Effects of a Fertilization Pulse on Migration of Nutrient and Trace Elements in Chernozem Soil Columns within a Vegetation Period

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Einfluss einer einmaligen Düngergabe auf die Migration von Nähr- und Spurenelementen in Tschernosem-Bodensäulen in einer Vegetationsperiode

1. Introduction

1.1 General

Application of mineral fertilizers, waste deposition and atmospheric deposition are the most important sources of input into topsoils. The most important pathways of output from soils include the transfer into biomass, as well as the transport into deeper layers and ground water. Losses of nutrients and essential elements from the root zone means loss of plant availability and thus decreased crop yield. Fertilization pulses may provoke migration to deeper layers and

Zusammenfassung

Die obersten Schichten eines Tschernosems, Paratschernosems und einer Feuchtschwarzerde wurden in Säulen von etwa 30 cm Länge und 125 cm² Querschnittsfläche in 3 Schichten gepackt, um die vertikale Ausbreitung von Nähr- und Spurenelementen im Zuge einer einmaligen Düngung zu untersuchen. Die Säulen wurden langsam im Dunkel mit etwa 5 Porenvolumina Wasser 2 Monate hindurch eluiert, um den natürlichen Regen zu simulieren. Nach dem Durchtritt etwa eines Porenvolumens sank der pH in den Eluaten, und eine Konzentrationsspitze nicht zugefügter Ionen Mg/Sr/Ba/Li trat in den Eluaten auf, erklärbar aus Ionenaustausch und Ansäuerung. Danach näherten sich die Konzentrationen in den Eluaten im Median durchwegs höheren Werten, als aus der Löslichkeit in den Standardwasserextrakten 1 + 9 ermittelt wurde. Auch die ausgewaschenen Frachten korrelierten kaum mit den für die gleiche Wassermenge aus dem Wasserextrakt berechneten.

Beträchtliche Mengen von aufgegebenem Phosphat wurden nur aus dem Paratschernosem ausgewaschen, während aufgegebenes Molybdän und Vanadium fast vollständig zurückgehalten wurden. Aufgegebenes Bor wurde rasch aus dem Paratschernosem, und auch noch innerhalb von 5 Porenvolumina aus der Feuchtschwarzerde ausgewaschen, während es im Tiefgründigen Tschernosem zurückgehalten wurde. Erhöhte Kupfergehalte des Tschernosems aus einer vormaligen Nutzung als Weingarten wurden nicht in die Eluate mobilisiert, fanden sich aber deutlich auch in den Extrakten mit Oxalat pH 3 und 1 M NaOH. Einfaches Modellieren der Desorption nach dem Ionenaustauschpeak gelang nur für Natrium.

Nach dem Experiment wurden die in den Säulen verbleibenden Festkörper trocknen gelassen und in 6 Tiefenstufen zerlegt, welche wie das ursprüngliche Material durch Königswasser-, Oxalat- und Natronlaugeextrakte charakterisiert wurde, um pedogene Oxide oder Huminstoffe als mögliche Ziele für Adsorptions- bzw. Desorptionsvorgänge innerhalb der Profile nachzuweisen. Oxalatlösliches Eisen stieg im Tschernosem und Paratschernosem nach dem Versuch auf das Doppelte an, hingegen hatten nicht zugegebene Co-Ni-Pb-Zn sinkende Tendenzen; in der Feuchtschwarzerde gab es in dieser Fraktion der pedogenen Oxide keine signifikanten Löslichkeitsänderungen. Obwohl keine organischen Substanzen aufgegeben noch durch Photosynthese gebildet wurden, stieg die Alkalilöslichkeit der verbleibenden Festkörper in vielen Fällen an. Die zusätzlich aufgegebenen Düngemittelanionen zielten in den 3 Bodentypen auf unterschiedliche Phasen, aber der Wiedererhalt aus Alkali war zumeist stärker als aus saurem Oxalat.

Schlagworte: Bodensäulen, Phosphor, Molybdän, Bor, Vanadium.

Summary

Topsoils of a Calcic, a Haplic and a Gleyic Chernozem were packed to columns of about 30 cm length and 125 cm^2 area in 3 layers and 4 replicates each, in order to investigate the vertical migration of nutrients and trace elements, added as a fertilization pulse. The columns were gradually eluted in the dark with about 5 pore volumes of water within 2 months to simulate natural rainfall. After passage of about one pore volume, pH in the eluate dropped and a pulse of non-added species Mg/Sr/Ba/Li appeared in the eluates, explainable from ion exchange and acidification. Then, most median concentrations in the eluates approached a level higher than obtained from standard water extracts 1 + 9. Similarly, the eluted loads did hardly correlate with solubilities obtained from water extracts.

Substantial amounts of added phosphorus eluted only from the Haplic Chernozem samples, whereas added molybdenum and vanadium were almost completely retained. Added boron was rapidly eluted from the Haplic, and still within 5 pore volumes from the Gleyic chernozem columns, but largely retained on the Calcics. Elevated Cu from former use of the Calcic Chernozem as a wineyard soil, was not mobilized to the eluates, but clearly extractable into oxalate pH 3 and 1 M NaOH. Simple mathematical modelling of desorption after the ion exchange peak could be only achieved for Na.

After the experiment, the solids remaining in the columns were let dry and sliced into 6 fractions, which were characterized by aqua regia, oxalate, and NaOH like the original materials, to reveal pedogenic oxides and humics as target phases of adsorption/desorption within the profiles. Oxalate soluble Fe increased in the Calcic and Haplic Chernozem samples to double amounts, whereas oxalate soluble non-added Co-Ni-Pb-Zn tended to decrease; in the Gleyics no changes in these pedogenic oxide fraction occurred. Though no organics were added nor formed by photosynthesis, alkali mobile forms of the remaining solids tended to increase. The target phases for the additional loaded fertilizer anions varied considerably between the 3 soil types, but alkali mobile recoveries were preferred over oxalate mobiles.

Key words: soil columns, phosphorus, molybdenum, boron, vanadium.

thus change groundwater composition. Investigation of the genesis of ground water is important to protect aquifers from environmental hazards, in order to save clean water reserves for future generations.

Mineral fertilizers may not only contain N, P, K and sulfate as the main nutrients, but also other trace elements required for optimum yields, like boron and molybdenum. As in soils many solid phases carry negative surface charges, the mobility of anions is generally higher than of cations. Great excess of phosphate, nitrate, and possibly sulfate may compete for adsorption sites and up the downward migration of anions, as well as influence pH and redox potential.

1.2 Merits of column experiments

For routine characterization of soils, numerous batch extraction methods have been established, which can be run for a large number of samples within some hours, and reflect the actual situation. On the other hand, lysimeters in the field are used to investigate transport phenomena of water and solutes at the climate, hydraulic conductivity, reaction time and microbial life close to natural conditions.

Column experiments link the gap between simple batch extraction techniques done in routine soil laboratories, and lysimeters in the field. As column experiments last for a long time, and many data have to be made from one column, detailed investigations are rather expensive. In order to predict vertical mobility of nutrients, main and trace elements, high amounts of solutes can be applied on top of the model columns in order to provoke marked effects, without doing any harm to the environment. After the experiment, it is much easier to slice the remaining solid in order to investigate changes in soil concentration profiles due to the treatment.

The conditions within a column cannot be fully simulated by batch experiments. Within a column, for each layer another kind of equilibrium can be reached, if any. The solid is in excess over dissolved complexants. Components dissolved by action of acid within an upper layer, move along with the water phase, which thus permanently changes its composition within the column. Sometimes even new solid phases may generate. On the other hand, within a batch experiment, equilibrium is reached between

liquid and solid phase within at least some hours. Duration of the column experiment of several weeks gives a more realistic view of transformations during the entire growth period, because soil life and respective metabolisms are maintained (SAGER, 1992).

1.3 Soil pH-changes

pH shifts in the soil column occur due to direct input of acids or bases (e.g. acid rain), application of fertilizers and microbial processes. Fertilizers may have a pH different to soil pH, and also cause pH-shifts by ion exchange reactions versus H^+ or OH^-. Microbial oxidation of ammonia with oxygen to nitrate, and of sulfide to sulfate directly produces acid. Similarly oxidation of Fe(II) to Fe(III), as well as degradation of Fe- and Al-organic complexes at neutral pH, leads to precipitation of the hydroxides, thus consuming hydroxyl ions and shifting the pH to more acid values (ROTH-KLEYER and WILKE, 1989).

As long as there is aerobic respiration, CO_2 is formed, which has acid properties. Microbial activity is governed by the availiability of nutrients and substrates, oxygen, temperature, water content and pH. In carbonaceous B-horizons, the pore water is often oversaturated with respect to $CaCO_3$ (HOLTHUSEN, 1982).

1.4 Phosphate mobility in soil columns

Beneath uptake by the biomass, migration of phosphate is limited by precipitation of Ca-, Al- and Fe-phosphates, by anion-exchange processes and by sorption processes on Fe-/Mn-/Al-oxides. As the limiting mineral phase, variscite $AlPO_4$ was calculated for pH = 5,5, and hydroxylapatite $Ca_5(PO_4)_3OH$ was calculated for pH = 7,4. In the core profile, the maximum P concentrations appeared in the calcite dissolution zone under neutral or slightly acid aerobic conditions (ISENBECK-SCHRÖTER et al., 1993). Whereas for a lot of aquatic ecosystems, phosphate has turned out to be the limiting nutrient, possible P-input via groundwater wells has been hardly investigated. Permeable sandy soils low in clay content and pH, which are more typical for deep soil layers, are particularly subject to phosphate leaching. Thus, after having passed the topsoil layers, P migration might happen appreciably faster.

1.5 Molybdate, vanadate and borate

Beneath phosphate, chemically similar oxyanions were included in this study for comparison, which may be present at enhanced levels in the phosphate fertilizers as well (SAGER, 2002a). Contrary to cationic trace elements, maximum mobilities of molybdate and vanadate occur at pH 4, and increase with increasing pH because of repulsion from the negatively charged adsorbent hydroxides. Mo-adsorption was negliglible at pH > 7, and V-adsorption was negligible at pH > 8 and pH < 3. Phosphate and molybdate sorption are competitive (MIKKONEN and TUMMAVUORI, 1993). Additional immobilisation may occur from reduction to Mo(V), which is more tightly bound N- and S-ligands within the organic substance, but in sewage sludge treated soils, the mobility of Mo and V obtained in batch experiments, was not affected by aeration (GERRITSE et al., 1982).

