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Contents

List of Figures

List of Tables

FAMEST Year 2 : Annual Report 1999

Project title: Fundamental Aspects of Metal Speciation and Transport in metal-contaminated soils and aquifers (FAMEST)

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This report covers the period December 1998 - December 1999.

SUMMARY

Overview

The aims of the FAMEST project are to apply the latest geochemical methods and models to practical problems of metal toxicity and pollution at metal-contaminated sites. Studies are taking place at sites in the UK, France, Switzerland and the Netherlands. The study areas include polluted sites near old metal smelters, an agricultural field heavily contaminated by sewage sludge some 20 years ago, and an experimental site where different amounts of copper had been added in a controlled way some years ago. One aim is to be able to predict from a minimum number of basic measurements of the affected soils or aquifer materials the present-day pore water concentrations and the speciation of the metals within this pore water. This gives a good idea of the potential toxicity of the water. Once this and the rate of water movement are known, it should also be possible to determine the transport of metals through the affected soils and hence estimate the persistence of the metals in the soils and their potential impact on local water bodies.

Key targets being addressed in the FAMEST project are:

- to derive a generic set of proton and metal ion interaction parameters for the binding of metal ions to natural organic matter, specifically to fulvic and humic acids and to use these data for the modelling the binding of metals to the organic component of soils and soil solutions (UK);

- to develop a set of procedures to characterize metal-contaminated soils using chemical extraction and spectroscopic techniques (EXAFS, EPR) and to use this information to predict the metal concentrations in pore water (soil solution) and its variation with depth (France);

- to develop methods for measuring and characterising the transport of metals through soils. In particular, testing various multicomponent transport models for predicting the results of transport experiments with contaminated and control soils (Switzerland);

- to develop a method for measuring 'free' (i.e. not complexed by organic matter) metal ion concentrations in soils and solutions using a novel Donnan membrane technique (the Netherlands).

The project is designed to cover field, laboratory and modelling studies in about equal measure. In particular, it is hoped that the considerable accumulated experience of the project team in modelling chemical speciation in laboratory systems can be applied to the 'real world'. We hope that the results of this work will be transferred to the wider world in terms of revised working procedures and improved computer models. These can then be incorporated by others into future risk assessments.

Progress in the reporting period

The principal progress is described below.

Derivation of a generic set of parameters for metal ion binding by humic materials

Natural organic materials ('humics') are powerful chelators of metal ions and can have a strong influence on the toxicity and mobility of metal ions in contaminated soils. However, the intrinsic heterogeneity of these materials makes modelling their proton and metal binding behaviour difficult especially in the natural environment where there are many ions competing for the same binding sites. Recently we have developed a new model, the NICCA-Donnan model, that attempts to do this. Recent results have been encouraging. However, determining all of the required parameters is a major exercise and is not feasible in most situations where rapid estimates of metal speciation and transport are required. Therefore the preparation of a database of generic humic-proton and humic-metal ion interaction parameters and the testing of this to 'real world' situations is an important goal.

Some 190 data sets of literature proton and metal ion binding by humics have been reviewed and digitised. These cover some 60 humic materials. The data have been split into those for humic acids (HAs) and those for fulvic acids (FAs) since their behaviours are distinctive. Within the FAs and HAs, the differences are relatively small.

Generic NICCA-Donnan proton and metal ion parameters were derived from these data sets. The proton data describe the basic charging properties of the humic material including the number of sites per kg of material while the metal ion parameters including a median binding affinity and non-ideality parameter for each metal ion. So far, parameters for Al, Ca, Cd, Co, Cu, Eu, Ni, Pb, UO_2 and VO have been estimated. Only the proton parameters and charge densities are different between FAs and HAs.

Future work is aimed at extending this database to a broader set of metals and testing its application to practical problems.

Characterization of metals in metal contaminated soils

The selective chemical extractions (calcium chloride, sodium pyrophosphate, citrate-dithionite-bicarbonate) of the project metal-contaminated soils have been completed.

These extractions allow some distinction to be made in terms of the forms of the metal present. In some cases, this speciation has also been estimated indirectly by EXAFS. The EXAFS spectra have been resolved with the aid of spectra of metal bound to model components such as iron oxides, clays and organic matter to give some guide to the dominant forms in the contaminated soils.

Large amounts of Zn/Al mixed hydroxides were identified in the smelter-contaminated soils from France and Switzerland. These are unlikely to be common forms of Zn in uncontaminated soils. The organic-rich woodland soils from France contained significant amounts of organic-Zn as detected by chemical extractions and EXAFS.

Soil water/soil partition coefficients (Kds) were estimated for Zn, Cd, Cu and Pb from a range of the contaminated French soils. This was done by both a combination of the chemical extraction data and pore water concentrations (determined by centrifugation), and by modelling using the NICCA-Donnan model. Agreement between observations and experiment was in most cases good apart from Pb for which the modelling underestimated the Kd. This is believed to have been due to Pb binding to manganese oxides which was not adequately captured by the model.

The data show that the metals are generally strongly bound to soils. Log10 Kd's are often 2-3. This accounts for the persistence of metals in soils.

Multicomponent transport and metal breakthrough curves

Sorption and transport of Cd and Zn were investigated using an uncontaminated soil material from northern Switzerland. The experimental sorption data were used to develop a simple competitive sorption model which can be applied to predict metal mobilization from contaminated soils in response to changes in soil solution chemistry. Cd sorption to the soil material was measured over wide concentration ranges in $CaCl_2$, $MgCl_2$, and NaCl electrolyte solutions. The model accurately describes sorption data in all background electrolytes over wide concentration ranges. To achieve a satisfying model description, competitive sorption sites with a small site concentration (2 mmol/kg) and high Cd affinity had to be introduced, in addition to conventional cation exchange sites. The model coupled to a numerical transport code was used to predict Cd transport in the presence of different Ca concentrations. With increasing $CaCl_2$ concentration, Cd retention was strongly decreased. Model predictions were generally in good agreement with experimental results.

In most contaminated soils, Cd occurs together with Zn contamination. The model was successfully extended to describe the competitive sorption and transport of Zn and Cd in the soil material.

To study the influence of changes in solution chemistry on metal mobilization and transport, a first set of column experiments was carried out with contaminated soil materials from the FAMEST field sites D1 (arable), CF1 (arable), P2 (woodland), and OQS (arable). Additional information was obtained from XRF analysis, $BaCl_2$ and sequential batch extractions.

In soil P2, very similar elution patterns were found for Cd and Zn. The concentration ratio of both metals in effluent solutions reflected their total concentrations in the soil material. Increasing the $CaCl_2$ concentration to 10^{-2} M resulted in a pronounced elution pattern. This pattern was similar for Cd and Zn, and can be explained by a simple cation exchange model accounting for sorption competition between Ca, Mg, K, Cd, and Zn.

Comparison with the total Zn and Cd contents showed that, at the end of the experiment, Cd was almost completely mobilized from the soil material, while around 500 ppm of Zn remained. Apparently, the remaining Zn is present in a less available form, possibly as Zn hydrotalcite. As $CaCl_2$ mobilizes mainly sorbed heavy metals, the similar concentration patterns of Cd and Zn agree well with the findings from the control transport experiments which showed a similar sorption behaviour for Zn and Cd.

A completely different elution pattern was found for the French soil OQS. Zn and Cd concentrations in the column effluent were approximately 1000 and 100 times smaller than in soil P2. A simple cation exchange model could not describe the elution curves. It is likely that precipitation/dissolution rather than sorption reactions determine the mobility of Cd and Zn in this soil material. These differences may be explained by the lower pH, higher organic matter content, and higher cation exchange capacity of soil P2 compared to soil OQS. These column results are in good agreement with speciation results found for both soils by the French project partner.

Mobilization and leaching of Pb was measured in experiments with soil P2. At the end of the experiment, only 22% of the total Pb was mobilized. The elution curve was completely different than for Cd and Zn, indicating either cation exchange reactions with a very high affinity for Pb, or dissolution reactions of Pb bearing mineral phases. In an additional long-term mobilization experiment 1200 ppm Pb were mobilized over 2000 pore volumes, corresponding to 80% of the total Pb in the soil material.

In all column experiments and batch extractions, Cd was found to be more exchangeable than Zn. Cd mobilization in the column experiments ranged from 40% to 100% of the total, Zn extraction from 0.8% to 72%.

In general, the ability of the model to fit the column breakthrough data was encouraging.

Measuring free metal ion concentrations in soil solutions

The Wageningen Donnan membrane technique (WDMT) is proving useful for measuring free metal ion concentrations in soil solutions – a long-standing challenge for soil chemists. However, because the total metal concentrations in soil solutions are normally small, the resulting metal ion concentrations are often at or below the chosen analytical detection limit even of ICP-MS. The small concentrations are also relatively poorly buffered and so are sensitive to small amounts of contamination or to adsorption on the apparatus. Therefore the use of the WDMT in combination with a soil column has been investigated (SC-WDMT). The soil provides much greater buffering of the low metal concentrations.

The optimum percolation rate through the soil column and the time needed to reach equilibrium were investigated. The results obtained were compared with the measurement of displaced soil solution after filtration through a 0.45 μm filter. The effect of mixing soil with quartz sand was investigated so that the SC-WDMT method can be also applied to soils with low permeability (e.g. clay soils). The amount of metal accumulated in the cation exchange membrane was also measured and the soil metal buffering capacity evaluated.

Another important aspect was to test the correction used for relative ionic strength differences between donor and acceptor solutions. This was based on using the activity ratio of the cations present and was investigated for the measured free Cu^{2+} concentration in the 'Wildekamp' soils. The activity ratio of potassium in the donor and the acceptor solution was used as a basis of the correction. Potassium always occurs in soils naturally, and is similar to sodium in that it has a very low tendency to form complexes with ligands in the soil solution. We therefore assumed that all potassium in the donor solution was in the form of the free ion. The potassium concentration in the donor and the acceptor solution was measured by ICP-AES along with the analysis of the other macro-elements and the correction carried out accordingly.

Finally the SC-WDMT results were compared with results those from the chemical equilibrium program ECOSAT which used the NICCA-Donnan model to describe metal binding to dissolved organic matter. Measured pH, dissolved organic matter content, total dissolved metal concentration in filtered donor solution were used as the input data. Dissolved organic matter was assumed to behave as purified peat humic acid (PPHA). The effects of pH, ionic strength, Ca and Al competition on Cu adsorption to dissolved organic matter were considered in the Cu speciation calculation. Free Cu^{2+} concentration was computed and the results were compared with the measured free Cu^{2+} concentration in the acceptor solution after correcting for the ionic strength difference. The agreement was reasonable if the complexity of dissolved organic matter was taken into account. The fraction of free copper at an initial salt concentration of 0.002M $Ca(NO_3)_2$ was 65.1% and 88.6% for the measured and calculated free ion, respectively. For soil 4D the measured and calculated free copper fractions were only 3.8% and 9.3%, respectively.

These results are encouraging.

FAMEST Year 2 : Annual Report 1999

British Geological Survey, Wallingford, Oxfordshire, UK, OX10 8BB

Objectives:

The objectives of the second year of the project were:

- Completion of database of metal-ion/humic-substance binding data and associated generalised NICA binding model parameters
- Investigation of the use of recirculating column experiments to measure metal leaching from field soil samples

Progress and achievements

- A thorough review of literature data for organic-metal ion and proton interactions has been undertaken. The raw experimental data has been obtained directly from the authors or extracted by digitisation from the original source. This resulted in 190 sets of experimental data. These data have been analysed using the NICCA-Donnan model to derive generic model parameters which can be used for modelling the speciation and transport of metal ions in soils and aquifers where detailed information about the organic present is not known.
- The desorption of metals from sewage sludge contaminated soil was studied using a recirculating flow-through reactor with a high solution/solid ratio. Unbuffered 0.01 M $CaCl_2$ was used in the system to desorb the metals. Steady state metal concentrations were achieved after about 100-200 pore volumes (1-2 hours) demonstrating that such a technique can be used to estimate the amount of labile metals present in a soil. It could easily be scaled-up to reduce the unit cost of the analysis.

1. UNITED KINGDOM

1.1 Derivation of general purpose parameter values for modelling of humic-ion interactions

Although a significant part of this project has involved detailed investigation of material from four field sites, the primary motivation has not been to learn about the specific soils in question. Rather, the aim is through these detailed case-studies, to identify those aspects of the soil character which particularly affect our ability to model the metal speciation and transport in 'real' soils and aquifers. Then, where possible to draw general conclusions so as to avoid the need for such detailed site investigations in future. One component of the soil-water system which strongly influences metal speciation and transport behaviour is the presence of humic material, as humic or fulvic acids. These can be present as mobile (soluble, particulate) or immobile (solid) compounds. These interactions a critical for determining the transport of many trace metals. The derivation of general purpose descriptions of the interactions between humic materials and metal ions is outlined. Such descriptions will be crucial in developing the ability to model real-life systems quickly and easily.

