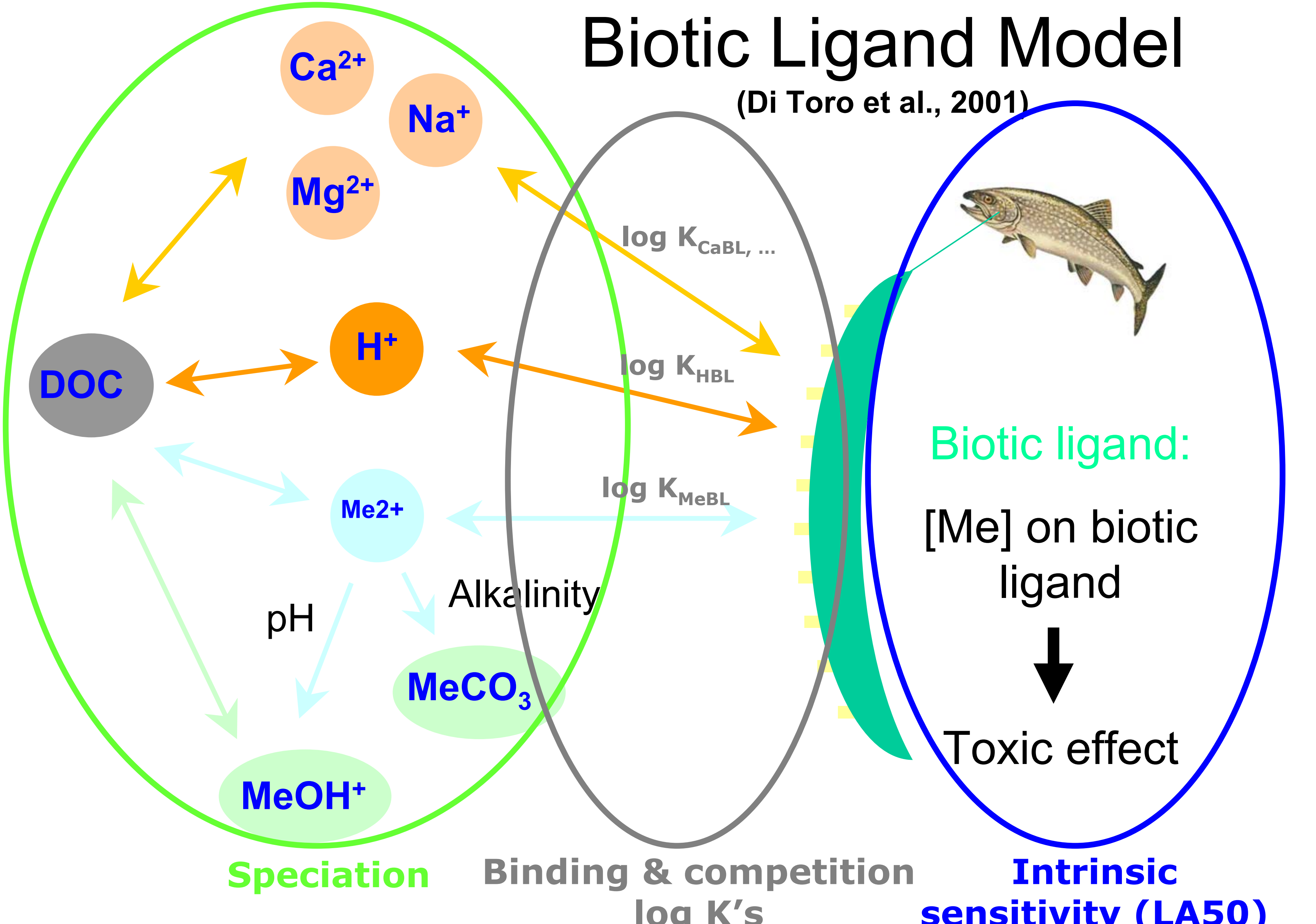
Simulation of metal binding to whole soils





Modelling ecotoxicity: Biotic Ligand Model

(Di Toro et al., 2001)