In some mineral fertilizers, boron may be present at the 0,1 % level, but on the other hand it is regarded to be of moderate toxicity. Boric acid is a neutral molecule at ambient levels, its retardation is usually low.

1.6 Selective leaching fractions

Changes in selective leaching fractions were used to investigate possible speciation shifts of phosphate and others from the loading and leaching experiment.

In soil analysis, alkaline extracts are used to extract humics from soils. Experiments with model substances showed that phosphorus, arsenic and many elements were released from oligochaetes, reed, or sewage sludge in cold 1 M- NaOH extracts (SAGER et al., 1990). Further alkali-soluble phosphate derives from ion-exchange versus OH- (PSENNER et al., 1984). 1 M-NaOH extractable phosphate had been the main fraction in sediments from crystalline areas, whereas the acid mobile phosphate fraction was dominant in carbonaceous sediments, like in the River Danube or the Lake Balaton (SAGER and PUCSKO, 1989). When P applied from anaerobically digested sewage sludge was applied to soil columns, P preferably moved to the NaOH-mobilizable fraction (HINESLY and JONES, 1990). Thus, the possible uptake of added phosphorus and other anions to organic solids or ion exchangeable sites might be visible in changes of NaOH extractable amounts in the soil profile.

Sorption processes on Fe-/Mn-/Al-oxides might be well characterized by means of oxalate leachates, which are known

to dissolve many Fe-oxide phases. Extraction into cold 0,2 M oxalate yielded the main P-fractions in the sediments of the River Danube and the River Po (SAGER and PUCSKO, 1989).

2. Material and Methods

Aims of this experiment were to investigate the fluxes of nutrients and selected presumably anionic trace elements within a vegetation period, both during periods of intense rainfall, as well as after 6 weeks of no precipitation. A quasi natural soil profile was simulated by filling 3 layers into the test columns in the same succession which was found in the field. Experimental variability was got from four replicates each. Contrary to short-time batch experiments with acids, alkalis or complexants, bacterial and fungal metabolism was tried to be maintained by discontinous addition of distilled water. As a worst-case scenario for downward migration, plant cover and algae growth were prohibited by keeping the model columns in the dark. Like in the field, periods of water flow and periods of aeration down from the surface should alternate, which seems to be closer to natural condi-

tions than to maintain a steady state flow. The amount of water added on top of the columns should be within the range of natural precipitation, simulating a "wet year". Chernozem topsoils were selected because of their known intense soil life and exchange capacities.

A haplic chernozem, calcic chernozem, and gleyic chernozem sample was taken by digging at depth 0–10 cm, 10–20 cm and 20–30 cm, from topsoils at Sierndorf/March, at the eastern border of Lower Austria, just before the begin of the growing season (Feb. 26th, 1998). After air drying at 35 °C over 2 nights in a drying chamber, recognizable plant material was removed by hand. The soils were characterized by aqua regia and water extracts, soil pH, clay and carbonate contents (Table 1).

As experimental setup, 12 cylindrical columns of 12,6 cm diameter (area = 125 cm^2) and 40 cm length made from transparent polypropylene were used. Plastic Büchner funnels with perforated plates were fitted with an O-ring to the bottom of the columns. Two layers of medium pore filter papers were placed at the bottom of each column. Then the air-dried soils were filled into the columns to a depth of 30 cm, maintaining the original profile of the 3 layers sep-

Table 1: Some characteristics of the soils investigated, and data from aqua regia extracts
Tabelle 1: Einige Kenndaten der untersuchten Böden, und Daten aus dem Königswasseraufschluss

		Gleyic chernozem			Haplic chernozem			Calcic chernozem		
		0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
pH CaCl$_2$		7,0	7,05	7,35	4,2	4,25	4,25	7,15	7,2	7,2
Carbonate %		0,9	1,1	0,7	0	0	0	1,3	1,1	1,2
Humics %		2,5	2,5	1,9	0,9	0,9	1,0	3,6	3,4	3,4
Clay fraction %		13	14	14	7	7	7	13	13	13
Cation exchange capacity cmol/kg		20,4	20,2	22,4	1,85	2,3	2,7	22,3	21,4	22,3
Ca	%	1,12	1,04	0,98	0,035	0,041	0,041	1,19	1,31	1,21
Fe	%	1,7	1,71	1,73	0,667	0,703	0,697	2,03	2,03	2,04
K	mg/kg	497	817	592	4280	3911	4541	917	932	544
Mg	mg/kg	4882	4963	4789	937	999	954	4934	4914	4998
Mn	mg/kg	498	446	398	257	262	253	589	590	593
P	mg/kg	528	541	342	361	376	372	796	811	831
S	mg/kg	27,5	26,7	20,8	5,5	5,9	5,8	32,9	33,1	33,3
Sr	mg/kg	590	577	588	112	114	108	423	430	418
As	mg/kg	19,1	19,1	16,3	4,83	5,05	4,83	10,7	11,8	12,6
Ba	mg/kg	112	104	106	33,7	37	36,2	96,5	98,6	95,9
Cr	mg/kg	29,3	29	28,4	10,2	11,2	11,2	33,8	34	34
Cu	mg/kg	18,2	16,3	14,9	22,4	23,1	23,9	61,8	61	61,7
Li	mg/kg	6,6	6,3	6,4	1,7	1,8	1,8	7,7	7,4	7,6
Ni	mg/kg	37,6	37,8	37,7	5,6	5,6	6	44,2	43,2	42,2
Pb	mg/kg	10	12,5	11,1	11,2	12,8	11,7	15,8	14,8	15,2
Se	mg/kg	0,222	0,163	0,107	0,085	0,087	0,067	0,251	0,243	0,215
V	mg/kg	30,2	29,7	30,9	10,3	11	11	37,3	37,6	37,8
Zn	mg/kg	47,1	47,3	43	19,6	20,7	20,7	56,9	57,3	56,6

arately sampled. Each column contained approximately 5 kg of soil. On top of each column, 100 g of pure quartz sand were evenly spread to facilitate uniform distribution of any solution applied among the entire cross-section. Then the columns were weighed, and saturated with distilled water from bottom to top for 2 days to displace all air, and to soak the clay minerals, but not covered with water. Each of the columns took about 1 l of water. In order to prevent algal growth, the soil columns were kept in a dark room in the cellar at approximately constant temperature (21–24 °C), and 55–90 % humidity.

At first, the effective pore volume of each column had to be determined in a pre-run. After opening the outlet of the columns to release non physically bound excess water by gravitation, 50 ml of 1.0 M KCl solution were added on top as marker substances for presumably non-retarded ions. Twice a day, each of the columns were eluted with portions of 50 ml distilled water by gravitational flow, leaving untouched inbetween. Before addition of new water portions, the eluate vessels were exchanged, weighed for evaporation, and the eluates analyzed for chloride, potassium and pH. The curve of eluate volume versus eluate concentration was fitted with a Gaussian function, and the volume at the fitted maximum of chloride concentration was taken as the effective pore volume. The effective pore volume for the chloride anion was slightly less than for the simultaneously added potassium cation, if both are regarded as non-retarded species. Whereas chloride yielded broad elution peaks in any case, the counter-ion potassium was completely absorbed in the gleyic chernozem, and eluted constantly from the calcic chernozem columns. Only for the haplic chernozem sample, a significant K-peak in the eluates could be observed.

Smoothing of the chloride elution curves by taking the average concentrations of three subsequent 50 ml fractions led to equally shaped elution curves. Therefore, 150 ml were chosen as added washout-volumes for the main experiment (SCHOISSENGEIER, 1999).

After a drying period of some weeks, the columns were saturated with distilled water from bottom to top again, excess water was released by gravitation, and finally 50 ml of liquid mineral fertilizer solution was added on top of the wet columns. Beneath main elements $K/Ca/Mg/NH_4/NO_3/PO_4/SO_4$, the test solution contained a cocktail of presumably anionic trace elements Mo, V, As, Se and B, in circumneutral solution. The application rate of nutrients at the column surface corresponded to an application rate of 160 kg N/ha as NH_4NO_3, 320 kg P_2O_5/ha as $Ca(H_2PO_4)_2$. H_2O, and 200 kg K_2O/ha (from this 20 % given as K_2SO_4 and

80 % as KCl, in order to avoid precipitation of gypsum). The trace elements were added in concentrations more than 100-fold above detection limit in the eluate solution, i. e. 50 mg/l B and V each, 20 mg/l Mo, and 10 mg/l As and Se each, within 50 ml of loading solution. This means in absolute terms per column: 2,5 mg B and V, 1 mg Mo, and 0,5 mg As and Se, resp. 2 g/ha, 0,8 g/ha and 0,4 g/ha (Table 2).

Every day except the weekends, 3 times (morning, noon, afternoon) 50 ml distilled water was added with a glass pipette slow enough to permit gradual seeping down, which matched about 1/10 of effective pore volume per day. Eluates from pure gravity were taken from the bottom of the columns. Before addition of eluent water in the morning, the eluate vessels were exchanged. About 4–5 effective pore volumes were collected in 40 fractions from each column, which took about 2 months (Table 3). Then the columns were left dry for 6 weeks, gradually rewetted from top to bottom with 350 ml water, and eluted at 4 subsequent days with 3 times 50 ml a day like above, in order to estimate the effect of drying and aeration. Mean recovery of the added water volume after the intermediate drying period ranged between 64–100 %, and precision among the 4 replicates was less than before.

The eluates were weighed, pH determined, and HNO_3 suprapure added for stabilization. Most of the analytical data (Al/As/B/Be/Ca/Cd/Co/Cr/Cu/Fe/K/Li/Mg/Mn/Mo/Ni/Na/P/Pb/S/Sr/V/Zn) were obtained from ICP-OES multi-element determination from undiluted and 1 + 4 diluted samples, to serve as controls. Some samples at 1 effective pore volume had to be diluted 1 + 9. Controls were done with flame-AAS and graphite furnace (in case of vanadium). Details referring to selenium, arsenic and sulfur are given elsewhere (SAGER, 2002b). Be, Cd, Cr, and Pb were often below detection limit of the ICP. Zinc desorbed from the vessels and gave too high results after storage.