The approach was to compile a database of available data for humic-ion binding reactions, then model all of the data using the NICCA-Donnan model to obtain a database of parameters to describe the ion-binding behaviour.

The published scientific literature was first reviewed to identify experimental studies of ion-binding by humic or fulvic acids and the data were collated into a database. Where possible the original raw experimental data have been obtained in electronic form from the authors. Otherwise the data have been recreated by scanning and digitizing plots or tables presented in the printed journal articles. The table below summarizes the data holdings:

Holdings include more than

(i) 850 literature references

(ii) 190 sets of experimental data

(iii) 19000 individual data points

(iv) 60 characterized humic and fulvic materials

(v) 45 sets of data for proton binding

(vi) 24 different cations represented

The databasing process included critical evaluation and standardization of the data. Evaluation to assess the quality of the data, e.g. purity of the humic material, resolution and uncertainty margins of the data, or the range of experimental conditions covered. Standardization to ensure that all the data in the database used consistent nomenclature, formats and units. Related datasets, such as separate studies on the same material were cross-referenced.

1.1.1 Proton binding

The NICCA-Donnan model, described in detail elsewhere, was used to model all the datasets collected. First the model was applied to data for proton binding (Kinniburgh et al., 1999). The description of proton binding is prerequisite for the descriptions of metal-ion binding.

The model was fitted to each individual dataset in turn, allowing full and free optimisation. This generated fits which were specific to the individual datasets, but measured the ability of the model to describe all the different experimental results, not only those on which the model was originally calibrated. Almost without exception the model could describe an experimental dataset very well, with a coefficient of determination of better than 0.99. The range of parameter values obtained for these individual fits is shown in Table 1.1.

Table 1.1 **Summary of NICA-Donnan fits to all suitable experimental datasets for proton-binding by humic and fulvic acids. The generic parameters are overall best fit parameters to the whole data ensemble and are suitable for use as default proton-binding descriptions.**

	RMSE	R2	b	Q1 mol/kg	Log K1	m1	Q2 mol/kg	Log K2	m2	Qtot mol/kg	Q1 %	Q2 %
FULVIC												
n	23	23	20	23	23	23	15	13	14	15	15	15
min	0.0160	0.67411	0.29	2.64	2.00	0.27	0.55	7.19	0.33	4.73	50.2	8.7
max	0.4906	0.99971	0.94	8.77	3.81	0.65	6.55	10.91	0.96	13.14	91.3	49.8
st dev	0.0927	0.06699	0.17	1.29	0.44	0.09	1.57	1.04	0.21	2.03	11.7	11.7
mean	0.0990	0.98049	0.63	5.62	2.67	0.40	2.31	8.71	0.60	7.84	72.3	27.7
median	0.0736	0.99656	0.67	5.79	2.61	0.39	1.93	8.68	0.62	8.00	74.5	25.5
mean			0.63	5.62	2.67	0.40	2.31	8.71	0.60	7.84	72.3	27.7
Generic	**0.4273**	**0.915**	**0.63**	**6.24**	**2.38**	**0.42**	**1.96**	**8.50**	**0.58**	**8.20**	**76.1**	**23.9**
HUMIC												
n	19	19	18	19	19	19	16	12	12	16	16	16
Min	0.0120	0.95616	0.21	1.89	1.94	0.39	0.76	6.06	0.20	3.45	35.4	14.8
Max	0.1719	0.99990	0.84	4.73	3.90	0.87	5.39	10.06	0.86	9.15	85.2	64.6
st dev	0.0424	0.01012	0.20	0.90	0.55	0.11	1.33	0.96	0.20	1.29	16.9	16.9
Mean	0.0584	0.99406	0.53	3.08	3.08	0.53	2.44	8.06	0.45	5.66	58.5	41.5
Median	0.0464	0.99838	0.59	2.78	3.03	0.52	2.36	8.05	0.51	5.55	56.3	43.7
Mean			0.53	3.08	3.08	0.53	2.44	8.06	0.45	5.66	58.5	41.5
Generic	**0.6466**	**0.728**	**0.43**	**2.76**	**2.56**	**0.49**	**3.24**	**7.74**	**0.24**	**6.00**	**46.0**	**54.0**

To obtain a single overall best parameter set suitable for use as the default description a two step strategy was used. The sixteen best available datasets each for humic and fulvic acids were modelled simultaneously. First single values for the shape of the site distributions were obtained whilst allowing each material to continue to have a different total number of binding sites available (i.e. single values for b, $\log K_i$ and m_i, but different Q for each material). The experimental evidence shows that the biggest single variable between materials is the total site density. Therefore the assumption is made that the chemical heterogeneity of the materials is formed of similar *distributions* of sites, regardless of the total *number* of sites i.e. the binding can be simply scaled to the site density. Second, the site densities (Q1 and Q2) were optimized using the established best log K and m values.

The combination of the two step fit to the complete data ensemble gives the optimum parameter values shown as generic fits in the table. These parameters are suitable for use as default descriptions of proton binding to humic or fulvic acids in the circumstance where no other specific information about the material was available. As can be seen, the quality of the generic fit is better to the fulvic acids than to the humic acids, i.e. the available data for fulvic acids fit a single model description more closely than the humics, which exhibit a greater variation in behaviour between the different materials. However, the generic descriptions do provide a physically realistic description, consistent with the observed experimental patterns of behaviour, and would simulate the proton binding to a previously unknown material to within a RMSE margin of 0.6 (humic) or 0.4 (fulvic) mol/kg over the entire pH range. As a fraction of the total proton binding (6-8 mol/kg), this represents an uncertainty of 10% or so and is good enough for generic modelling.

Simulated proton titration curves for the humic and fulvic acids, derived from the generic parameters are shown in Figure 1.1. The figures show the data over the observation window which can be typically achieved experimentally, and successfully reproduce all the key features of observed experimental data, providing additional confidence in the validity of the generic descriptions.

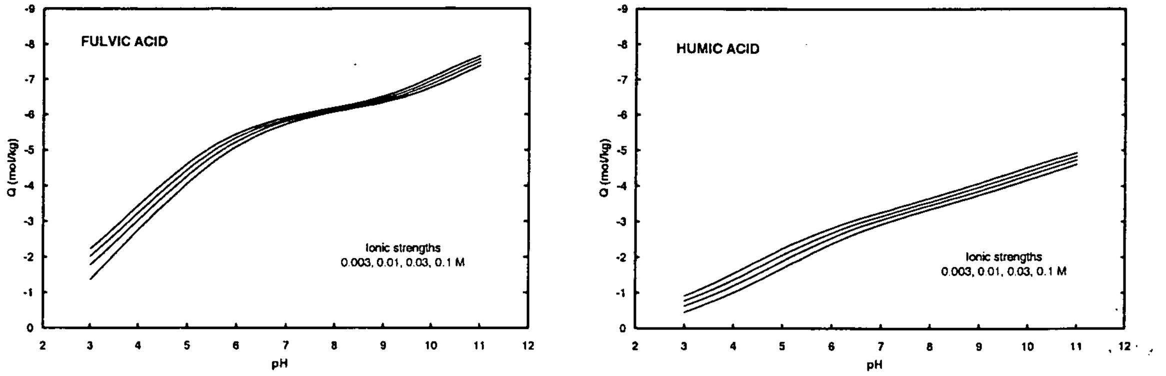

Figure 1.1 **Simulated proton titration curves for fulvic and humic acids, generated using the generic set of default proton-binding parameters listed in Table 1.1.**

1.1.2 Metal binding

With the generic proton-binding descriptions established the modelling can be extended to cover metal-ion interactions with humic and fulvic acids. Again individual datasets were fitted to identify the range of parameter values which could be expected and then aggregated sets of data for individual ions, or where possible multiple ions were fitted simultaneously. The strongest sets of metal data were used to establish the p parameter, describing the intrinsic heterogeneity of the substrate material. Then this was fixed while the affinities and site distributions accessible to individual ions were modelled. The preliminary best estimates for the default parameters are shown in Tables 1.2 and 1.3. Figure 1.2 shows the comparison between the default model descriptions and two representative metal binding datasets. It can be seen that while the model fit to the Ca-HA system is good, that for the Cd-FA system is poorer, but still usable. Validation of these estimates is continuing in order to assess whether the default parameters can be improved or whether this represents the limit that can by achieved by this technique. The parameter sets are also being extended to cover other metals with poorer data coverage.

Table 1.2 **Preliminary default heterogeneity parameters obtained using the 50 most extensive datasets for metal-binding**

	p1	p2
min	0.46	0.33
max	0.97	0.79
st dev	0.08	0.17
mean	0.62	0.58
median	0.62	0.61

Table 1.3 **Preliminary default log K and n_M values for metals with the most extensive datasets. Using P1=0.62 and p2=0.58 from Table 1.2 and generic proton parameters from Table 1.1**

	Al	Ca	Cd	Co	Cu	Eu	Ni	Pb	UO_2	VO
log KM1	nd	-1.4	-0.2	-4.5	0.6	2.9	-4.1	0.6	0.2	1.7
nM1		0.7	0.6	0.5	0.4	0.6	0.4	0.6	0.3	0.6
logKM2	11.5	-1.4	2.9	-1.7	7.4	3.9	0.5	7.0	1.5	8.7
nM2		0.4	0.5		0.7	0.3	0.7	0.4	0.5	

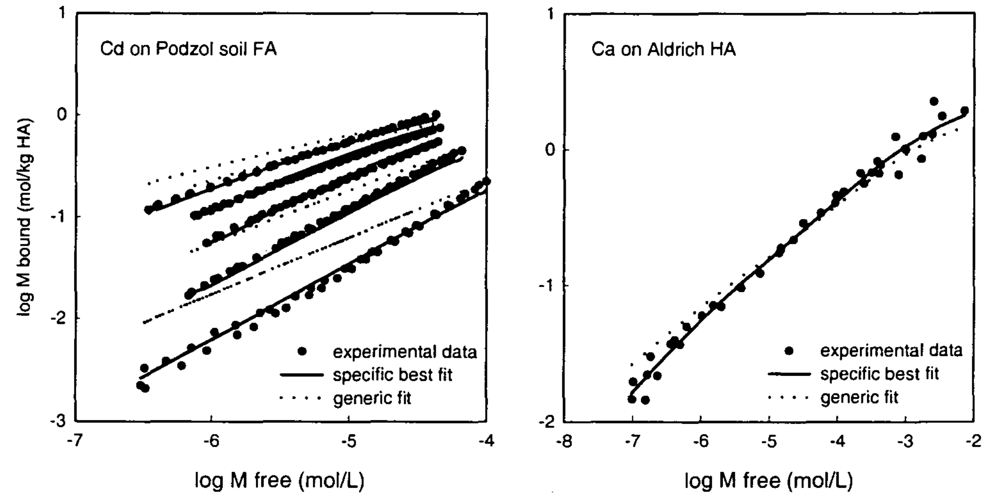

Figure 1.2 **Examples of NICCA-Donnan fits using default parameter sets to two representative experimental datasets for metal-ion binding by humic and fulvic acids.**

1.2 Investigating the use of recirculating column experiments to measure metal leaching from field soil samples

1.2.1 Introduction

Description of sorption and desorption process involving a fluid phase and a solid matrix are of particular importance in soil science and subsurface hydrology. This type of information is essential to estimate the toxicity and mobility of pollutants such as heavy metals, radionuclides, and other organic compounds in soils and aquifers systems. Such results allow the long term estimation of subsurface water quality risks from contaminated sites.

The amount of sorbed species present is commonly determined in the laboratory by using batch experiments. There are a number of problems with such methods, not least that of particle breakdown during shaking. This has been the driver for the development of less disruptive techniques such as the use of flow-through reactors (Burgisser et al., 1993). We describe the use of such a flow through reactor and present some of our preliminary findings.