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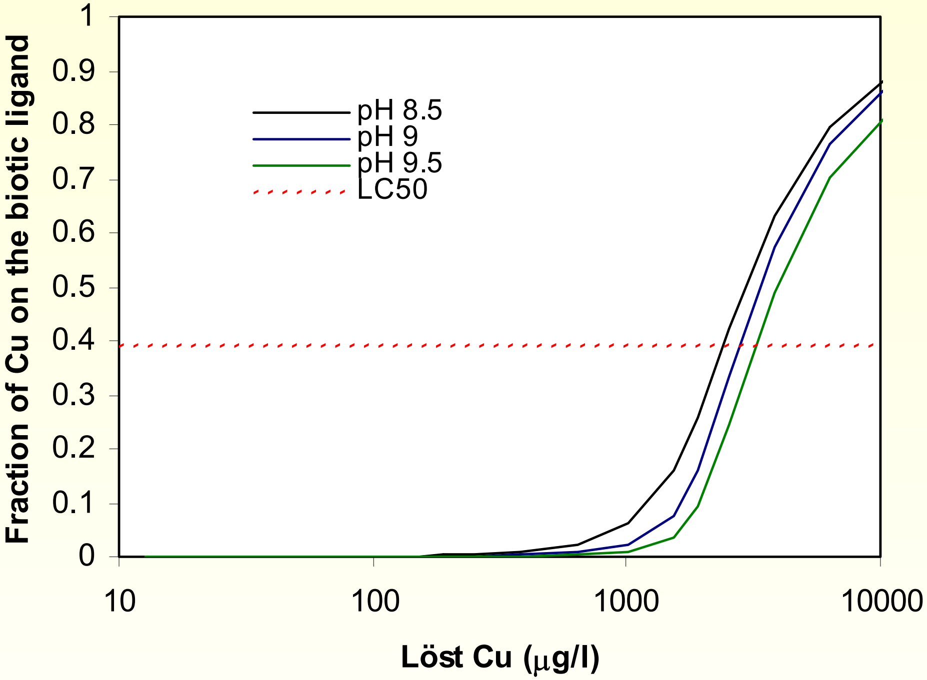
Simulation of ecotoxicity, example



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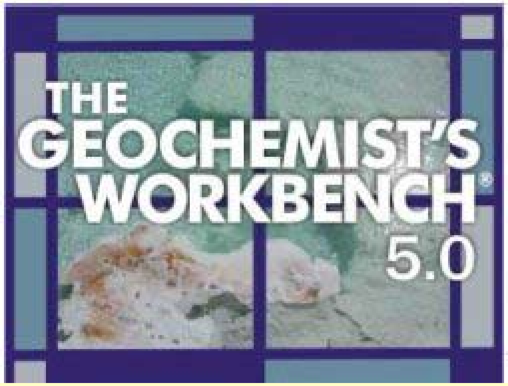
Examples of computer programs



Visual MINTEQ	PHREEQC	GWB
(*free*)	(*free*)	(*commercial*)
Speciation	All 4 model types	All 4 model types
Reaction path (limited)		

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Visual MINTEQ

- Developed from MINTEQ and MINTEQA2
- Well adapted for students – simple to learn
- Up-to-date models for organic complexation and surface complexation
- No transport, no kinetics; simple titration / mixing simulations possible

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PHREEQC

- USGS. Developed from WATEQ by David Parkhurst
- More difficult to learn, but very flexible. Very often used in geochemistry
- Many more functions than in MINTEQ; e.g. kinetics and transport simulations possible
- Unfortunately, not very updated concerning models for organic complexation / surface complexation

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WHAM 6

Windermere Humic Aqueous Model

Equilibrium chemical speciation for natural waters

Version 6.0

- Developed by Steve Lofts and Ed Tipping, UK; commercial software
- Easy to learn
- Centered around Model VI for organic complexation; surface complexation available but only as a simplified model
- Limited precipitation of solid phases, the database is small

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Thermodynamic databases I

Different programs use different databases !!!!

The databases can be edited by the user

Most databases rely on compilations of constants by: NIST, LLNL, NEA, Lindsay (for soils)

It is **always** the responsibility of the user to check the validity of the constants used!!

Thermodynamic databases II

The ”thermo” database in Visual MINTEQ

Open Visual MINTEQ

The information is stored as ASCII files that can also be edited in WordPad

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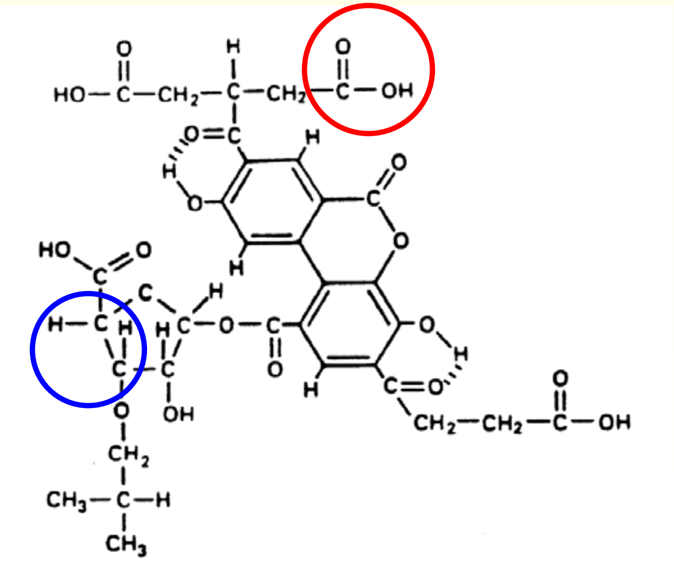
Physical / chemical surface reactions of natural organic matter