About one week after the last fraction was collected, the columns were dismantled and cut into 6 equal slices, which were air dried in the drying chamber again. The 6 slices correspond to profile depths of 0–5/5–10/10–15/15–20/

Table 2: Amounts added to each column
Tabelle 2: Die auf jede Säule aufgebrachten Mengen

Nutrient salts per Hectare		absolute amounts
160 kg/ha N as NH_4NO_3		
320 kg/ha P_2O_5 as $Ca(H_2PO_4)_2$.H_2O	113 mg Ca	175 mg PO_4-P
200 kg/ha K_2O as K_2SO_4 + KCl	208 mg K	17 mg SO_4-S
2 g/ha B		2,5 mg B
0,8 g/ha Mo and V		1,0 mg Mo and V
0,4 g/ha As and Se		0,5 mg As and Se

20–25/25–30 cm in the original column; when the columns were dismantled, the original 30 cm had declined to 27 cm for the gleyic, and to 24 cm for the haplic and calcic chernozem samples. The filter paper had completely disappeared at the bottom of the the haplic and calcic chernozem samples. Ochres inside the funnels were collected, dissolved in hydrochloric acid, and submitted to multi-element analysis; they were carbonaceous from the calcic and gleyic, and non carbonaceous from the haplic chernozem samples.

The air dried slices were homogenized and extracted with aqua regia, oxalate buffer and sodium hydroxide like the original soil samples, to detect possible differences in speciation.

For aqua regia extracts, 21 ml conc. HCl and 7 ml conc. HNO_3 were added to 2 g samples. After pre-reaction overnight, the samples were pre-heated for 30 min at 60 °C and refluxed for 90 min, filtered and made up to 100 ml.

Oxalate extracts were obtained by shaking 2 g sample in capped plastic vessels with 20 ml of 0,2 M oxalate buffer pH = 3 (25,2 g oxalic acid + 28,4 g ammonium oxalate in 1 liter for 4 hours at ambient temperature), and filtered.

NaOH extracts were obtained by shaking 5 g sample in capped plastic vessels with 50 ml 1 M NaOH (40g NaOH in 1 liter) for 4 hours at ambient temperature. The brown extracts were almost neutralized with 1 M HNO_3, and aliquots were dried and ashed in a drying oven and the muffle furnace (4 hours at 560°) after addition of magnesium nitrate solution, dissolved with 30 ml 1 + 1 HCl for 1 hour at the boiling water bath, and made up to 50 ml.

For ICP-OES determination in the oxalate buffer, calibrants were made in oxalate buffer also. The calibration blank for trace elements was 1 µg/lg of Fe and Mn each. Use of plastic vessels and milli-Q purified water enabled reasonable readings for boron because of sufficient low blanks. For ICP determination in the NaOH-extract, the calibrants were matrix matched with magnesium, and a shorter program for the non-distorted lines was used, covering Ca/Cd/Cr/Cu/Fe/Mn/P/S/Zn.

Molybdenum was determined by graphite furnace AAS (Perkin Elmer 3030 Z) and standard addition, because the ICP-line was interfered from the salt matrices. K was determined by flame AAS (Perkin-Elmer 3030) in presence of 450 µg/ml Cs as a matrix modifier.

Methods and results for selenium, sulfur and arsenic have been treated elsewhere (SAGER, 2002b).

3. Results and Discussion

3.1 Water flow and pH-effects

The columns were weighed air dried and after water saturation and free drainage. This difference of weights was only some percent higher than the pore volumes fitted from the chloride elution curves. Effective pore volumes were in the range of 1,0–1,2 liter.

Details of the hydraulic conditions are given by SCHOISSENGEIER (1999). After initial saturation with water, drain of the columns was achieved by gravity only. All concentration data refer to the actual eluate volumes. Evaporation (= difference between added water and eluate weight) during the main run was lower than during the pre-run, because the columns were fed faster (Table 3).

pH-effects may serve as an easily determinable parameter to predict mobilities of solutes in soils. pH measurement inside the column would be preferable, because pH turned out to be not stable in the eluates on storage. In the pre-run, pH of each eluate fraction was determined immediately after collection, and 3 days afterwards. After 3 days, the pH was less variable, and generally higher, except for the calcic chernozem after 0,6–0,7 pore volumes, but the pH taken immediately after collection is presumably closer to the conditions in the column. The increase of eluate pH on storage clearly indicates oversaturation with CO_2, whereas precipitation of hydroxides in the eluate would lead to a pH decrease. In the pre-run, no trends in pH versus elution volume could be recognized (for details, see SCHOISSENGEIER, 1999).

In the main run, after the addition of the fertilizer solution, the pH in the eluates dropped slightly until one effective pore volume had passed, and further on steadily increased (see Figure 1).

Table 3: Evaporation of water during the experiments – range obtained from 4 columns each
Tabelle 3: Wasserverdunstung während des Versuchs – Bereich aus je 4 Säulen

	Pre-run			Main-run		
	Added	Duration	Evaporation	Added	Duration	Evaporation
Haplic chernozem	2600 ml	53 days	18,8–22,1 %	6000 ml	57 days	10,4–11,3 %
Gleyic chernozem	2600 ml	53 days	18,8–21,7 %	6000 ml	57 days	5,0–14,3 %
Calcic chernozem	2600 ml	53 days	23,2–24,2 %	6000 ml	57 days	10,7–15,2 %

Lower pH in the standardized $CaCl_2$ extract obtained from the original samples, reflect both an ion exchange reaction of Ca^{2+} versus $2 H^+$, and the buffer capacity (Table 4).

Table 4: Range of pH in the eluates and standardized $CaCl_2$ solution
Tabelle 4: pH-Werte in den Eluaten und in standardisierter $CaCl_2$-Lösung

	pH $CaCl_2$	pH-range in pre-run	pH-range in main-run
Haplic chernozem	4,2	5,8–7,6	6,2–7,7
Gleyic chernozem	7,1	7,6–9,2	7,7–8,9
Calcic chernozem	7,2	7,4–9,0	7,5–8,8

Among reactions in soils, reduction of nitrate, sulfate and Fe(III) would consume H^+ or liberate OH^-, and thus increase the actual pH. On the other hand, addition of previously aerated waste deposit leachate to a luvisol significantly lowered the pH, because of intense microbial oxidation of the input of ammonium to nitrate, and of sulfide to sulfate in the soil (ROTH-KLEYER and WILKE, 1989). Compared with other soil types from various countries, Austrian chernozem had extraordinary high oxygen diffusion coefficients. Enzymatic activities were higher in aerated soils (RAMPAZZO et al., 1998).

3.2 Leaching of non-added main and trace elements with vertical water flow and comparison of water extracts obtained from batch versus column mode

The multi-element capability of the ICP enabled the simultaneous measurement of a lot of element concentrations in the eluates, which were not added during the experiment.

It was, however, interesting to observe, whether the release of these main and trace elements was influenced by the input of the liquid fertilizer solution. Degradation of complexants, active uptake by micro-organisms, and dissolution/precipitation reactions steadily change the transport conditions in the column. Selective leaching of the remaining solid core revealed (see Tables 12–14) an increase in oxalate-extractable Fe in the haplic and calcic chernozem columns, which are weathering products. This can largely change the conditions for retardation in the column. In some cases, the aqua regia extract, too, does not reflect the total contents (like e.g. for Ba, Cr, Li, Sr), and shifts in aqua regia leachable amounts might occur.

The sum of eluted amounts and contents of the ochres collected in the Buechner funnels below the soil columns was lower than 0,1 % of the absolute amounts present in the entire samples in most cases. Exceptions were manganese and strontium.

The water soluble fraction (batch extraction 1 + 9), which might be favourably eluted along with the vertically moving water (Table 5), was mainly below 0,2 % of aqua regia. Maximum mobilities in the water extract were 2 % Zn, 1 % Cu, 0,6 % Li in the gleyic chernozem, 4 % Li, 2 % Zn and Ni, and 1 % Mn in the haplic chernozem, and just 0,6 % Zn and 0,5 % Cu in the calcic chernozem (Table 5). As expected, the acid soil yielded higher water soluble concentrations of Al, Fe, Mn, and P in the batch mode.

Within Tables 6A/6B/6C, the recovered eluate volumes, the eluted loads and their precision obtained from the 4 replicates are presented. If the samples would have been just cored at the sampling sites, precision is expected to be

Table 5: Solubilities in the water extract 1 + 9 before the column experiment
Tabelle 5: Löslichkeiten im Wasserextrakt 1 + 9 vor dem Säulenversuch

		Gleyic chernozem			Haplic chernozem			Calcic chernozem		
		0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
Al	mg/l	0,16	0,193	0,167	1,31	0,97	0,99	0,36	0,21	0,23
Ca	mg/l	25,8	27	27,7	5,68	8,77	8	32,2	31,9	32,9
Fe	mg/l	0,01	0,05	<	0,35	0,34	0,41	0,1	X	0,06
K	mg/l	3,07	2,39	1,08	4,54	4,49	7,77	9,36	7,59	11,25
Mg	mg/l	7,42	7,56	8,59	3,81	2,49	4,43	2,74	3,1	2,93
Na	mg/l	1,57	1,87	3,55	1,36	1,17	1,14	1,52	1,63	1,82
P	mg/l	0,214	0,17	0,044	2,01	1,91	2,14	0,72	0,79	1,14
S	mg/l	0,65	0,82	0,82	0,48	0,46	0,55	0,89	1,03	1,34
B	µg/l	63	58	42	X	55	46	41	37	39
Ba	µg/l	42	44	37	42	42	42	38	61	75
Li	µg/l	4	4	4	16	4	4	3	2	3
Mn	µg/l	28	39	17	247	240	289	21	14	17
Sr	µg/l	98	101	112	33	30	27	63	64	64
V	µg/l	12,4	11,8	3,2	1,3	<	<	9,9	8,2	11,6

lower because of inhomogeneities from stones and rests of maize leaves. For calculation of eluted loads, concentration values below detection limits were replaced by half the detection limit throughout. Be-Cd-Co-Cr-Mo-V were below the detection limit many times, and thus precisions are worse. Elements tending to ochre formation (see below), like Fe-Al-Mn-As, yielded lower precisions. When the recovered eluate loads are compared with both the added amounts and the soluble amounts calculated from the water extracts, the columns released significantly more Ca-Mg-Sr-Ba-Li-Mn-S from the two weakly alkaline soils, than predicted from batch design for the same amount of water. For the acid soil (haplic chernozem), however, much more Fe-Mn-Ba-S were found in the eluates. Significant retention within the columns occurred for the added K, P, As, B, Mo and V. Just from the gleyic chernozem, boron was completely recovered.