1.2.2 Method

We have used a method similar to that developed by Grolimund et al (1995) and used recently by Freese et al (1999). The experimental setup is shown in Figure 1.3. The principal component is a flow-through reactor cell that consists of a modified, three-piece air monitor cassette and a filter holder. A cellulose-nitrate membrane filter (0.45 μm) and a silicon gasket were placed on the filter

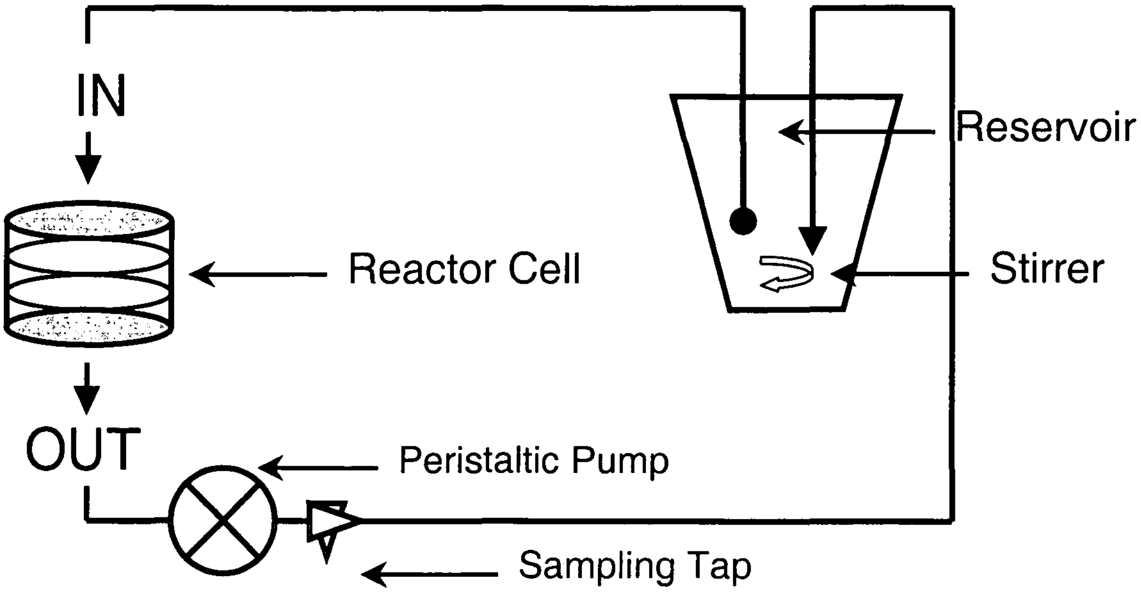

Figure 1.3 **Schematic of recirculating reaction cell apparatus used in preliminary leaching studies. Reactor cell dimensions approximately 37mm x 40mm. Figure is not to scale.**

holder and fixed in place by the intermediate piece of the air monitor cassette. The inlet of the reactor cell was connected to a reservoir vessel, and the outlet was connected to a peristaltic pump using low pressure fittings and silicon tubing.

In our experiments the reservoir contained 150 mL of 0.01M $CaCl_2$ which was circulated at a rate of 2.5 mL per minute (roughly 1.25 pore volumes min^{-1}) through 10 g of soil. The soil used was heavily contaminated by zinc from sewage sludge and was from Carlton Forest Farm; details of some of its properties are shown in Table 1.4.

When packed the flow-through reactor had a porosity of roughly 20%. The system was initially run in an open mode with the first five samples of 5 mL each taken consecutively. The system was then allowed to recirculate and 18-20 samples were then taken over the next 24 hours. The pH was continuously monitored by glass electrode placed in the reservoir. Samples were filtered (0.45 μm), acidified and then analysed for cations by ICP-AES.

Table 1.4 **Carlton Forest Farm CF1 C (90-110 cm) Sample Properties**

	Concentration
Total	76 mg/kg Zn
0.01m $CaCl_2$	34 mg/kg Zn
Porewater Zn	1.1 mg/L Zn
DOC	27.7 mg/l
C_{org}	0.067 %
pH (porewater)	6.9
pH ($CaCl_2$)	5.6
LOI	1.35 %
CEC	0.026 mol_c/kg

1.2.3 Results and Discussion

Time series data for selected cations are presented in Figure 1.4 with results shown as duplicates. Calcium is shown since it is present in the background electrolyte. After roughly 30 pore volumes calcium concentrations can be seen to be reaching a fairly steady state, this happens as calcium is exchanged for other cations. All other cations show a characteristic fall in concentration as the number of pore volume passed through the reactor increases. By roughly 100 pore volumes, most elements have reached a near constant concentration. Measurement of pH during the first experiment (white circles in Figure 1.2) was disappointing with a large discrepancy between the initial and final buffer concentrations. A summary of the total extract in the leachate is presented in Table 1.5. This excludes the amount of extracted material still present in the reservoir at the end of the experiment. Clearly good agreement can be seen between the two runs of the experiment.

Table 1.5 Amount Extracted After 1800 Pore Volumes

	Run 1	Run 2	Average
		mg kg^{-1}	
Zn	12.2	12.2	12.2
Sr	1.39	1.12	1.26
Cu	0.059	0.073	0.066
Ni	0.076	0.051	0.0635
Co	0.008	0.009	0.0085

Figure 1.5 shows normalised concentrations against total pore volumes. This demonstrates the relative binding strength for this particular soil at this pH (roughly 5.4) and at these concentrations. In this example, magnesium is released first, followed by copper, potassium, aluminium and finally zinc.

1.2.4 Concluding Remarks

We have demonstrated through the use of multi-element techniques and small volume reactor-cells a reproducible method for determining relative rates of desorption from a soil. Due to the small volume of the cell, a large number of pore volumes can be passed in a relatively short period of time (roughly 24 hours for 1800 pore volumes). A near steady state was achieved after one hundred pore volumes making this a rapid method. For our soil at these concentrations we found the following series of binding: Zn>Al>K>Cu>Mg. This procedure (without the recirculation) enables the reservoir of 'labile' metals to be estimated. This is a necessary input for further modelling.

In retrospect the partial recirculation aspects of the experiments has complicated the interpretation and analysis of the data. It would probably be better to have no recirculation. However, such experiments demonstrate that quantitative estimates of the labile metal content of soils can be made in a couple of hours without the need for potentially damaging batch desorption methods. The approach could be easily adapted to run a number of such flow through reactors in parallel and thereby reduce the unit cost of analysis.

1.3 Future work

- complete data analysis of literature data for humic-metal interactions to derive generic parameters for a greater range of metals

- apply these results to model metal mobility using literature data and examples from the project sites, including the possible impact of the contaminated soil to groundwater quality

- Produce the Final Report

1.4 References

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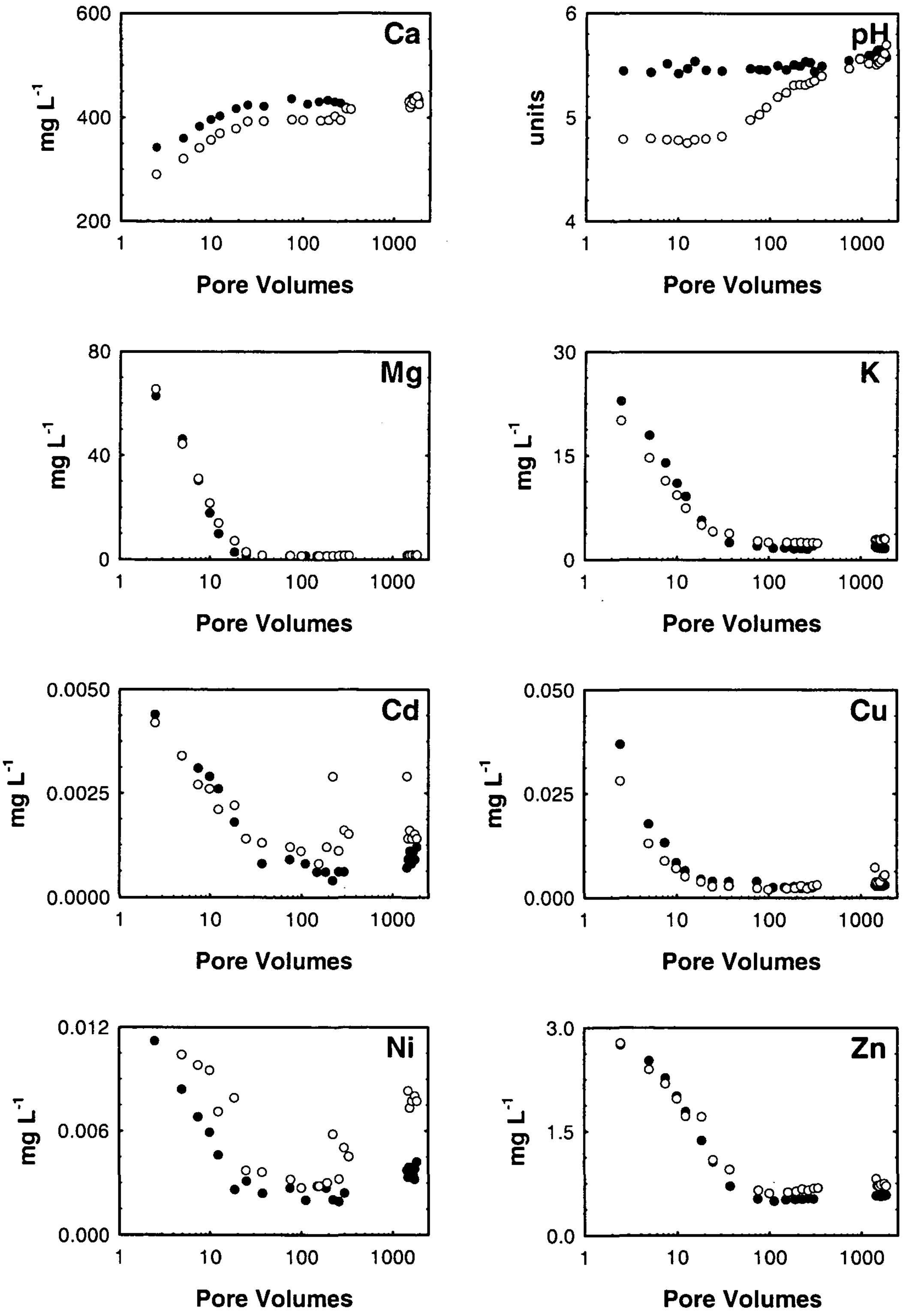

Figure 1.4 Selected cations concentrations (measured by ICP-AES) against pore volumes passed over flow through reactor. Unfilled and filled symbols denote runs 1 and 2 respectively. Note Log scale for pore volumes.

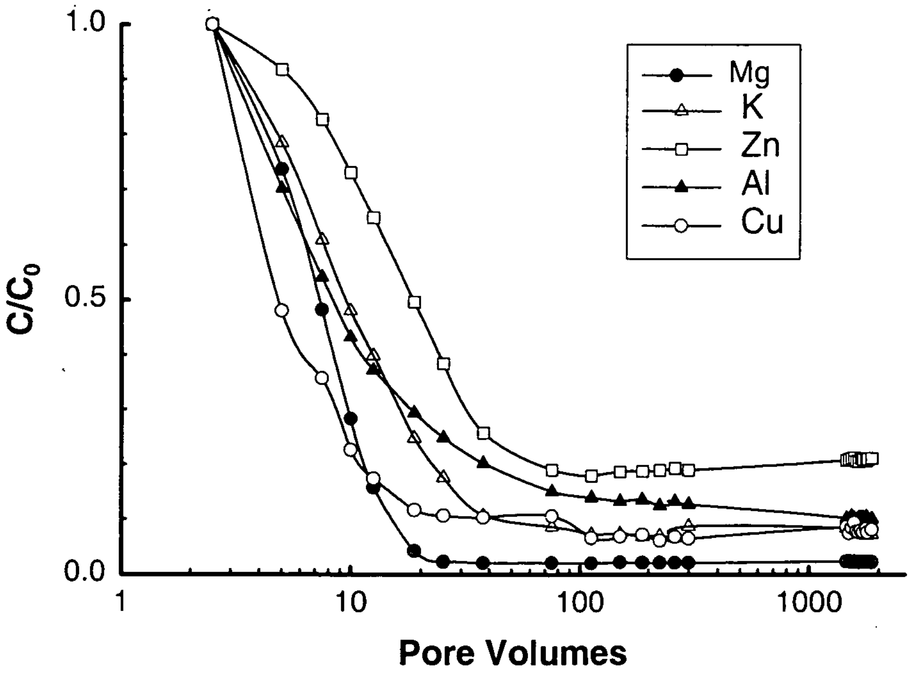

Figure 1.5 Normalised concentrations for selected elements against total number of pore volumes passed through reactor. The curve shape is an indication of the binding strength of a given element under these experimental conditions.