a) Complexation (for metals)

b) Hydrophobic interactions (organic pollutants)

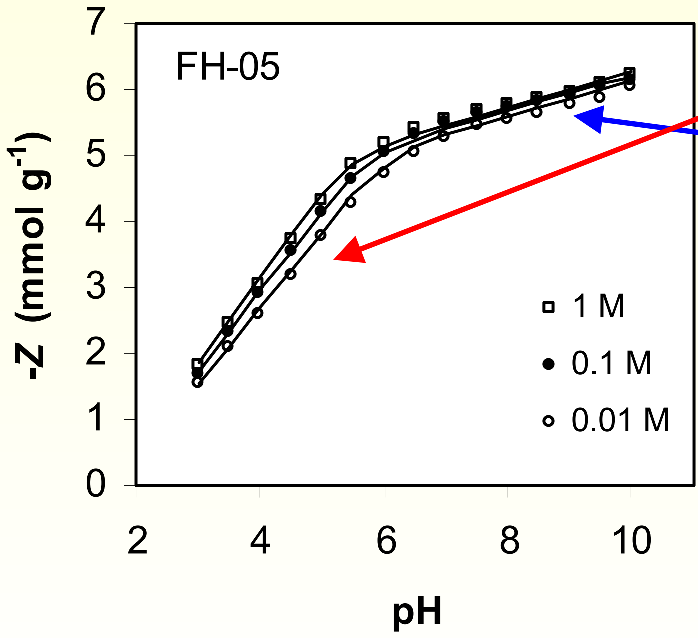


Carboxylic acid groups that bind metals

Non-polar structures that bind organic compounds

Complexation

Caroboxylic and phenolic acid groups are important. These are common in *humic* and *fulvic acids* and their charge is pH-dependent

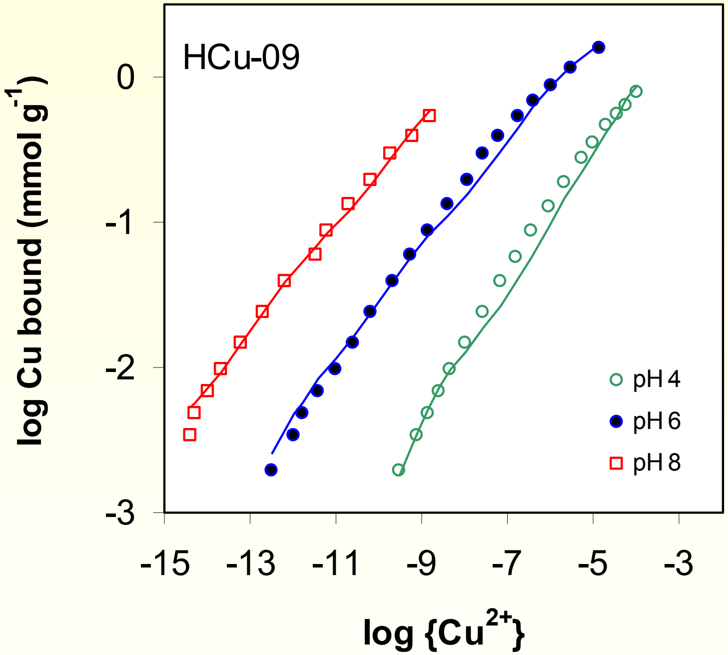


R-COOH ⇔ R-COO$^-$ + H$^+$; pH 2-7

R-OH ⇔ R-O$^-$ + H$^+$; pH > 7

The charge density as a function of pH for isolated fulvic acid from Göta river.