3.3 Mobility of a pulse of added nutrient K and P with vertical water flow

From the haplic chernozem a rather narrow and pronounced peak of K appeared in the eluate at about 1 effective pore volume, with a subsequent decline to low levels. From the calcic chernozem, washout was appreciable throughout, but no significant peak appeared. Release from the gleyic chernozem was negligible throughout. Summing up the amount of eluted K minus the amount soluble in the respective water extracts, 50 % of added K were eluted from the calcic and the haplic chernozem, but for the gleyic chernozem, complete retention took place. After drying and aeration, K-release strongly enhanced for the haplic and the calcic chernozems, but K-release was unchanged low for the gleyic chernozem.

Added phosphate was detectable in the eluate after 2 pore volumes and remained at about constant level, the eluted amounts were highest in the haplic chernozem. The calcic

Table 6A: Comparison of the total load eluted by the 40 eluates with the load obtained from standard water extraction 1 + 9 in the same volume of water, for the **gleyic** chernozem

Tabelle 6A: Vergleich der durchschnittlichen Gesamtfracht aus den 40 Eluaten mit der aus dem Standard-Wasserextrakt im selben Wasservolumen berechneten Fracht, für die **Feucht-schwarzerde**

	Column elution	% std dev	added	batch H_2O soluble
ml total	5207 ± 104	2,0		5207
mg Na	21,5 ± 1,5	6,9		12,1
mg K	5,0 ± 1,2	24,2	208	11,4
mg Ca	620 ± 32	5,1	113	140
mg Mg	291 ± 22	7,6		40,9
mg Fe	2,74 ± 1,55	56,6		0,104
mg Mn	10,36 ± 5,13	49,5		0,146
mg Al	0,48 ± 0,16	9,4		0,90
mg P	0,096 ± 0,012	12,1	175	0,74
mg S	55,9 ± 4,0	7,2	17	3,97
µg As	37,8 ± 14,2	37,4	500	
µg B	2484 ± 234	9,4	2500	283
µg Ba	409 ± 53	13,0		214
µg Be	1,15 ± 0,07	6,3		
µg Cd	6,03 ± 0,84	14,0		
µg Co	10,5 ± 3,2	30,6		
µg Cr	3,02 ± 1,12	37,0		
µg Cu	41,1 ± 3,9	9,5		
µg Li	68,8 ± 7,8	11,3		20,8
µg Mo	17,3 ± 9,5	54,9	1000	
µg Ni	67,4 ± 5,6	8,3		
µg Pb	11,7 ± 3,2	27,4		
µg Sr	3672 ± 309	8,4		540
µg V	7,29 ± 3,29	45,1	1000	47,6
µg Zn	43,6 ± 5,8	13,3		

Table 6B: Comparison of the total load eluted by the 40 eluates with the load obtained from standard water extraction 1 + 9 in the same volume of water, for the **haplic** chernozem

Tabelle 6B: Vergleich der durchschnittlichen Gesamtfracht aus den 40 Eluaten mit der aus dem Standard-Wasserextrakt im selben Wasservolumen berechneten Fracht, für den **Para-tschernosem**

	Column elution	% std dev	added	batch H_2O soluble
ml total	5347 ± 22	0,4		5347
mg Na	1,6 ± 0,2	10,8		6,4
mg K	118 ± 15	12,8	208	29,2
mg Ca	186 ± 10	5,4	113	39
mg Mg	23,5 ± 2,6	11,1		18,6
mg Fe	177 ± 21	11,9		1,91
mg Mn	93,2 ± 8,9	9,6		1,35
mg Al	3,5 ± 3,8	3,3		5,83
mg P	30,7 ± 8,1	26,3	175	10,52
mg S	43,4 ± 1,3	3,1	17	2,59
µg As	137 ± 12	9,1	500	
µg B	1632 ± 55	3,3	2500	262
µg Ba	330 ± 66	19,9		219
µg Be	1,43 ± 0,12	8,5		
µg Cd	7,46 ± 1,24	16,7		
µg Co	513 ± 45	8,8		
µg Cr	9,15 ± 6,26	68,4		
µg Cu	59,7 ± 23,5	39,3		
µg Li	18,8 ± 9,4	49,9		41,7
µg Mo	33,0 ± 21,4	64,8	1000	
µg Ni	416 ± 36	8,8		
µg Pb	19,2 ± 2,5	12,8		
µg Sr	756 ± 34	4,5		156
µg V	12,8 ± 7,4	57,4	1000	2,3
µg Zn	86 ± 19	22,1		

Table 6C: Comparison of the total load eluted by the 40 eluates with the load obtained from standard water extraction 1 + 9 in the same volume of water, for the **calcic** chernozem

Tabelle 6C: Vergleich der durchschnittlichen Gesamtfracht aus den 40 Eluaten mit der aus dem Standard-Wasserextrakt im selben Wasservolumen berechneten Fracht, für den **tiefgründigen Tschernosem**

		Column elution	% std dev	added	batch H_2O soluble
ml	total	5232 ± 140	2,7		
mg	Na	12,4 ± 4,6	36,8		8,7
mg	K	137 ± 16	11,8	**208**	49,2
mg	Ca	962 ± 89	9,3	**113**	169
mg	Mg	142 ± 118	82,9		15,3
mg	Fe	26,7 ± 5,6	20,9		0,42
mg	Mn	32,3 ± 5,7	17,7		0,09
mg	Al	0,4 ± 0,2	43,4		1,40
mg	P	1,16 ± 0,10	8,9	175	4,62
mg	S	44,9 ± 5,4	12,1	17	5,68
µg	As	60,6 ± 15,2	25,1	500	
µg	B	722 ± 313	43,4	2500	204
µg	Ba	619 ± 97	15,6		303
µg	Be	0,62 ± 0,32	50,8		
µg	Cd	3,78 ± 1,70	44,9		
µg	Co	44 ± 9	20,8		
µg	Cr	2,04 ± 0,84	41,1		
µg	Cu	89 ± 38	43,1		
µg	Li	22,7 ± 2,8	12,4		14,0
µg	Mo	51,1 ± 36,9	72,3	**1000**	
µg	Ni	90,1 ± 13,0	14,5		
µg	Pb	9,9 ± 1,1	11,2		
µg	Sr	2296 ± 124	5,4		333
µg	V	6,9 ± 3,9	56,4	1000	51,8
µg	Zn	60,2 ± 5,9	9,8		

chernozem steadily released minor amounts of P, whereas the gleyic chernozem strongly retained nearly all solutes; only sulfate passed as a steep peak. After the drying period, phosphate elution was significantly lower (Figure 4).

Ochre precipitates in the run-off as an effect of oxidation of divalent Fe or loss of excess CO_2, have caught substantial amounts of eluted P, and may thus lead to artefacts (Table 7).

From the (alkaline) calcic and gleyic chernozems, the amount of P coprecipitated with Fe/Mn-hydroxides/carbonates after aeration, was appreciably higher than the amount found in the eluates, which surely distorts the results. From the (acid) haplic chernozem, coprecipitation of phosphate after aeration was much lower, thus indicating a pH-effect. Mobilization of phosphate caught in the precipitate cannot be assigned to a certain pore volume. It just gives an indication about fixation of already mobilized P on aeration. This has certain implications on the phosphorus cycle. In case, well water or spring water would appear on surface, the formed sinter will scavenge some of the load transported through the soils and subsoils. The composition of this sinter material mainly depends on the soil pH (see also Table 9).

With respect to the amount added, the release of phosphate from the haplic chernozem within the 4–5 pore volumes elution volume was appreciable.

Though the composition of the gleyic and the calcic chernozem samples was similar for many parameters, phosphate retention in the gleyic sample was much more pronounced. This has to be attributed to differences in sorbing phases: the gleyic was higher in clay contents, whereas the calcic had double amount of Fe/Mn oxides (oxalate soluble Fe/Mn), more humics and slightly carbonate. Strikingly, P retention at this slightly alkaline pH at moderate aeration seemed to be stronger at the clay fraction, than at the Fe/Mn oxides.

3.4 Ion exchange phenomena

After addition of the artificially mixed fertilizer solution containing the cations $K/Ca/NH_4$ on top of the soil columns investigated, enough Ca remained in the eluate to move with the water front. Simultaneous liberation of non-added Mg/Sr/Ba/Li/Na yielded elution curves rather similar in shape, which can be explained by ion-exchange. With respect to the area of the peaks obtained after 1 pore volume, haplic chernozem exchanged 3,9–6,0 % of the equivalents added, calcic chernozem exchanged 6–16 %, and gleyic chernozem even 28–45 %, which was not predicted from the cation exchange capacity versus Ba (Table 1). Only for the calcic chernozem, magnesium co-precipitated in the run-off, might influence the ion balance in significant amounts. The equivalent sum of Li + Sr + Ba was only in the range of 1 % of the total, und thus lower than the Mg-equivalents scavenged in the run-off precipitates (Table 8). Discharges of Ba from the column were about constant for

Table 7: P budgets in the column experiments
Tabelle 7: Phosphorbilanzen der Säulenexperimente

Soil type	Originally mg (aqua regia)	Added mg	Eluted mg	Ochre residue mg
Gleyic chernozem	1733 ± 35	175	0,08 ± 0,03	0,85 ± 0,44
Haplic chernozem	1672 ± 16	175	31 ± 8	29 ± 4
Calcic chernozem	3197 ± 27	175	1,2 ± 0,2	5,2 ± 0,5

the three soil types investigated, whereas the discharges for Sr and Li depended on the soil characteristics, but the proportion Sr/Li remained fairly constant.