FAMEST Year 2 : Annual Report 1999

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and

Laboratoire de Minéralogie et Cristallographie, Univ. Paris 6 et 7, UMR CNRS 7590, IPGP

Objectives:

The objectives of the second year of the project were:

- Completion of analyses of samples
- Measure labile cations for all samples from UK, FR, CH and NL sites
- Modelling desorption data (Kd)
- Measure desorption isotherms for key metal contaminants (Completed next period)

Progress and achievements:

- Analyses of samples complete for all sites
- Desorption data modelled for Fr and UK

2. FRANCE

2.1 Selective chemical extractions

The chemical extractions used aimed at identifying the chemical forms (speciation) of the various pollutants and at comparing these data with those obtained by *in situ* spectroscopy. Table 2.1 summarises the results for all sites for the samples that were or will be studied by *in situ* spectroscopy. Data are available for all elements at all sites but the complete set are not shown here because of lack of space. The chemical speciation was determined as follows: for each chemical extract we propose the following procedure to obtain the quantity of metal associated with: the Exchangeable fraction = $CaCl_2$ extract; the Organic Matter (OM) fraction = NaPP extract - $CaCl_2$ extract; the (hydr)Oxides fraction (without distinction between amorphous and crystallised oxides) = DCB extract - $CaCl_2$ extract.

The results for the French site were presented last year and are given for completeness in Table 2.1.

The results for the English site show that for zinc, the major pollutant, the speciation is dominated by the Oxide fraction (>50%) while Zn associated with OM or in exchangeable form represents a similar amount in the plough horizon. Below the plough horizon the speciation seems to be similar. For Pb which is probably of atmospheric origin for this site since the uncontaminated sites contains as much Pb as the polluted site, the distribution is also dominated by oxides and some OM for the plough horizon while the OM contribution disappears below this horizon.

The results for the Swiss sites (CHD1 and CHD2) show no exchangeable metal ions in the polluted horizons. The OM and the Oxide fractions dominate the metal ion speciation (i.e. Cu, Pb, Zn). The nitric acid extraction results (Table 2.1) suggest that some resistant forms of Zn and Pb exist. The resistant forms could be clay or phosphate minerals.

The results for the Dutch site only concern surface samples where the pollutant (Cu) was derived from Cu nitrate application to different experimental plots having different monitored pHs (Table 2.1). The data show a consistent poor mass balance for the recovery. The sum of OM and oxides extracts is always greater than 100%. This means either that the extractions procedures are not selective for this soil or that Cu is also associated with a fraction which is different from OM and oxides but has a similar solubility with respect to both extraction procedures. This point should be clarified by spectroscopic data that will be obtained during the final year of the project.

2.2 Modelling chemical extractions.

The partition coefficient (K_d) is a key parameter for understanding the retardation of a metal ion during transport. From pore-waters results (given in 1st year report) the K_d is defined as: $K_d = m_{labile}/c_T$, where m_{labile} = metal mobilised by a chemical c_T = total concentration of the metal in pore-waters expressed as L kg^{-1} of soil. Log K_d calculated for the French and Swiss sites having a similar type of source for the pollutant (i.e. smelters) are given in Figures 2.1 and 2.2 as function of depth (Figure 2.1 French site for Zn, Cd, Cu, and Pb; Figure 2 Swiss sites for Zn and Cu). The data show an increasing mobility going from Zn, Cd, Cu to Pb for the French site irrespective of the nature of the carrier (Figure 2.1. OM or oxides). The results also show no variation of mobility with depth for the wooded site (P2 in Figure 2.1). For the Swiss sites a different behaviour is observed for Zn and Cu. The difference in mobility between Cu and Zn is much less important than the variation measured for the French site (Figure 2.1). But the mobility of both elements is changing with depth as log Kd decreases with increasing depth, meaning that the elements become more mobile in the deeper horizons.

In order to be able to predict metal contaminant mobility with changing conditions, the modelling of the partition coefficient (K_d) was done using the recently developed NICCA-Donnan approach. The results of the modelling are shown in Figure 2.3 for one of the French sites. Agreement between model and data is good for Cu, Cd and Zn. This means that the NICCA-Donnan approach used to simulate metal ion speciation in the soils and the soil solution is robust even when using parameters calibrated with measurements of metal ion binding to purified humic substances made in the laboratory. For lead, the model systematically underestimates the value of Kd. This means that either the modelling is not adapted or that the extraction is not specific for organic matter. For instance, Pb sorbed by manganese oxides could explain these systematic discrepancies. A new modelling effort is currently being undertaken to verify this hypothesis which seems to be supported by *in situ* spectroscopic data.

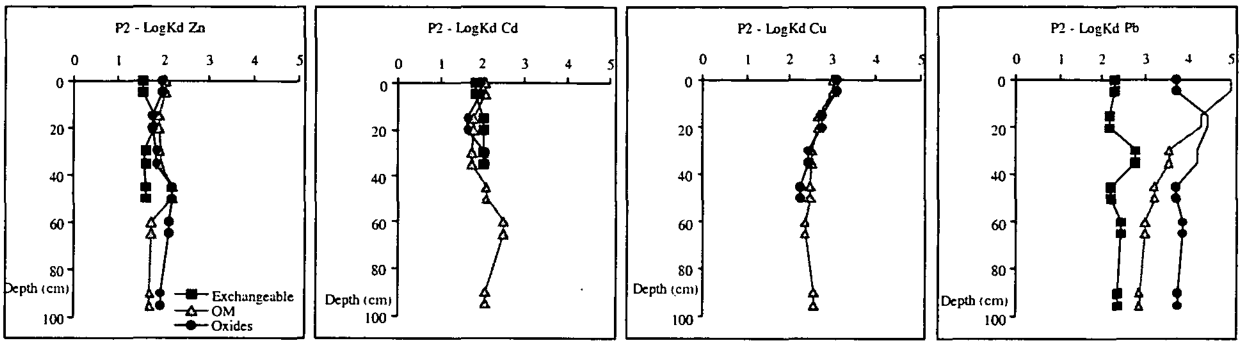

Figure 2.1 Partition coefficient (K_d) as function of depth for the French soil (wooded site P2)

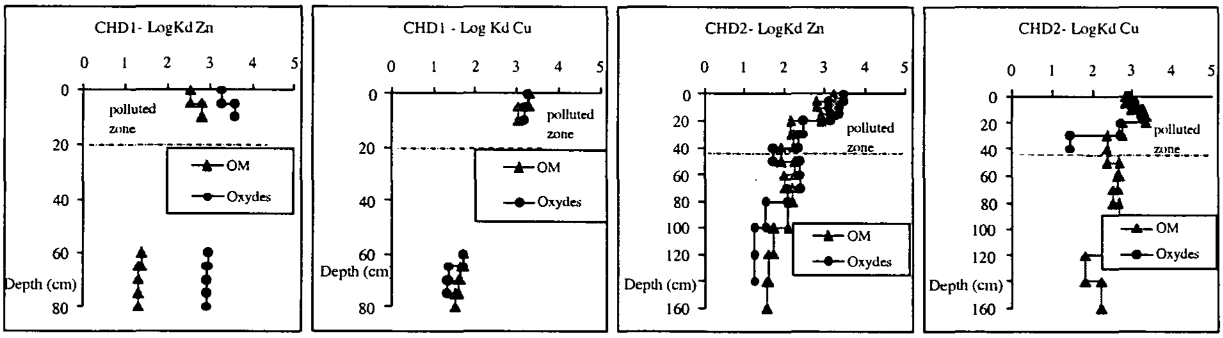

Figure 2.2 Partition coefficient (K_d) as function of depth for the Swiss soil (sites CH1 and CH2)

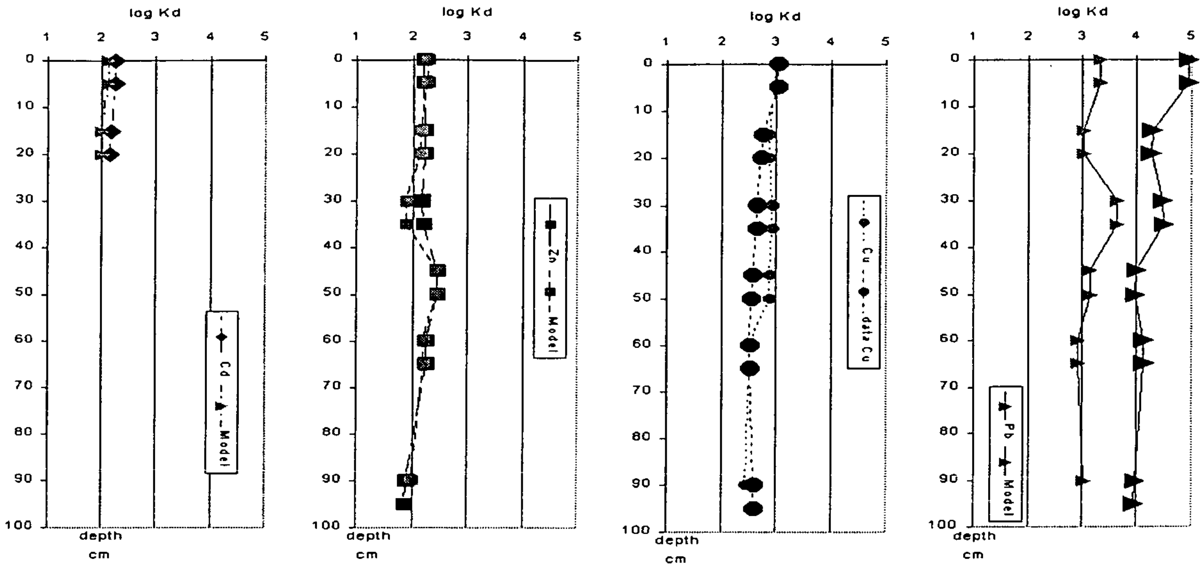

Figure 2.3 Modelling log(K_d) for metal ions associated to OM. Location : wooded French soil (site P2) Grey symbols corresponding to the model and black symbols to the experimental data. Calculation made with NICCA-Donnan model.

Table 2.1 Summary of chemical extractions for samples studied by in situ spectroscopy. Exch : metal ion in exchangeable form; OM bound to organic matter; Ox. Bound to metal oxides; HNO_3 in acid soluble forms

		% Exch.	% OM	% Ox.	% HNO_3	Notes
FRENCH SOIL:						
	Zn	12	38	31	60	40% in resistant phase (slag, clay, PO4)
P2	Cd	23	40	32	98	Present as acid-soluble forms
0-5 cm	Pb	-	73	4	105	Present as acid-soluble forms
	Cu	-	51	62	60	40% in resistant phase (slag ?)
	Zn	32	42	29	84	15% in resistant phase (slags ?)
P2	Cd	42	25	17	93	Present as acid-soluble forms
15-20 cm	Pb	-	54	84	84	Present as acid-soluble forms
	Cu	-	41	48	40	60% in resistant phase (slags ?)
	Zn	-	21	46	67	30% in resistant phase
OQS	Cd	-	-	82	100	Present as acid-soluble forms
0-30 cm	Pb	-	26	95	86	Mainly as acid-soluble forms
	Cu	-	29	55	67	30% in resistant phase
UK SOIL:						
CF1 A	Zn	18	30	57	110	Present as acid-soluble forms
0-30 cm	Pb	-	21	82	95	Present as acid-soluble forms
CF1 B	Zn	21	10	48	70	30% in resistant phase (clays or PO4)
30-90 cm	Pb	-	-	69	0	Associated to resistant forms
CF2	Zn	< 5	19-21	70-90	6-7	Mainly associated to resistant Oxides
0-40 cm	Pb	-	18-27	65-95	30-40	Mainly associated to resistant Oxides
SWISS SOIL:						
CHD1 A	Zn	-	41	49	68	Highly acid-soluble (30% in slags ?)
0-5 cm	Pb	-	20	35	72	Highly acid-soluble (30% in slags ?)
	Cu	-	58	26	86	Distributed between OM and oxides
CHD1 P3	Zn	-	7	94	89	Mainly associated to oxides
10-15 cm	Pb	-	< 5	73	41	Mainly associated to resistant oxides
	Cu	-	38	62	72	Distributed between OM and oxides
CHD2 A	Zn	-	24	42	54	45% in resistant phase (clays or PO4)
0-20 cm	Pb	-	11	40	68	30% in resistant phase (clays, ...)
	Cu	-	46	64	79	Distributed between OM and oxides
DUTCH SOIL:						
3D-0-20 cm	Zn	6	22	23	30	70% in resistant phase (clays, PO4 ,...)
pH = 6.1	Pb	-	39	69	100	Totally acid-soluble
500ppmCu	Cu	-	76	75	105	Totally acid-soluble
4D 0-20 cm	Zn	7	8	38	37	60% in resistant phase (clays, PO4 ,...)
pH 6.1	Pb	-	46	71	100	Totally acid-soluble
750ppm Cu	Cu	-	58	70	109	Totally acid-soluble
4A 0-20 cm	Zn	8	46	21	20	80% in resistant phase (clays, PO4 ,...)
pH 4	Pb	-	33	68	106	Totally acid-soluble
750ppm Cu	Cu	11	87	66	109	Totally acid-soluble

2.3 In situ spectroscopic data

Extended X-ray Absorption Fine Structure (EXAFS) data were recorded on raw soil samples and on chemically treated samples in order to accurately determine the chemical forms of Pb and Zn in the soils studied. Both elements were chosen because they occur at high concentrations in the soils studied. The lack of sensitivity of the method meant that the <2μm fraction, where metals concentrate had to be studied. Data were recorded at 10K on second and third generation Synchrotron sources (SSRL, CA and ESRF, France, respectively). Such spectroscopic data are essential to check for the reliability (selectivity) of the chemical extraction procedures and they yield a solid basis for modelling pore water chemistry.