Metal-organic complexation



Copper complexation to a Swiss humic acid

The extent of complex formation is strongly pH-dependent. Two reasons :

The chemical reaction is pH-dependent

2R-COOH + Cu^{2+} ⇔ $(RCOO)_2Cu$ + $2H^+$, , *i.e.*, H^+ ions are "exchanged" in the reaction

The electrostatic effect:

For humic substances, as is the case for oxides, a charge of the opposite sign *enhances* complex formation through electrostatic attraction

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Models for metal-organic complexation

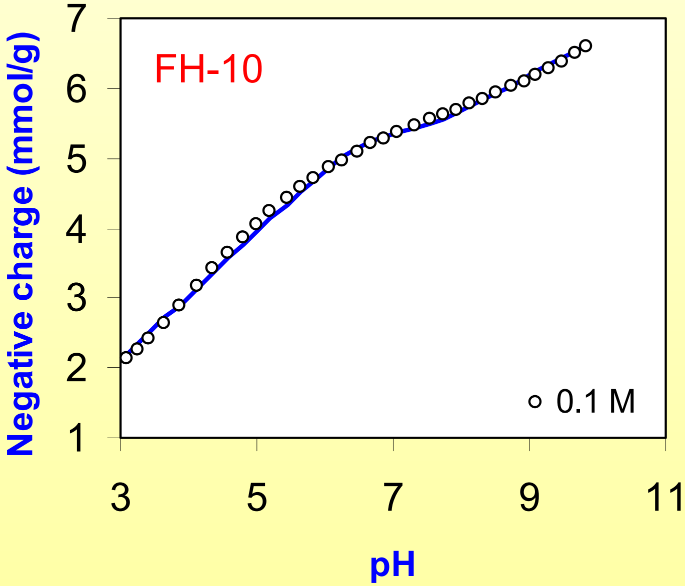
- **Model V (Tipping, 1994); Model VI (Tipping, 1998)**
- **NICA-Donnan (Kinniburgh et al., 1999)**

+ *a few others, including*...

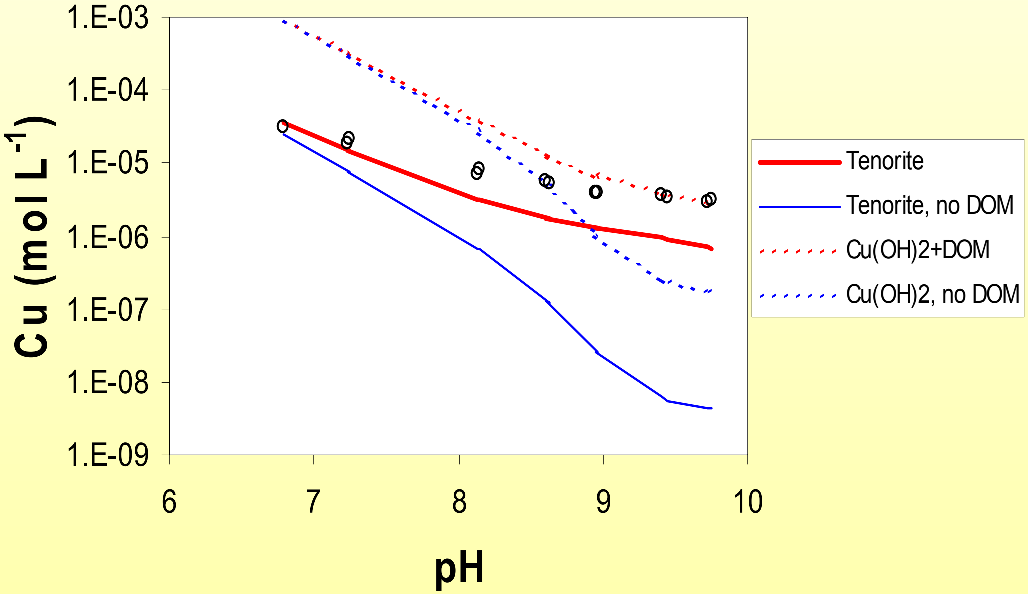
- **SHM (Gustafsson, 2001)**

Acid-base characteristics of isolated fulvic and humic acid

- Dissociation of carboxylic and phenolic functional groups
- Described by a 8 discrete pK_a values (WHAM-6, SHM), or with an isotherm approach (NICA-Donnan); 5-6 adjustable parameters



Example: Cu release as a function of pH from MSWI bottom ash



- Mineral equilibria alone (without considering organic complexation) cannot describe Cu release.
- The trends were described better with DOM and when $Cu(OH)_2$/CuO with a range of solubilities determined the leaching.

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Words of caution

All models have deficiencies and uncertainties

A model result is NOT a scientific finding, but it can support other data and help us understand what is happening

Do not trust the thermodynamic databases; always check them for your problem

Complicated model descriptions (for example, coupled chemistry-transport models) may provide interesting simulations, but are nearly impossible to ”validate”

Despite all this, it is nearly always better to try than not to try at all!!!