Table 8: Ion exchange peak area at 1 pore volume of eluate
Tabelle 8: Ionenaustausch-Peakfläche bei 1 Porenvolumen Eluat

Column	meq in the eluate	meq in the residue at the column outlets	% exchanged for K + Ca
Gleyic 1	7,823	0,556	81,1
Gleyic 2	4,859	0,632	53,2
Gleyic 3	7,646	1,443	89,0
Gleyic 4	6,646	0,631	70,4
Haplic 1	0,915	0,269	11,5
Haplic 2	0,776	0,164	9,1
Haplic 3	0,679	0,249	9,0
Haplic 4	1,042	0,086	10,9
Calcic 1	2,863	1,117	38,5
Calcic 2	1,107	0,612	16,6
Calcic 3	–	–	–
Calcic 4	1,283	–	–

In spite of considerable variations of exchanged equivalents among each other, the columns from different soils were still significantly different. In columns Calcic 3 and Calcic 4, the residue was not collected.

3.5 Proportion of Fe/Mn in the eluates

After the addition of the artificial fertilizer solution, appreciable release of Fe took place from the haplic chernozem, whereas it was moderate for the calcic and negligible for the gleyic chernozem samples (see Figure 2; the Y-axis had to be stretched 10-fold for the gleyic and calcic samples).

The Fe/Mn-ratio in the eluates may give insights into redox and phase transformation reactions in the columns. Steady release of Fe and Mn at constant ratio indicates destruction of organic material, and thus a decrease of the number of chelating groups and adsorption sites, and further on, the redox potential is not high enough to enable subsequent precipitations of FeOOH and MnOOH. In case Fe and Mn derive from hydroxide phases, however, at beginning reduction manganese is released first, and Fe afterwards, the ratio thus increases with increasing elution. In the first eluate fractions, the Fe/Mn proportion widely scattered and was rather high, but it stabilized at about half a pore volume after addition of the test solution. The Fe/Mn proportion in the gleyic chernozem was minor 0.5, for the calcic chernozem it was about 1, and for the haplic chernozem it was 2–4, the latter showing a slightly increasing trend (see Figure 3).

3.6 Ochre formation at the column outlet

After 9 months of drying, the soil columns were dismantled und cut into 6 aliquots in order to enable investigations of the respective soil profiles. Compared with the original lengths of the columns of 30 cm of air-dried soil, the cores shrinked to 27 cm length for the gleyic, and to 24 cm for the haplic and calcic chernozem samples. In the depicted soil profiles (figs. 5–9), however, the lenght axis is taken as the original one. The paper filter, which was inserted at the soil bottoms to prevent wash-out of fine particles, was not visible any more, except for the haplic chernozem. The quartz sand cover on top, which should lead to a homogenous distribution of the applied eluents on the entire cross-section,of the columns could be removed easily. The cores were surprisingly compact. Veins of suspended quartz from the top layer were visible from outside, but they were present just on the mantle.

In the bottom plates and the outlets of the funnels, which carried the soil columns, brown precipitates occurred, which were carbonaceous from the calcic and gleyic, and non carbonaceous from the haplic chernozem samples. The funnels were separated from remaining soil material as well as possible, and the brown residues were dissolved with hydrochloric acid on the boiling water bath, made up to 250 ml, and submitted to multi-element analysis. In case, Fe is calculated as FeOOH, manganese as MnOOH, aluminum as $Al(OH)_3$, magnesium as $MgCO_3$, calcium as $CaCO_3$ and phosphorus as P_2O_5 (to allow addition of the weights together with FeOOH und MnOOH), and take the sum of these 6 main elements as 100 % (silicon is lacking; the weight of the traces is negligible), this leads to the results of the composition of the precipitates given in the subsequent Table 9. The precipitate formed on contact with air after exiting the soil column was identified as a Fe/Mn-hydroxide carrying appreciable amounts of phosphate for the (acid) haplic chernozem, and a Ca-carbonate for the (slightly alkaline) calcic and gleyic chernozems. Co-precipitated Al was variable and seemed to be accidental.

These precipitation products can be explained by oxidation of soluble divalent Fe and decline of CO_2 partial pressure on the air. Some of the eluted trace elements are caught in these precipitates, others are not, which could lead to artefacts in the interpretation of the elution curves. For alkali and alkaline earth elements (except Ca), the precipitated quantity in the run-off was, however, marginal.

Precipitations between the end of the soil column and the elution vessels may cause artefacts. Transported loads are

Table 9:   Calculated composition of the brown precipitates in the outlets of the columns
Tabelle 9: Berechnete Zusammensetzung der braunen Niederschläge an den Säulenausläufen

% of precipitate	P1	P2	P3	P4	F1	F2	F3	F4	T1	T2
$Al(OH)_3$	5,3	4,2	8,0	2,9	4,4	3,0	17,4	3,6	7,1	2,6
FeOOH	67,7	69,9	63,4	65,3	7,1	6,5	9,2	6,2	10,9	11,4
MnOOH	3,5	3,5	4,3	4,2	2,6	2,4	1,0	2,0	3,4	3,7
$CaCO_3$	6,5	5,4	7,0	7,4	80,5	83,3	64,9	83,4	75,6	80,3
$MgCO_3$	3,0	1,4	2,2	1,1	5,3	4,7	7,4	4,8	2,9	2,1
P calculated as P_2O_5	14,1	15,6	15,1	9,0	<	<	<	<	<	<
Fe + Mn + Al	76,5	77,6	75,7	72,4	14,1	11,9	27,6	11,8	21,4	17,7
Ca + Mg	9,5	6,8	9,2	8,5	85,8	88	72.3	88,2	78,5	82,4

not recognized as such, if they remain scavenged in the run-off. These observations were done after the end of the column experiments presented. Purging the lower end of the columns with nitrogen might prevent the oxidation of Fe^{2+} in the run-off, but also provoke more anaerobic conditions.

3.7 Mathematical modelling of desorption

For many analytes, a peak after one effective pore volume appeared, due to ion exchange reactions because of the input of fertilizer solution. Then a hyperbolic decline of the analyte concentrations in the eluate was observed. These data can be used to investigate the desorption reaction of solutes in the column design. The experimental data were fitted to suit the hyperbolic equation of Langmuir $Y = A/(B + X)$

Utilization of this Langmuir equation is justified, if all adsorption sites are equal, and if the curves approach a constant value.

X-Axis: sum of ml
Y-Axis: measured concentration of the analyte

The first data point after the ion exchange peak, which was included in the fitted curve is also given in the subsequent Table 10 for Na, and in Table 11 for Mg.

Coefficient A reflects the amplification in the Y-axis (analyte concentration), and is termed the capacity criterion. Coefficient B reflects the shape of the hyperbel, and is termed affinity criterion. Enlarging of B means flattening of the hyperbel.

The results of the fittings show coefficient A presumably to derive from the soil type, and coefficient B presumably to derive from the ion investigated. From this, the capacity criterion increases in the order haplic < calcic < gleyic chernozem, which looks realistic, but again does not correlate with cation exchange capacities (Table 1).

Among the main elements eluted, only the curves Na versus pore volume could be fitted for all samples, and Mg versus pore volume only for the calcic chernozem. Lack of fit for the Mg data for the other soil samples can be recognized from low correlation and scatter of coefficients of the 4 experiments in parallel. The elution data of Sr, Ba, and Li could not be fitted at all, because there eluate concentrations rapidly decline to an approximately constant value.

Table 10:   Fitted curves for Na desorption from the columns
Tabelle 10: Kurvenanpassung für die Na-Desorption aus den Säulen

Column	1. data point (Pore vol.)	A	B	Correlation
F1	1,054	3,6747	-0,5826	0,9865
F2	1,109	4,5860	-0,5495	0,9878
F3	1,407	4,0476	-0,8307	0,9796
F4	1,181	3,6468	-0,6404	0,9631
P1	1,240	0,3192	-0,5814	0,8982
P2	1,373	0,2863	-0,5713	0,9438
P3	1,289	0,2830	-0,6880	0,9487
P4	1,111	0,3551	-0,6352	0,8571
T1	1,207	1,7890	-0,5336	0,9748
T2	1,282	2,2444	-0,2617	0,9432
T3	1,488	1,8910	-0,6104	0,9720
T4	1,351	2,1035	-0,4589	0,9553

Table 11:   Fitted curves for Mg desorption from the columns
Tabelle 11: Kurvenanpassung für die Mg-Desorption aus den Säulen

Column		1. data point (Pore vol.)	A	B	Correlation
F1	Plateau	1,309	200,1	1,864	0,8016
F2		1,386	329,8	3,939	0,7380
F3	Plateau	1,407	128,1	0,173	0,9226
F4		1,567	172,1	2,187	0,8319
P1	Plateau	1,373	8,641	0,760	0,7309
P2		1,512	12,53	3,405	0,7408
P3	Plateau	1,425	7,767	0,396	0,7350
P4		1,383	13,63	2,668	0,7296
T1		1,486	66,61	2,116	0,9599
T2		1,513	69,42	3,169	0,8711
T3		1,488	83,92	4,701	0,9003
T4		1,351	83,15	2,650	0,9183

3.8 Changes of mobile fractions in the soil profile during the column study

The aqua regia extract of the samples before and after the column experiments were not significantly different, because the amount of dissolved solid was too low in most cases. Only for Sr, Na and Mn, lower contents after the elution experiments were notable. Oxalate soluble Fe, however, increased in the calcic and haplic chernozem samples to double amounts, whereas it remained constant in the gleyic chernozem.

Tables 12–14 contain concentrations in the solids obtained before and after the addition/elution experiments by selective leaching, averaged over the entire profile and all 4 soil columns.

After the experiment, added As, Mo, Se and V were rather inhomogenously distributed along the profiles, because the added amounts were fixed in the upper layers. Whereas Mo and Se additions increased both oxalate, NaOH and aqua regia mobile forms, P addition mainly moved to NaOH-mobile forms. V and As additions were noticeable along the profile, but they were compensated by washout from deeper layers.