2.3.1 Lead speciation in the French soil.

EXAFS data at the Pb L_3 edge on the French soil were presented in the previous report. They indicated that Pb speciation differs between the cultivated F-OQS and the wooded F-P2 soils (Figure 2.4).

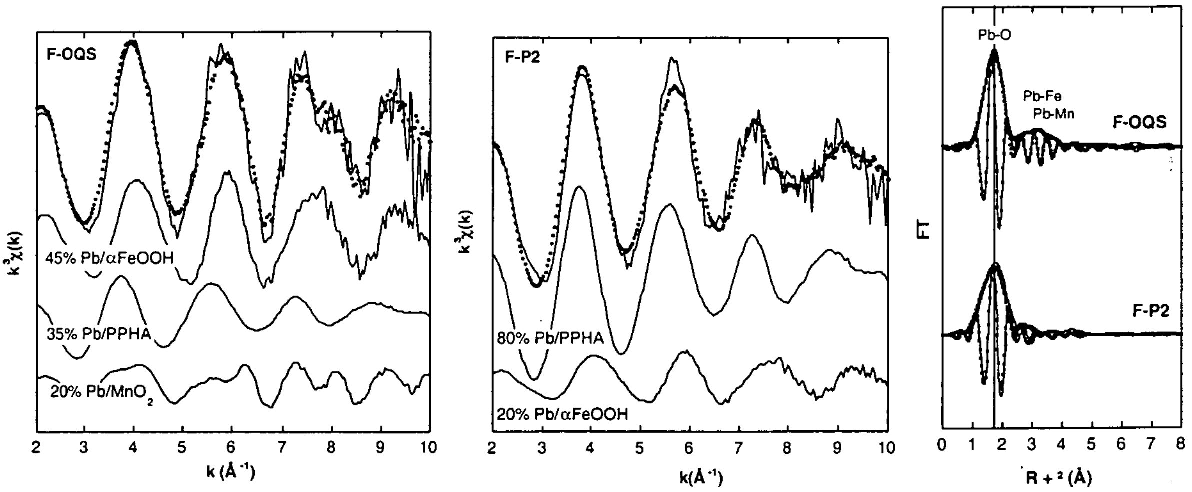

Figure 2.4 Pb L_3 edge EXAFS data (dotted) on the <2 μm fraction of the F-OQS and F-P2 top soil. Experimental spectra are modelled (plain) by linear combinations of model compound spectra, including Pb(II) sorbed on α-FeOOH, on MnO_2 and on PPHA. Pb(II) ions mainly sorb onto organic surfaces in F-P2 and on mineral surfaces in F-OQS. Additional data on NaPP treated F-OQS samples indicate that this reactant also extracts the Pb/MnO_2 contribution (Morin et al. 1999).

2.3.2 Zinc speciation in the French and Swiss soils

New data were recorded at the Zn K edge on the < 2 μm fraction of the smelter-impacted soils (French and Swiss). EXAFS data on the English site (sewage sludge-impacted soil) are currently being interpreted. EXAFS data were interpreted according to a large set of EXAFS spectra from various model compounds including, oxides, hydroxides, carbonates, phosphates, Zn-bearing clay minerals, as well as sorption samples such as Zn on goethite, Zn on ferrihydrite, Zn on purified peat humic acid (PPHA), Zn on MnO_2 and Zn on kaolinite.

Our results show strong similarities between Zn speciation in the French and Swiss smelter impacted soils (Fig. 2.5 and 2.7). EXAFS data indicate that zinc occurs in three main forms : Zn-organic complexes, Zn/Al mixed hydroxides (hydrotalcite-like structure), Zn-bearing clay minerals (probably dioctahedral smectites). Zn-bearing natural illite (Illite from Le Puy, France, 150 ppm Zn) was taken as analogue for 3-layer TOT clays (e.g. illite, smectites and so on).

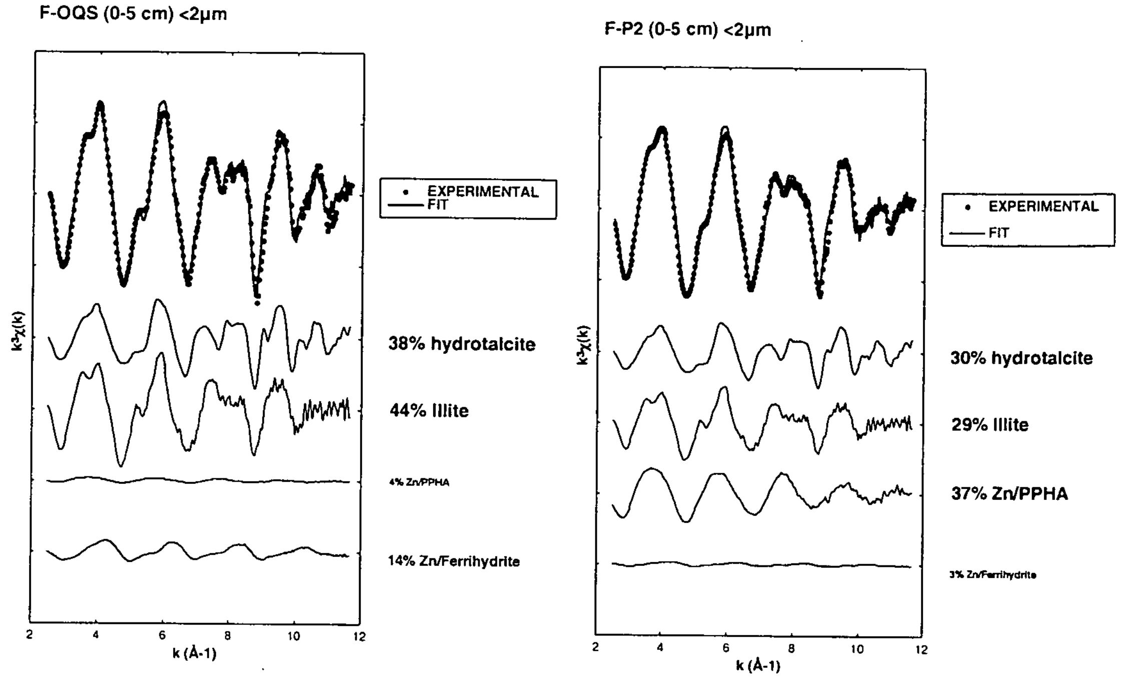

Figure 2.5 **Zn K edge EXAFS data (dotted) of the <2 µm fraction of the F-OQS and F-P2 topsoils. Experimental spectra are modeled (plain) by linear combinations of model compound spectra, including Zn(II)/Al(III) hydrotalcite, Zn(II)-bearing clay (illite, le Puy France 150ppm Zn), Zn(II) sorbed on ferrihydrite (Fh) and Zn(II) sorbed on PPHA. Zn(II) ions are mainly incorporated in hydrotalcite and clays. However, F-P2 soil exhibits a significant Zn-organic contribution.**

The largest proportion of Zn-organic complexes, as determined by EXAFS, was found in the wooded F-P2 topsoil (37 wt.%) compared to the cultivated French soil F-OQS (<5 wt.%) and the Swiss soils (11 and 24 wt.% for CHD1 and CHD-2 resp.). In addition F-P2 was the only soil containing "exchangeable" Zn (10 wt.%). This specific behaviour can be related to both its low pH (pH 5.5) and its high TOC content (6 wt%). EXAFS analysis of NaPP extracted samples suggested that this reactant is specific to the Zn-organic complexes but may also solubilise surface complexes of Zn sorbed onto ferrihydrite. Indeed the Zn-organic contribution as well as the minor Zn-ferrihydrite contribution are both removed from the spectra after extraction and the residual contributions of both the Zn/Al mixed hydroxides and the Zn-clay are enhanced (Figure 2.6).

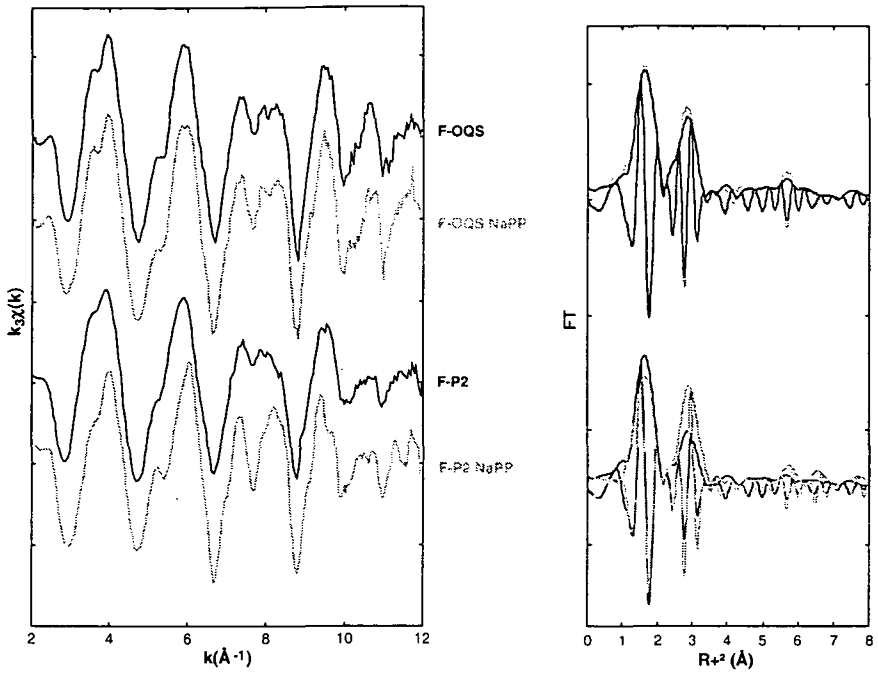

Figure 2.6 **Zn K-edge EXAFS data of the <2 μm fraction of the F-OQS and F-P2 topsoils before and after NaPP treatment. For F-P2 topsoil, note the strong increase in the 2nd neighbour contributions after removing organic mater using NaPP treatment. The spectra confirm the significant Zn-organic contribution in this soil.**

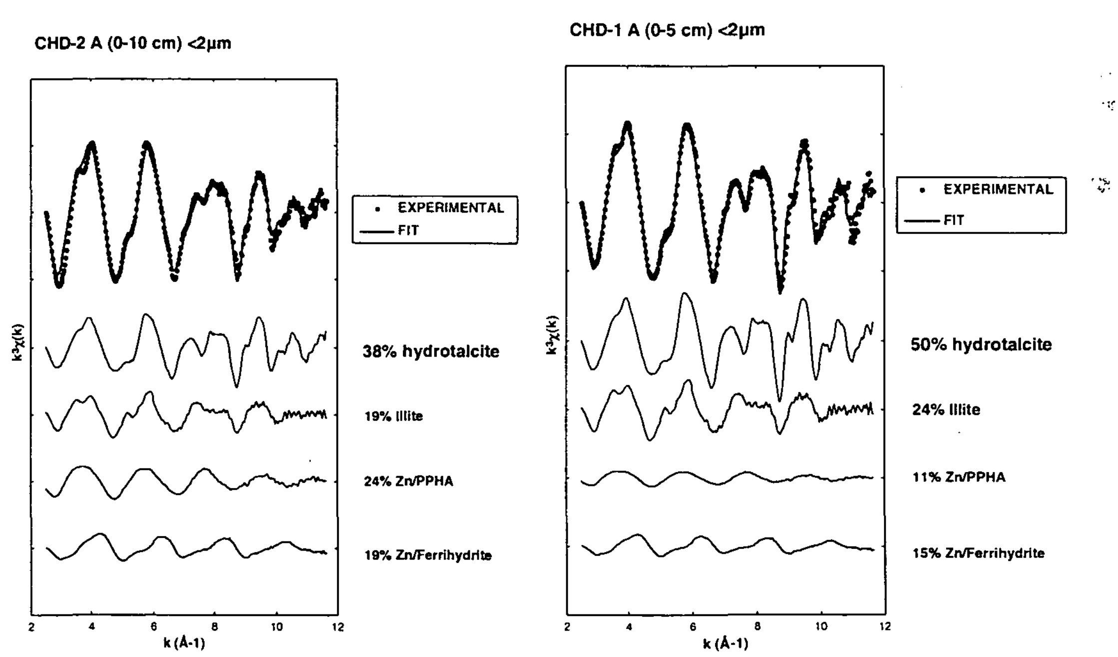

Figure 2.7 **Zn K edge EXAFS data (dotted) of the <2 μm fraction of the CHD-1A and CHD-2A topsoils. Experimental spectra (dotted) are modelled (full) by linear combinations of model compound spectra, including Zn(II)/Al(III) hydrotalcite, Zn(II)-bearing clay (illite, le Puy France 150ppm Zn), Zn(II) sorbed on ferrihydrite (Fh) and Zn(II) sorbed on PPHA. Zn(II) ions are mainly incorporated in hydrotalcite and clays. However, F-P2 soil exhibits a significant Zn-organic contribution.**

Large amounts of Zn/Al mixed hydroxides were found in both the Swiss soils (50 and 38 wt.% for CHD1 and CHD-2 resp.) and the French soils (38 and 30 wt.% for F-OQS and F-P2 resp.). It is now generally accepted from laboratory experiments, that such mixed M^{2+}/Al^{3+} hydroxides easily precipitate at room temperature when an Al-bearing phyllosilicate mineral or an Al (hydr)oxide reacts with a diluted M^{2+} salt solution, (where M can be Co, Ni, Zn ...). However, our data yield the first evidence of naturally occuring Zn-hydrotalcite. Moreover, the occurrence of this mineral phase, in four distinct contaminated soils differing in pH, TOC and CO_3 content, strongly suggests that it may be a major sink for Zn in a wide range of Zn-contaminated soils.

In addition, the presence of Zn-bearing clay-like structures in mixture with Zn-hydrotalcite, could be related to the possible role of hydrotalcite as a precursor for the formation of clay-like minerals.

2.4 Future Work

(i) Zn-EXAFS data for UK site will be interpreted

(ii) EPR will be used to tentatively investigate the speciation of Cu in the Dutch soils.

(iii) Desorption isotherms with the WDTM cell for a selected number of soil samples and under controlled pH conditions

(iv) Modelling of Kd as function of depth for other soils and others selective extractions (i.e. oxides)

FAMEST Year 2 : Annual Report 1999

Institute of Terrestrial Ecology, Swiss Federal Institute of Technology, Grabenstrass 3, CH-8952 Schlieren, Switzerland

Objectives:

The objectives of the second year of the project were:

- to complete the controlled multi-component column transport experiments with major cations (Ca, Mg, Na) and trace metals (Cd and Zn) using uncontaminated soil material from Switzerland.

- to development a competitive sorption and transport model which accurately describes trace metal behavior in complex multicomponent soil systems over wide concentration ranges.

- to conduct first leaching experiments with contaminated soils from the FAMEST field sites, concentrating on Cd and Zn mobilization and leaching behaviour in response to changes in soil solution chemistry.

Progress and achievements:

- completed multicomponent transport experiments with major cations and trace metals (Cd, Zn).

- developed and calibrated combined cation exchange and competitive adsorption model to describe Cd and Zn transport in soil columns.

- conducted leaching experiments with contaminated soils from France (P2, OQS), England (CF1) and Switzerland (D1).

- obtained first modelling results for leaching experiments.

3. SWITZERLAND

3.1 Cadmium and Zinc Sorption and Transport

Sorption and transport of Cd and Zn were investigated using an uncontaminated soil material (Riedhof soil) from northern Switzerland. The experimental sorption data were used to develop a simple competitive sorption model which can be applied to predict metal mobilization from contaminated soils in response to changes in soil solution chemistry. Cd sorption to the soil material was measured over wide concentration ranges in $CaCl_2$, $MgCl_2$, and NaCl electrolyte solutions. Figure 3.1 shows experimental sorption data (symbols) and model calculations (lines). The model is based on cation exchange and competitive adsorption reactions. As shown in Figure 3.1, the model accurately describes sorption data in all background electrolytes over wide concentration ranges. To achieve a satisfying model description, competitive sorption sites with a small site concentration (2 mmol/kg) and high Cd affinity had to be introduced, in addition to conventional cation exchange sites. The model coupled to a numerical transport code was used to predict Cd transport in the presence of different Ca concentrations. Figure 3.2 shows transport experiments and corresponding model predictions. With increasing $CaCl_2$ concentration, Cd retention was strongly decreased. Model predictions were generally in good agreement with experimental results.

In most contaminated soils, Cd occurs together with Zn contamination. Thus, the model should also describe competitive sorption of different heavy metals. Figure 3.3 shows the coupled breakthrough of Cd and Zn in $CaCl_2$ background electrolyte solution. The model was successfully extended to describe the competitive sorption and transport of Zn and Cd in the soil material.

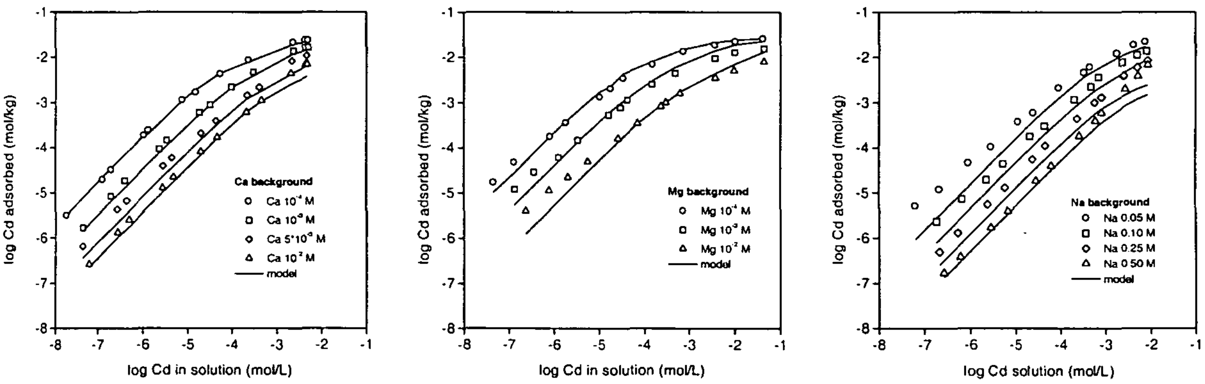

Figure 3.1 **Cd sorption in different $CaCl_2$, $MgCl_2$ and NaCl background electrolyte. Symbols: experimental data. Lines: model description accounting for cation exchange and specific Cd adsorption.**

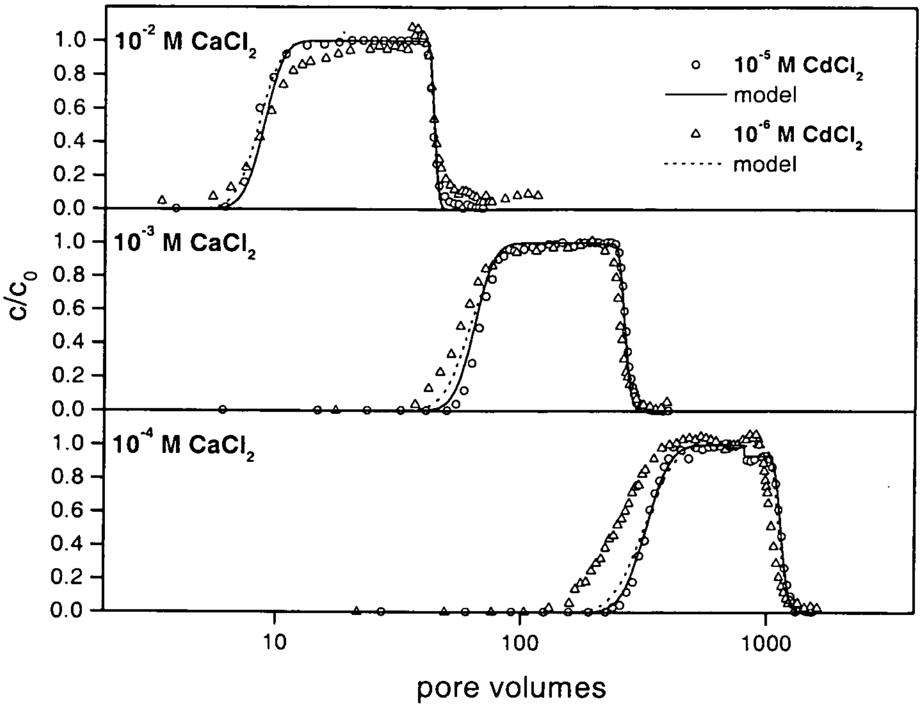

Figure 3.2 Cd breakthrough curves at different Cd concentrations in different $CaCl_2$ backgrounds. Symbols: experimental data. Lines: model predictions.

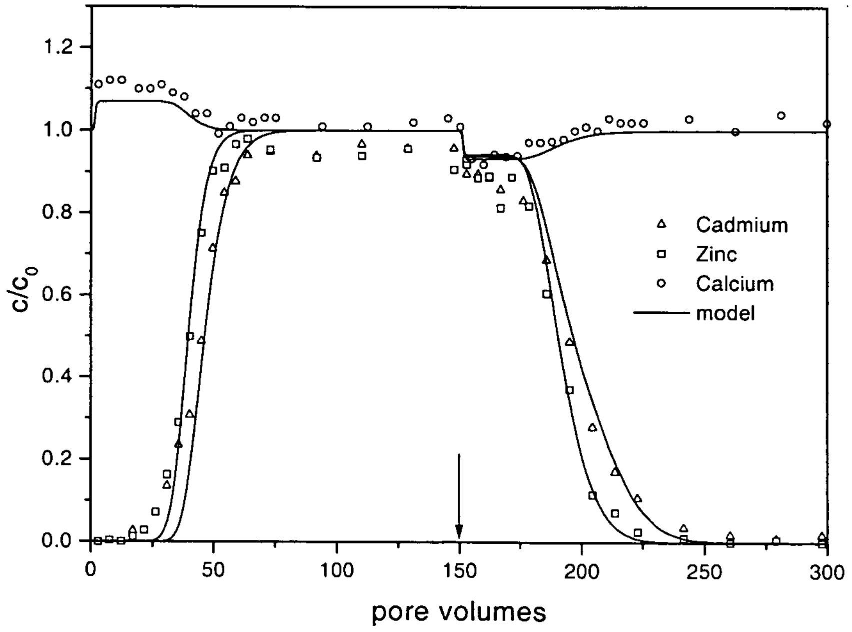

Figure 3.3 Coupled breakthrough of Cd (1• M) and Zn (100• M) in 10^{-3} M $CaCl_2$ background. Symbols: experimental data. Lines: model predictions.

3.2 Mobilization of heavy metals contaminated soils

To study the influence of changes in solution chemistry on metal mobilization and transport, a first set of column experiments was carried out with contaminated soil materials from the FAMEST field sites D1, CF1, P2, and OQS. Additional information was obtained from XRF analysis, $BaCl_2$ and sequential batch extractions. Figures 3.4 and 3.5 show experimental results from mobilization experiments at increasing $CaCl_2$ concentrations with soils P2 and OQS, respectively. Table 3.1 lists selected properties of all soil materials used. Table 3.2 contains a comparison of Zn and Cd concentrations mobilized in soil columns with results from batch extractions and total contents.

In soil P2 (Figure 3.4), very similar elution patterns were found for Cd and Zn. The concentration ratio of both metals in effluent solutions reflected their total concentrations in the soil material. Increasing the $CaCl_2$ concentration to 10^{-2} M resulted in a pronounced elution pattern.. This pattern was similar for Cd and Zn, and can be explained by a simple cation exchange model accounting for sorption competition between Ca, Mg, K, Cd, and Zn. The shoulder in the Cd and Zn elution peaks at approximately 26 to 34 pore volumes was related to the replacement of K and Mg from the exchanger phase by Ca. When Mg and K were depleted, Cd and Zn concentrations started to increase. This trend overlapped with the depletion of the exchangeable Cd and Zn pools. After around 38 pore volumes, the concentrations of Cd and Zn in the column effluent decreased sharply. Increasing the $CaCl_2$ concentration to 10^{-1} M resulted a second Cd and Zn peak and accelerated further depletion of the exchangeable pools. A comparison of the cumulative loads of Zn and Cd with batch extractions showed that more Cd and Zn were mobilized in column experiments than were extracted by $BaCl_2$ or NH_4NO_3 solutions in batch extractions (Table 3.2). The cumulative loads, however, were comparable to the sum of the first two fractions of sequential extractions, which are assumed to correspond to non-specifically and specifically adsorbed metal cations, respectively. Comparison with the total Zn and Cd contents showed that, at the end of the experiment, Cd was almost completely mobilized from the soil material, while around 500 ppm of Zn remained. Apparently, the remaining Zn is present in a less available form, possibly as Zn hydrotalcite. As $CaCl_2$ mobilizes mainly sorbed heavy metals, the similar concentration patterns of Cd and Zn agree well with the findings from the controlled transport experiments showing similar sorption behaviour for Zn and Cd (Figure 3.3).