Oxalate extractable amounts are indicative as bound to Fe-oxides within the soil. In the haplic and calcic chernozem samples, oxalate extractable Fe significantly increased during the column experiment, but strikingly, Co-Ni-Pb-Zn, which should be substantially bound to these oxides, decreased. Release into oxalate was higher for the

haplic chernozem than for the other 2 samples. This reflects the affinity of the respective trace elements towards Fe/Mn oxides, and the abundance of Fe/Mn oxides relative to clays and humics on the other. With respect to aqua regia, the oxalate leachable fraction was highest for Mn, about half for Co and Cu, and rather low for Pb, Cr and Zn.

After the experiment, oxalate-leachable Zn, Cu, and Cr increased from top to bottom after the experiment in the haplic and calcic chernozems, and Ni in the gleyic chernozems, which may indicate a preferable washout from deeper layers, whereas in the gleyic chernozems, oxalate-mobile Zn decreased from top to bottom after the experiment.

The calcic chernozem had been contaminated with Cu some years before, because the field had been used as a wineyard. This is recognized in the oxalate and NaOH extracts, but it did not lead to increased elution in the column experiment.

When the difference of mobile fractions obtained before and afterwards in the soil profiles is taken, the P load from the experiment was seen only in the alkali extract of the haplic, and slightly in the alkali extract of the gleyic chernozem, but there was hardly any change in the other extracts (Figs. 10–12). As the washout is low, P must have gone to very residual fractions. The iron oxides often have a key part in the phosphorus cycle of sediments and soils, but within this experiment, P added on top of the soil columns moved to a non-oxalate-mobile fraction. In case anaerobic conditions would have occurred, P would have been released from Fe-oxides (= oxalate soluble fraction),

Table 12:　Concentration changes in the gleyic chernozem
Tabelle 12:　Konzentrationsänderungen in der Feuchtschwarzerde

mg/kg	oxalate pH 3 Before	oxalate pH 3 After	1 M NaOH Before	1 M NaOH After	aqua regia Before	aqua regia After
As	1,91 ± 0,41	1,91 ± 0,38	1,82 ± 0,28	1,83 ± 0,18	5,83 ± 0,45	5,08 ±0,25
B		2,19 ± 0,38	X	X	X	X
Ca	X	X	208 ± 22	191 ± 30	10500 ± 700	9697 ± 348
Cd		0,008 ± 0,007	0,043 ± 0,013	0,041 ± 0,025	X	0,066 ± 0,065
Co	2,1 ± 0,3	2,33 ± 0,41	X	X	6,1 ± 0,1	6,9 ± 0,9
Cr	1,0 ± 0,3	1,15 ± 0,22	0,49 ± 0,06	0,78 ± 0,06	28,9 ± 0,5	27,9 ± 2,2
Cu	9,0 ± 1,4	8,4 ± 1,4	5,5 ± 0,7	7,9 ±0,3	16,5 ± 1,7	18,0 ± 1,5
Fe	1177 ± 90	1178 ± 99	7,0 ± 2,5	8,3 ± 3,4	17100 ± 150	17530 ± 1111
Li	X	X	X	X	6,4 ± 0,2	10,7 ± 2,8
Mn	X	302 ± 50	0,09 ±0,03	0,21 ± 0,17	447 ± 50	412 ± 48
Mo	<	0,29 ± 0,17	0,02	0,22 ± 0,13	0,18 ± 0,05	0,43 ± 0,13
Ni	4,4 ± 0,2	5,0 ± 1,3	X	X	37,7 ± 0,1	20,5 ± 1,8
P	84,0 ± 10,5	85,4 ± 12,3	18,1 ± 6,4	31,1 ± 13,5	470 ± 111	517 ± 105
Pb	0,4 ± 0,1	0,5 ± 0,1	X	X	11,2 ± 1,3	10,2 ± 2,0
S	X	X	3,90 ± 0,85	4,08 ± 1,1	X	X
Se	0,0063 ± 0,0008	0,025 ± 0,015	0,068 ± 0,011	0,106 ± 0,054	0,164 ± 0,058	0,221 ± 0,086
V	8,43 ± 0,27	7,96 ±1,30	X	X	30,3 ±0,6	27,6 ± 1,1
Zn	4,6 ± 0,8	3,4 ± 1,0	17,7 ± 2,0	3,3 ± 1,3	45,8 ± 2,4	43,7 ± 3,9

Table 13:   Concentration changes in the haplic chernozem
Tabelle 13: Konzentrationsänderungen im Paratschernosem

Mg/kg	oxalate pH 3 Before	oxalate pH 3 After	1 M NaOH Before	1 M NaOH After	aqua regia Before	aqua regia After
As	1,02 ± 0,01	1,10 ± 0,15	0,69 ± 0,58	1,03 ± 0,18	2,48 ± 0,06	2,21 ± 0,09
B	X	0,15 ± 0,15	X	X	X	X
Ca	X	X	107 ± 56	77 ± 19	390 ± 35	778 ± 46
Cd	X	0,029 ± 0,007	0,034 ± 0,008	0,053 ± 0,017		0,096 ± 0,091
Co	2,0 ± 0,1	1,16 ± 0,10	X	X	3,0 ± 0,2	3,1 ± 0,3
Cr	1,0 ± 0,2	0,77 ± 0,12	0,87 ± 0,10	0,97 ± 0,19	10,9 ± 0,6	10,1 ± 1,1
Cu	3,3 ± 0,3	3,0 ± 0,6	5,1 ± 0,5	5,8 ± 1,2	23,1 ± 0,8	8,1 ± 0,4
Fe	1058 ± 14	1696 ± 208	55 ± 4	51 ± 17	6890 ± 190	7095 ± 221
Li	X	X	X	X	1,8 ± 0,1	2,9 ± 0,4
Mn	X	X	2,1 ± 0,2	2,6 ± 0,7	257 ± 5	217 ± 18
Mo	0,011 ± 0,003	0,19 ± 0,22	0,10 ± 0,03	0,24 ± 0,26	0,10 ± 0,03	0,29 ± 0,32
Ni	1,8 ± 0,1	1,2 ± 0,2	X	X	5,7 ± 0,2	7,4 ± 0,7
P	90,7 ± 1,5	97,8 ± 10,0	165 ± 5	223 ± 19	370 ± 8	451 ± 31
Pb	2,8 ± 0,3	1,9 ± 0,3	X	X	11,9 ± 0,8	6,6 ± 1,7
S	X	X	4,27 ± 0,17	4,26 ± 0,43	X	X
Se	0,0053 ± 0,0022	0,014 ± 0,018	0,032 ± 0,019	0,067 ± 0,052	0,080 ± 0,011	0,122 ± 0,084
V	3,06 ± 0,05	2,68 ± 0,56	X	X	10,8 ± 0,4	10,6 ± 0,7
Zn	3,2 ± 0,1	2,60 ± 0,44	20,0 ± 5,7	18,1 ± 5,0	20,3 ± 0,6	20,8 ± 1,6

Table 14:   Concentration changes in the calcic chernozem
Tabelle 14: Konzentrationsänderungen im Tiefgründigem Tschernosem

mg/kg	oxalate pH 3 Before	oxalate pH 3 After	1 M NaOH Before	1 M NaOH After	Aqua regia Before	Aqua regia After
As	2,05 ± 0,09	2,27 ± 0,44	1,25 ± 0,29	1,57 ± 0,33	9,02 ± 0,75	7,04 ± 0,33
B	X	2,40 ± 0,44	X	X	X	X
Ca	X	X	274 ± 27	299 ± 50	12570 ± 640	X
Cd	X	<	0,050 ± 0,007	0,055 ± 0,019	X	
Co	4,4 ± 0,1	2,93 ± 0,56	X	X	8,2 ± 0,1	9,8 ± 0,8
Cr	2,2 ± 0,3	1,60 ± 0,29	0,57 ± 0,10	0,68 ± 0,21	33,9 ± 0,1	37,0 ± 0,7
Cu	37,6 ± 1,3	35,8 ± 4,2	20,6 ± 1,8	18,5 ± 3,1	61,8 ± 0,2	67,7 ± 2,2
Fe	1375 ± 38	2690 ± 692	12,6 ± 0,8	12,5 ± 2,7	20300 ± 60	X
Li	X	X	X	X	7,6 ± 0,2	12,6 ± 0,3
Mn	X	X	0,46 ± 0,08	0,24 ± 0,18	579 ± 3	581 ± 30
Mo	<	0,32 ± 0,14	0,22 ± 0,03	0,35 ± 0,06	0,44 ± 0,04	0,71 ± 0,19
Ni	6,1 ± 0,1	4,4 ± 0,8	X	X	43,2 ± 1,0	28,2 ± 1,3
P	130 ± 2	139 ± 11	42,2 ± 2,9	48,5 ± 8,1	813 ± 18	
Pb	0,6 ± 0,1	0,5 ± 0,1	X	X	15,3 ± 0,5	14,5 ± 1,9
S	X	X	7,74 ± 0,49	7,21 ± 1,04	X	X
Se	0,014 ± 0,004	0,015 ± 0,013	0,081 ± 0,025	0,108 ± 0,056	0,236 ± 0,019	0,237 ± 0,080
V	10,6 ± 0,3	9,0 ± 1,7	X	X	37,6 ± 2,5	37,9 ± 1,2
Zn	5,5 ± 0,2	4,1 ± 0,7	14,8 ± 3,5	14,5 ± 7,8	56,9 ± 0,4	57,1 ± 0,9

but as this fraction remains rather constant throughout the profile, no redox gradient was superimposed.

NaOH mobile fractions indicate humic bound amounts, or anions exchangeable versus OH-, unless they are reprecipitated again (e.g. as $AlPO_4$, see PSENNER et al., 1984). No organic compound was added, nor there was photosynthesis, thus degradation and washout of humics was expected, resulting in a decrease in alkali soluble fractions: this was clearly not the case. Though alkali mobility varied between the soil types investigated, the added anions P and Mo tended towards increased alkali mobility (no data about vanadium in NaOH). In the calcic chernozem, added Mo was also oxalate-mobile, thus it aimed at different targets. Speciations of sorbed As, Se and S have been treated elsewhere (SAGER, 2002b).

Among non-added species, Cu and Zn were appreciably alkali mobile as well.