A completely different elution pattern was found for the soil OQS (Figure 3.5). Zn and Cd concentrations in the column effluent were approximately 1000 and 100 times smaller than in soil P2. A simple cation exchange model could not describe the elution curves. It is likely that precipitation/dissolution rather than sorption reactions determine the mobility of Cd and Zn in this soil material. These differences may be explained by the lower pH, higher organic matter content, and higher cation exchange capacity of soil P2 compared to soil OQS. The column results are in good agreement with speciation results found for both soils by the French project partner.

Mobilization and leaching of Pb was measured in experiments with soil P2 (Figure 3.4). At the end of the experiment, only 22% of the total Pb were mobilized. The elution curve was completely different from that for Cd and Zn, indicating either cation exchange reactions with a very high affinity for Pb, or dissolution reactions of Pb bearing mineral phases. In an additional long-term mobilization experiment 1200 ppm Pb were mobilized over 2000 pore volumes, corresponding to 80% of the total Pb in the soil material. Further experiments are needed to clarify which chemical processes govern Pb mobilization in relation to Pb speciation in the soil materials.

In all column experiments and batch extractions, Cd was found to be more exchangeable than Zn. Cd mobilization in the column experiments ranged from 40% to 100% of the total, Zn extraction from 0.8% to 72%. Mobilization experiments with soils P2 and CF1 with $CaCl_2$ were initially controlled by cation exchange reactions. In soils OQS and D1, dissolution reactions rather than cation exchange are likely to control Zn and Cd release. Pb mobilization was observed in soil P2. Spectroscopic data which provides information about the chemical speciation of metals in the soil materials will be of great help in interpreting the findings of the column experiments.

Table 3.1 Selected properties of topsoil materials from soils P2, OQS, CF1, and D1 (<2 mm).

	P2	OQS	CF1	D1
[a]pH	5.2	7.3	5.5	7.1
[b]C_{org} (%)	4.3	1.6	1.5	5.5
[b]CEC (mol_c/kg)	0.216	0.133	0.062	0.300
[b]$CaCO_3$ (%)	0.2	0.9	0.4	6.6

[a]pH in 0.01 M $CaCl_2$.[b]From FAMEST Annual Report 1998.

Table 3.2 Comparison of column mobilized Zn and Cd with amounts mobilized by batch extractions and total contents (aggregate fraction 0.1-1 mm: in ppm).

	P2			OQS		CF1		D1	
	Zn	Cd	Pb	Zn	Cd	Zn	Cd	Zn	Cd
[a]Column	1300	29.1	315	5.0	3.5	280		138	2.6
[b]$BaCl_2$	986	25.7	250	1.0	1.5	237		34	0.9
[c]NH_4NO_3 (F1)	915	18.6	151	5.0	1.2	140	0.4	23	0.5
[d]F1+NH_4OAc (F2)	1150	27.8	945	93	6.5	283	0.7	315	2.5
[e]Total	1807	25.2	1464	657	8.7	703	0.6	1713	[f]5

[a]Cumulative extraction in mobilization experiment (Figures 4 to 7). [b]0.1 M unbuffered $BaCl_2$ (30 mL/g). [c]1 M NH_4NO_3 (25 mL/g), first fraction of the sequential extraction (F1). [d]F1 and 1 M NH_4OAc, pH 6 (25 mL/g), sum of first and second fraction of sequential extraction. [e]For Zn, Pb: XRF data, for Cd: <2 mm fraction ICP-MS data. [f]2 M HNO_3 extract of a close soil profile, different study.

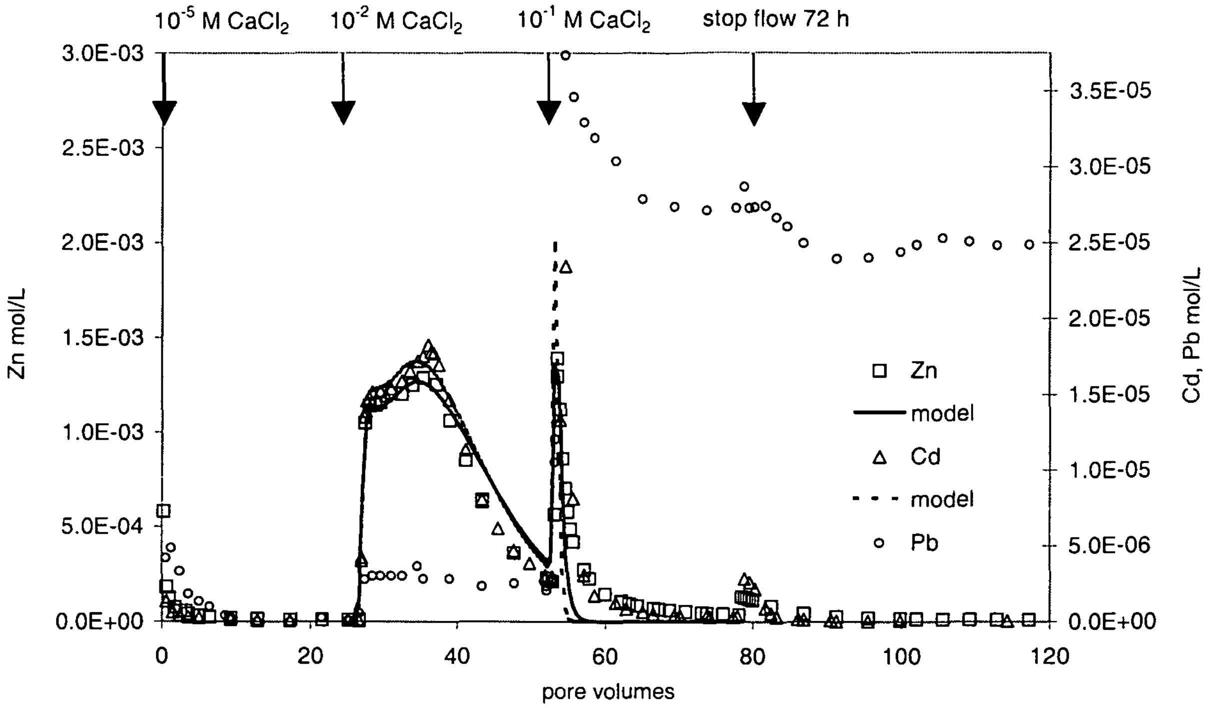

Figure 3.4 **Heavy metal mobilization experiment at increasing $CaCl_2$ concentrations from topsoil material of soil P2. Symbols: experimental data. Lines: model description (see text).**

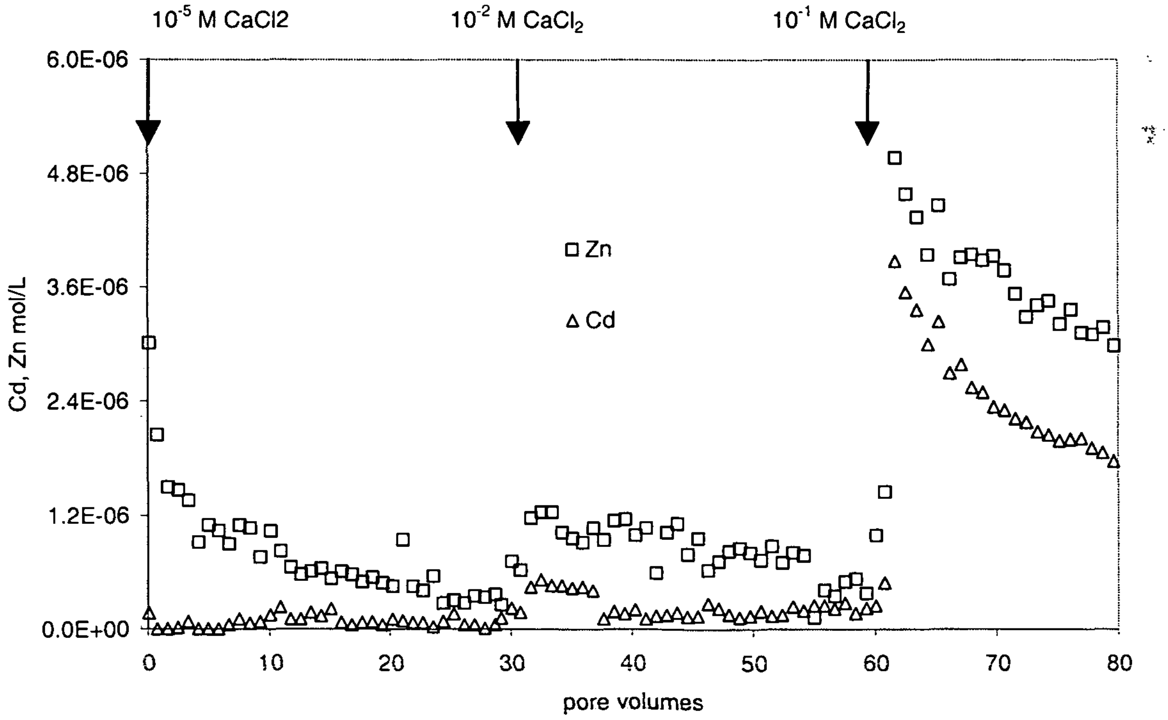

Figure 3.5 **Heavy metal mobilization experiment at increasing $CaCl_2$ concentrations from topsoil material of soil OQS. Symbols: experimental data.**

3.3 Future Work

For the third year, the following work is planned:

(i) Refinement of the competitive metal sorption and transport models to include additional factors, such as solution pH.

(ii) Testing of the sorption and transport models, in combination with metal speciation results (F), for predicting metal mobilization and transport in contaminated soils.

(iii) Additional column experiments to investigate dissolution of Zn bearing mineral phases (e.g., Zn hydrotalcite) in selected contaminated soils from the FAMEST project (D1, OQS).

3.4 Recent Publications

Christl, I. and Kretzschmar, R. (1999) Competitive sorption of copper and lead at the oxide-water interface: Implications for surface site density, *Geochim. Cosmochim. Acta*, 63, 2929-2938, 1999.

Voegelin, A., Vulava, V.M., Kuhnen, F., and Kretzschmar, R. (2000) Multicomponent transport of major cations predicted from binary sorption experiments (submitted).

Vulava, V.M., Kretzschmar, R., Rusch, U., Grolimund, D., Westall, J.C., and Borkovec, M. (2000) Cation competition in a natural subsurface material: Modeling of sorption equilibria (submitted).

3.5 Conference Presentations

Voegelin, A., Vulava, V.M., and Kretzschmar, R. Predicting cadmium transport in a non-calcareous soil from competitive sorption isotherms. *Paper presented at*: 5th International Conference on the Biogeochemistry of Trace Elements, Vienna, Austria, July 11-15, 1999.

Kretzschmar, R., Voegelin, A., Vulava, V.M. und Borkovec, M., Kompetitive sorption und Transport von Cadmium in Böden: Experimente und Modellierung. *Vortrag anlässlich der* Jahrestagung der Deutschen Bodenkundlichen Gesellschaft (DBG), Hannover, 1999.

FAMEST Year 2 : Annual Report 1999

Department of Environmental Science, Sub-Department of Soil Science and Plant Nutrition, Wageningen University, Wageningen, The Netherlands

Objectives:

The objectives of the second year of the project were:

- to develop a new methodology for the analysis of free metal activity (concentration) in the soil solution as a tool for soil quality assessment. For this objective, the Wageningen Donnan Membrane Technique (WDMT) method, which was developed in the first year, was linked to a soil column. Up untill now, free metal activity analysis with the Donnan membrane technique was conducted only with artificial solutions or soil extracts separated from solid phase.

- to compare the experimental SC-WDMT results with model calculations.

Progress and achievements:

- A paper about the WDMT technique was written and submitted to a journal for publication.

- The WDMT technique was further developed by linking a soil column to the WDMT cell. Different optimizations, like flow speed, filtering, salt level, mixing quartz sand etc., were carried out to optimize the SC-WDMT system.

- Results were compared with model calculations.

- Paper about linking a soil column to the WDMT is in preparation.

- Technique was presented at the conference 'Natural waters and water technology' in Italy and a poster was presented at the 12^{e} International Environmental Chemistry Conference in China.

4. NETHERLANDS

4.1 Summary of Results

The problem of using displaced pore solutions for WDMT analysis is twofold. First of all there is problem of phase separation that may introduce artefacts, and secondly the buffering capacity of the solution for trace metals often very low. In the WDMT, two sources of metal mass balance interference occur. One is due to transfer of the metal ions into the acceptor solution, and the other is due to accumulation of the cations in the membrane. Because of the negative charge of the cation exchange membrane, cations can accumulate in the Donnan phase of the membrane. For a reliable measurement of the free metal ion activity in the soil solution by the Donnan membrane technique, the chemical equilibrium in the substrate solution should not be disturbed by the method so that sufficient buffering capacity of the soil solution is a prerequisite.