Table 15: Median concentrations of eluates obtained from the columns after the ion exchange peak versus concentrations in the water extract from the original samples

Tabelle 15: Mediankonzentrationen in den Eluaten nach dem Ionenaustauschpeak im Vergleich mit dem Wasserextrakt der Originale

|		Gleyic chernozem					Haplic chernozem					Calcic chernozem				
		From columns				Water extract H$_2$O	From columns				Water extract	From columns				Water extract
Al	µg/l	28	63	18	36	**173**	223	277	375	2066	1,1	48	30	68	28	0,3
Ba	mg/l	0,058	0,061	0,055	0,040	0,041	0,028	0,020	0,019	0,035	0,042	0,082	0,111	0,105	0,083	0,058
Be	µg/l	0,06	0,09	0,05	0,07	< 0,04	0,10	0,11	0,14	0,11	< 0,04	0,08	0,09	0,07	0,069	< 0,04
Ca	mg/l	87,8	95,0	74,4	78,2	26,8	18,1	14,3	15,8	16,1	7,5	168,8	145,3	143,0	164,7	32,3
Cd	µg/l	0,9	1,5	0,8	1,1	< 0,4	1,0	1,1	2,0	1,2	< 0,4	1,24	1,24	1,04	1,79	< 0,4
Co	µg/l	2,2	1,1	0,8	2,5	< 0,3	69,0	56,0	58,5	43,1	< 0,3	5,75	7,13	5,57	5,49	< 0,3
Cr	µg/l	0,5	1,1	1,4	0,9	< 0,5	1,3	1,7	2,0	4,9	< 0,5	0,77	2,95	0,57	1,43	< 0,5
Cu	µg/l	5,28	6,80	3,32	3,30	< 0,6	5,73	6,14	11,17	14,65	< 0,6	23,43	7,87	18,96	6,05	< 0,6
Fe	mg/l	0,62	0,56	0,08	0,79	0,030	23,0	16,2	14,9	10,1	0,37	4,16	3,95	1,71	3,82	0,08
K	mg/l	0,74	0,95	0,66	0,44	3,54	15,1	15,7	14,2	22,1	1,7	19,3	29,3	20,7	19,3	4,1
Li	µg/l	0,013	0,010	0,011	0,009	0,004	0,002	0,002	0,002	0,006	0,008	0,003	0,005	0,003	0,003	0,0027
Mg	mg/l	41,8	46,6	34,4	31,1	7,86	2,21	1,84	2,07	2,28	3,58	13,15	11,48	10,42	14,38	2,92
Mn	µg/l	2073	1213	449	1778	28	9389	7289	7236	6070	259	4590	4230	4638	4476	17
Na	mg/l	1,25	1,44	1,16	1,40	2,33	0,13	0,12	0,11	0,16	1,22	0,68	0,79	0,75	0,82	1,66
Ni	µg/l	13,4	11,1	9,5	12,4	< 5	65,95	57,13	65,78	51,22	<	13,22	15,03	17,44	13,23	<
Pb	µg/l		4,2	11,8	3,8	< 3	6,45	5,45	6,00	8,62	<	5,81	4,75	7,34	3,61	<
S	mg/l	1,17	1,90	1,06	0,79	0,76	0,50	0,52	0,52	0,62	0,50	0,67	1,30	0,85	0,68	1,09
Sr	µg/l	0,539	0,625	0,458	0,416	0,104	0,069	0,052	0,057	0,060	0,030	0,358	0,349	0,316	0,375	0,064
Zn	µg/l	2,3	2,1	2,0	2,1	<	8,2	6,1	5,9	12,7	<	2,8	2,8	3,0	2,5	<
Added trace elements																
As	µg/l	9,5	8,0	4,4	10,8	< 6	30,8	34,7	28,5	27,2	<	10,8	12,6	15,1	13,6	<
B	µg/l	699	646	651	545	54	221	208	189	157	51	135	282	252	84	39
K	mg/l	0,74	0,95	0,66	0,44	3,54	15,13	15,66	14,16	22,11	1,67	19,30	29,30	20,73	19,26	4,12
Mo	µg/l	3,1	5,0	1,5	4,4	< 0,9	6,5	5,7	13,5	3,1	<	15,1	3,8	28,1	7,5	<
P	mg/l	0,022	0,026	0,038	0,033	0,14	7,27	9,98	4,82	10,32	2,02	0,24	0,25	0,18	0,22	0,88
V	µg/l	2,4	1,7	3,0	1,2	9,13	2,2	3,1	2,8	7,4	1,3	1,3	1,3	2,8	1,4	9,9
Se	µg/l	1,56	0,86	1,81	0,97	<	1,76	1,94	1,79	1,83	<	1,01	0,88	1,16	0,99	<
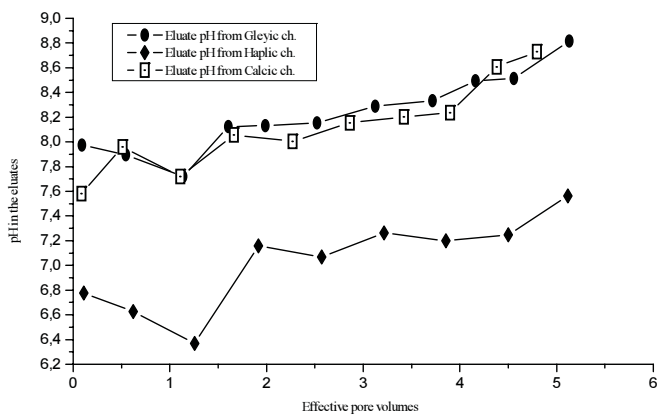
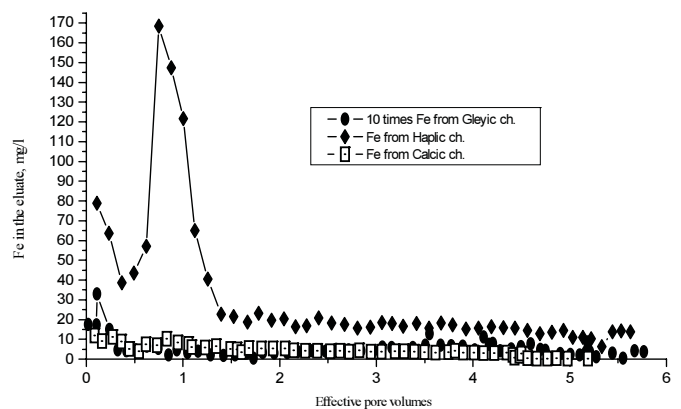Figure 1: pH in the eluates
Abbildung 1: pH in den Eluaten

Figure 2: Iron in the eluates
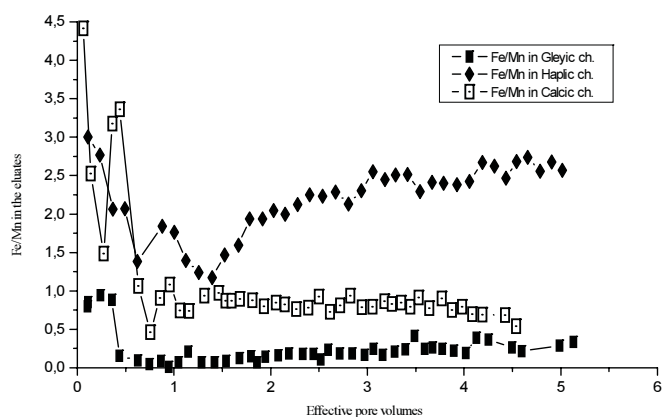Abbildung 2: Eisen in den Eluaten

Figure 3:   Fe/Mn proportions in the eluates
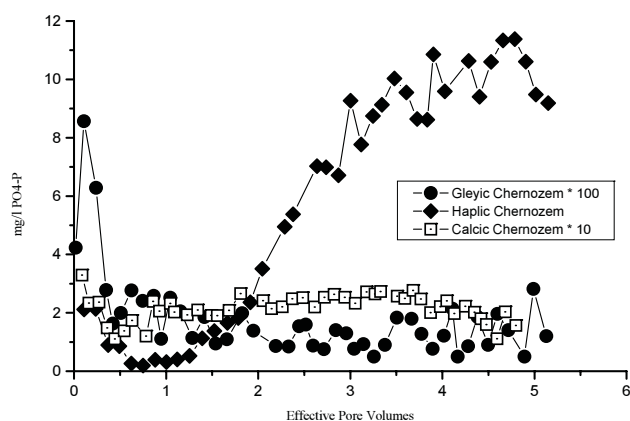Abbildung 3: Fe/Mn-Verhältnis in den Eluaten

Figure 4:   Phosphate in the eluates
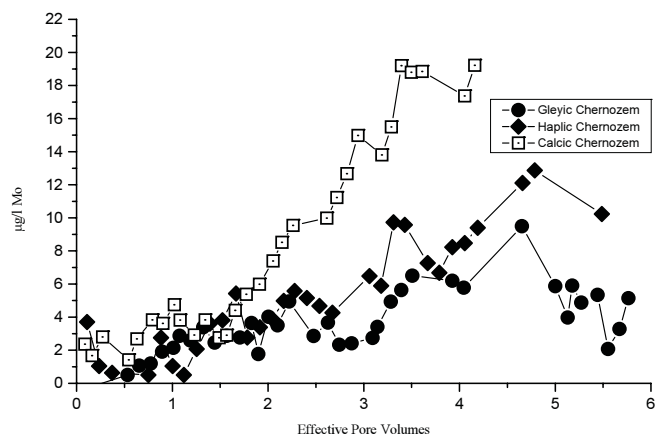Abbildung 4: Phosphat in den Eluaten

Figure 5:   Molybdenum in the eluates
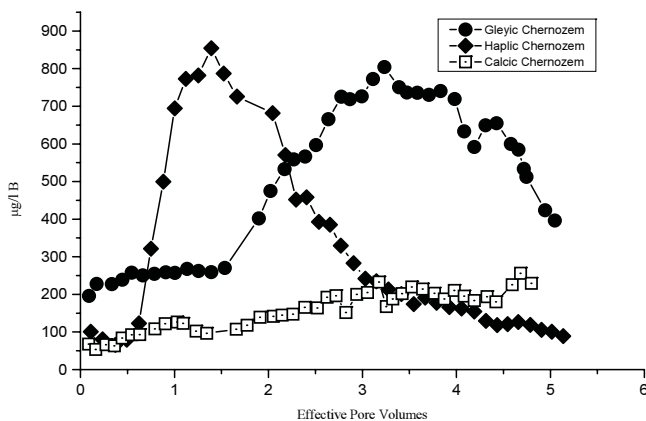Abbildung 5: Molybdän in den Eluaten

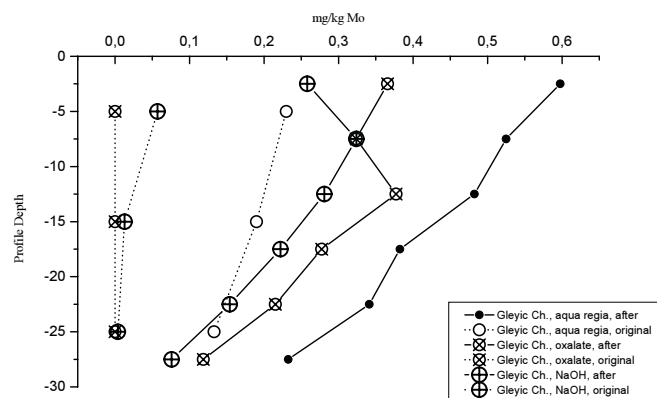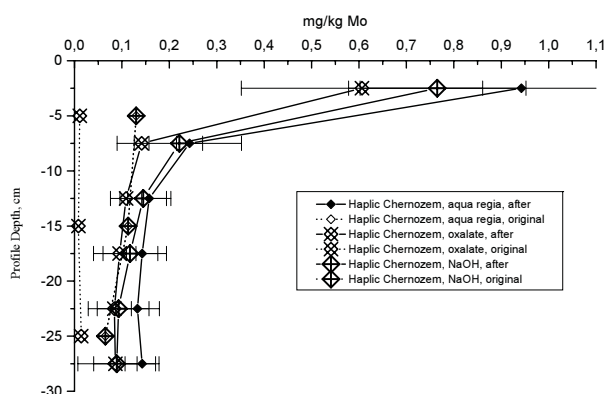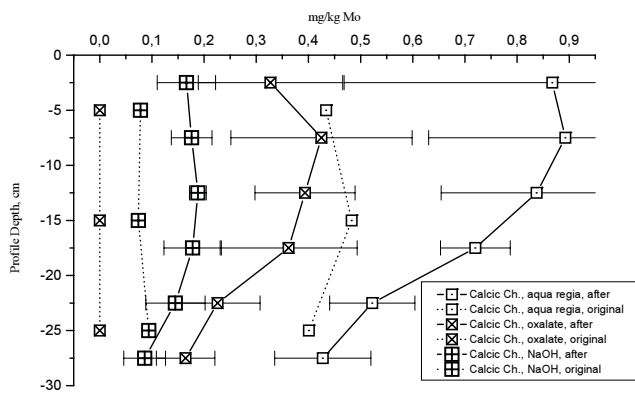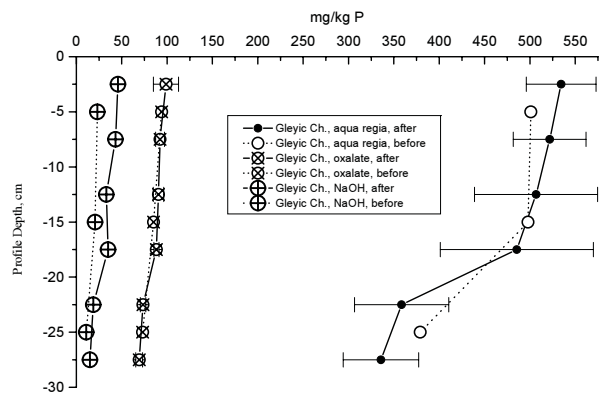Figure 6:   Boron in the eluates
Abbildung 6: Bor in den Eluaten

Figure 7:   Changes in Mo concentrations within the gleyic cherno-
               zem soil profile in various extracts
Abbildung 7: Veränderungen der Mo-Konzentrationen im Feucht-
               schwarzerdeprofil mit unterschiedlichen Extrakten
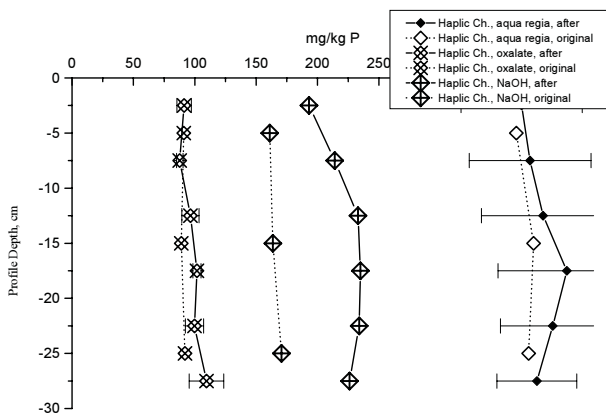

Figure 8:   Changes in Mo concentrations within the haplic cherno-
               zem soil profile in various extracts
Abbildung 8: Veränderungen der Mo-Konzentrationen im Paratscher-
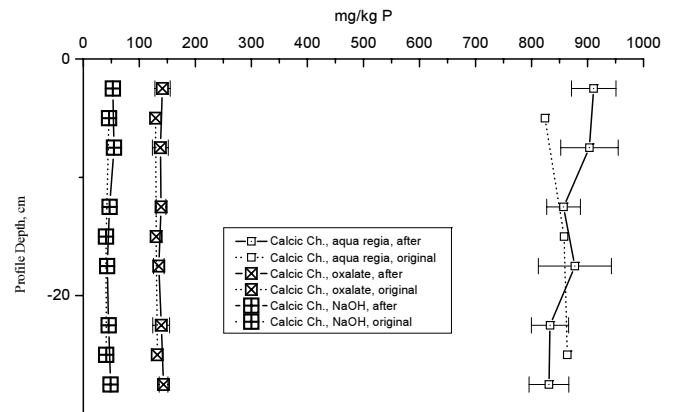   nosemprofil mit unterschiedlichen Extrakten

Figure 9:   Changes in Mo concentrations within the calcic cherno-zem soil profile in various extracts

Abbildung 9: Veränderungen der Mo-Konzentration im Profil tiefgründiger Tschernozems mit unterschiedlichen Extrakten

Figure 10:   Changes in P concentrations within the gleyic cherno-zem soil profile in various extracts

Abbildung 10: Veränderungen der P-Konzentrationen im Feucht-schwarzerdeprofil mit unterschiedlichen Extrakten

Figure 11:   Changes in P concentrations within the haplic cherno-zem soil profile in various extracts

Abbildung 11: Veränderungen der P-Konzentrationen im Paratscher-nozemprofil mit unterschiedlichen Extrakten

Figure 12:   Changes in P concentrations within the calcic cherno-zem soil profile in various extracts

Abbildung 12: Veränderungen der P-Konzentrationen im Profil tiefgründigen Tschernozems mit unterschiedlichen Extrakten

4. Conclusions

Model soil columns without plant cover can be operated to investigate the vertical migration of added solutes with a precision of about ± 10 %, unless ochre formation occurs. Contrary to steady state flow conditions, 6 liters of water (= the annual precipitation) were applied discontinously upon 125 cm^2 area within 2 months, yielding more realistic conditions, and aerobic conditions; no sulfides were formed. Much rain and no plant cover might favour vertical migration, but all added species (K, P; Mo, V, As, Se) were largely retained, except borate. The anions phosphate, arsenate, vanadate and molybdate were predicted to be moderately mobile. The release of alkali, alkaline earths, Fe,

Mn and S was higher than predicted from the water extracts, whereas release of K and P was lower, but these differences varied between soil types. Also, pH of the eluates were higher than the pH obtained from the standard CaCl$_2$ procedure. Thus, groundwater composition formed from arable soils seems hardly predictable from standard water extracts and standard pH. When time scales of some months are taken into account, uptake of added P and K by soil biota, as well as degradation of humics and sulfate release take place, which is not the case during 2 hours of batch extraction with water. Bio-processes have a lag phase, a phase of increase, and a saturation phase, depending on available nutrients, which can clearly not easily be modelled by physical concepts.

The addition of fertilizer salt pulse led to a pulse of exchangeable cations into the eluate, like Mg-Sr-Ba-Li-Na. The amount of this ion exchange between the 3 soil types was significantly different, and did not correlate with the standard cation exchange capacity versus Ba. After this ion exchange peak, most eluate concentrations approached a constant value which was higher in most cases than the water extracts from the original samples; just Na, as well as K-P-V from the haplic chernozem were lower. Na-desorption could be reproducibly fitted by Langmuir desorption, and is thus a physical phenomenon, whereas others were released from originally less-soluble fractions. As a result, the water extract obviously under-estimates the release into the ground water in most cases, depending on the soil type.

Ochre formations in the column outlet scavenged mainly Cr-Al-Pb-P-V-Fe-Zn from the eluates (data not given), but had negligible influence on the mobility of borate. This would also happen within wells, when seepage water enters the surface again. Ochre from the acid soil was mainly Fe-oxide, whereas from the weakly alkaline soils, it was mainly $CaCO_3$.

After dismantling of the cores, selective leaching may be a valuable tool to indicate speciation changes, when the results are compared with data from the original samples, and the conditions of remobilization. Selective leaching was done to estimate the roles of humics (1 M NaOH extract) and pedogenic oxides (oxalate buffer pH 3) in the adsorption and transport along the cores during the experiment. Extracts with oxalate buffer pH 3 revealed the formation of Fe oxides in the gleyic and calcic chernozem samples during the experiment, whereas oxalate extractable non-added trace elements tended to decrease. In the haplic chernozems, conditions with respect to oxalate leach remained rather constant.

Though no organic compounds were added nor formed by photosynthesis, alkali mobile fractions tended to be higher after the experiment than before, in particular from the added anions. In batch experiments, anions should exert maximum mobility at pH 9, and are scavenged at Fe-oxides under weak acid conditions, which is about the case for Mo, but clearly not for P. As a conclusion, the remobilisation conditions of added anions depend on the soil type and soil life, degradation of humics and formation of new phases, and did not match all predictions from short time shakings.

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