The optimum percolation rate and the time needed to reach equilibrium were investigated. The results obtained were compared with the measurement of the soil solution after filtration through a 0.45μm filter. The effect of mixing soil with quartz sand was investigated so that the Soil Column WDMT method can be also applied to soils with low permeability (e.g. clay soils). The amount of metal accumulated in the cation exchange membrane was also measured and the soil metal buffer capacity was evaluated. Another important aspect is the test of the correction for relative ionic strength difference in the donor and acceptor solution on the activity ratio of concerned cations. Results are shown for the measured free Cu^{2+} concentration in the 'Wildekamp' soils. For information about this soil see progress report of Year 1. Finally the SC-WDMT results are compared with computed results with the computer implemented chemical equilibrium program ECOSAT (Keizer and Van Riesdijk, 1994). In this computation, the NICCA-Donnan model (Kinniburgh et al, 1999) was adopted to describe metal binding to dissolved organic matter.

Linking a soil column to WDMT introduces an aspect of equilibrium time, because the donor solution is not in equilibrium with soil solid phase at the beginning of the analysis. To avoid a prolonged period to reach Donnan membrane equilibrium, rapid equilibrium between the donor solution and the soil solid phase is preferred. The effects of percolation rate through the soil column on the equilibrium time between the donor solution and the solid phase were therefore studied. The setup of the Soil Column WDMT system is shown in Figure 4.1.The solution was pumped (B) from bottle (E) into the soil column (D) from below, and then sucked out from the top of the soil column (A) and circulated through the donor side of the cation exchange cell (FI) and back to the bottle again. The acceptor side of the cell (FII) was connected with a test tube for ICP-MS measurement (G) and circulated constantly by pump C.

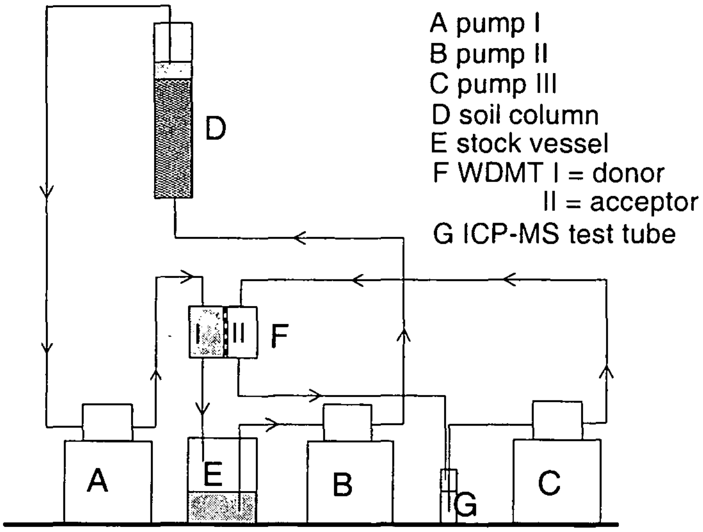

Figure 4.1 **Scheme of the Soil Column WDMT system**

4.1.1 Equilibrium Time

Column percolation with different rates were tested for two different sandy soils. At high rates (> 2.0 ml/min) too high a pressure in the soil column was built up and the soil column was damaged. Both contact time and percolation rate are important in determining the equilibrium time. A column percolation rate of 2.0 ml/min was chosen as standard in the other experiments. A flow rate of 2.5 ml/min was used for the pumping rate of the donor and acceptor solution over the WDMT cell.

The time to reach Donnan membrane equilibrium in this experiment system was analyzed. The results show that Donnan membrane equilibrium was reached within 24 hours in 0.002M $Ca(NO_3)_2$ and 48 hours in 0.01M $Ca(NO_3)_2$ (Figure 4.2). The salt concentration of the background electrolyte solution influences the Donnan membrane equilibrium time in two opposing ways. First, at a lower salt concentration, the Donnan potential of the cation exchange membrane is higher, and a higher Donnan potential favors faster cation flux. Second, at a lower salt concentration, the retardation of cations in the membrane is increased due to the high Donnan potential and less competition from the cations in the solution. Increased accumulation of cations will slow down the cation flux. The overall effect of the salt concentration on the Donnan equilibrium time is the combination of the influences on the Donnan potential and on the cation accumulation in the membrane.

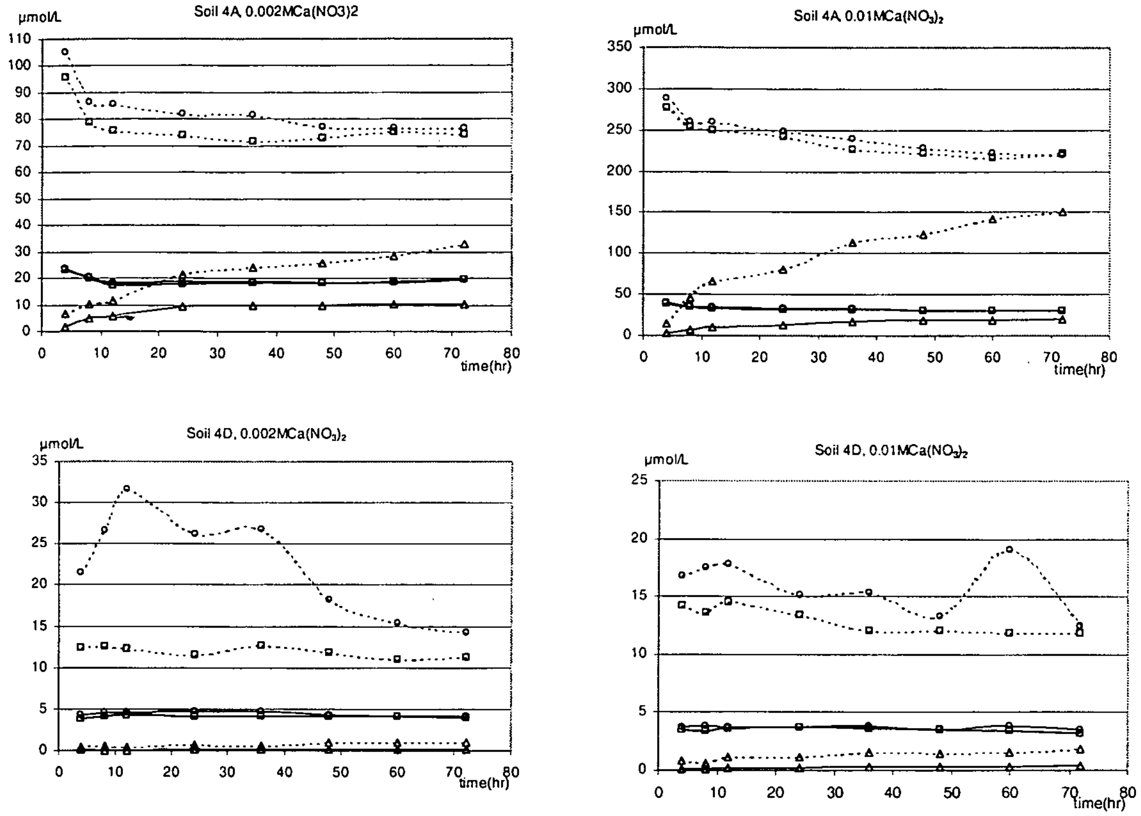

Figure 4.2 Donnan membrane equilibrium time in the Soil Column WDMT analysis and effect of filtration over o.45µm on Cu, Al concentration in donor solution

(o in donor solution; □ in filtered donor solution; △ in acceptor solution; —— Cu; .... Al)

Soil 4A: Cu$_{total}$ 1.70 mmol/kg; pH 3.99
Soil 4D: Cu$_{total}$ 2.22 mmol/kg; pH 5.39

4.1.2 *Filtration over 0.45µm*

Soil solutions and natural waters are generally prepared for analysis by filtration through a 0.45 µm filter. The aim of filtration is to separate "particulate" and "dissolved" matter. The cut off size is arbitrary but conventional (Buffle, 1988). Dissolved organic matter in soil solution is also mostly defined as the fraction of soil organic matter that can pass through a 0.45µm filter. In this investigation, the donor solutions were analyzed both without filtration and after filtration through a 0.45 µm filter. Filtration through a 0.45 µm filter has no effect on the content of dissolved organic matter (denoted by DOC). Aluminum concentration in filtered donor solution was much lower than without filtration. The reduction of Al concentration by filtration was more significant for soil 4D than soil 4A, probably because the pH of soil 4D was higher. At pH > 4, as in soil 4D, (hydro) oxide species of Al dominate and colloids may be formed. Cu concentration in donor solution was also reduced by filtration but much less significant compared with Al. Metal concentrations in filtered donor solutions were more stable than in the solution without filtration (Figure 4.2). Therefore, for speciation computation, we considered it necessary to pass the donor solution through a 0.45 µm filter.

4.1.3 Mixing Soil with Quartz Sand

It is problematic to apply the soil column method to soil samples that have too low a permeability, such as heavy clay soils. We have shown that if the percolation rate through the soil column was too low, it took too long to reach chemical equilibrium in the donor solution. Compared to other soil constituents such as organic matter, clay and metal oxides, quartz sand has a very low chemical reactivity and has been used in many batch and column experiments to modify the matrix texture or alter porous media permeability. In this research, the possibility of mixing quartz sand with soil samples for SC-WDMT analysis was studied. No significant influence on the content of DOC and metals was observed.

4.1.4 Correction for Ionic Strength Differences

It is difficult to maintain exactly the same ionic strength in the donor and acceptor solutions. We use the activity ratio of potassium in the donor and acceptor solutions as basis for the correction for ionic strength differences in SC-WDMT analysis. Potassium always occurs in soils naturally, and like sodium has a very low potential to form complexes with ligands in the soil solution. We therefore assume that all potassium in the donor solution is in the form of the free ion. The potassium concentration in the donor and the acceptor solution can be measured with ICP-AES, simultaneously with the other macro-elements.

4.1.5 Comparison of Measured and Modeled Free Copper

In the soil solution, both inorganic ligands, such as OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and organic ligands such as humic acid, fulvic acid exist and react with the dissolved metal ions. When metal-organic complexes are important, model calculations are difficult. The newly developed NICCA-Donnan model includes site binding heterogeneity, electrostatic effects, competitive binding, and ion specific non-ideality and it was reported that the prediction by this model matched the field observations rather well. In this research, the model calculations were done by the computer-implemented chemical equilibrium program: ECOSAT, in which the NICCA-Donnan model can be used. The NICCA-Donnan parameters were taken from Kinniburgh et al., (1999). Measured pH, dissolved organic matter content, total dissolved metal concentration in filtered donor solution were used as the input data. Dissolved organic matter was assumed to behave as purified peat humic acid (PPHA). The effects of pH, ionic strength, Ca and Al competition on Cu adsorption to dissolved organic matter were considered in the Cu speciation calculation. Free Cu^{2+} concentration was computed and the results were compared with the measured free Cu^{2+} concentration in the acceptor solution after correcting for the ionic strength difference (Table 4.1). The agreement was reasonable if the complexity of dissolved organic matter was taken into account. The fraction of free copper at an initial salt level of 0.002 M $Ca(NO_3)_2$ was 65.1% and 88.6% for the measured and calculated free ion in soil 4A. For soil 4D the measured and calculated free copper fractions were 3.8% and 9.3% respectively.

Table 4.1 Comparison of the measured and modelled free Cu^{2+} concentration in the soil solution

$Ca(NO_3)_2$ Donor-acceptor (M)	Soil 4A			Soil 4D		
	Cu in donor (µmol/L)	free Cu^{2+} (µmol/L)		Cu in donor (µmol/L)	free Cu^{2+} (µmol/L)	
	Measured	Measured	Computed	Measured	Measured	Computed
0.002	17.55±0.64	11.43±0.69	15.55±0.78	5.58±0.30	0.21±0.05	0.52±0.16
0.010	30.39±0.49	20.20±2.55	29.05±0.79	5.40±0.39	0.36±0.06	0.74±0.00

4.2 Future Work

In the third Year of the project more experiments will be carried out with the SC-WDMT. Special attention will be paid to aluminium speciation in soil since measurements of 'free' aluminium is difficult due to (in)organic complexation and the absence of an Al electrode. Also more soils will be analyzed with the SC-WDMT to get an insight into metal speciation in the soil environment. These results will be compared with model calculations. Papers will be prepared and a contribution will be given to the final report.

4.3 References

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