

Vertical mobility of Selenium, Arsenic and Sulfur in Model Soil Columns

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Vertikale Mobilität von Selen, Arsen und Schwefel in Modellbodensäulen

1. Introduction

In Europe, low selenium levels in soils and human nutrition has led to discussions about the need of additional fertilization of soils with selenium, e.g. as easily soluble sodium sele-

nate. In order to judge transfer to green plants and losses to the groundwater from agricultural soils, background levels, as well as pathways of input from atmospheric deposition, fertilization and irrigation water, as well as vertical mobility in the soil column, have to be considered.

Zusammenfassung

In Europa ist das Vorkommen von Selen in Böden, Erntegut und Grundwässern ziemlich niedrig, könnte aber durch Gabe organischer Düngemittel oder selenhaltiger Mineraldünger erhöht werden. Zum Vergleich wurde Selen zusammen mit Arsen und Schwefel untersucht, die ähnliche Eigenschaften aufweisen, und einander konkurrieren könnten. Um Mobilitäten und mögliche Verluste in das Grundwasser vorherzusagen, wurden Oberschichten von Schwarzerden (Paratschernosem, Feuchtschwarzerde und Tiefgründiger Tschernosem) aus dem Osten Österreichs in je 4 Säulen gepackt, um die höchstmögliche Beweglichkeit von als Düngemittel aufgegebenem Selen, Arsen und Schwefel durch Auswaschen mit dem natürlichen Regen zu untersuchen. Die Säulen enthielten etwa 5 kg Boden bei 30 cm Säulenlänge, und erhielten den Jahresniederschlag innerhalb von 2 Monaten. Sie wurden im Dunklen bei Zimmertemperatur ohne höhere Pflanzen und Algen gehalten, um möglichst hohe vertikale Mobilität zu erzielen. Die potentiell anionischen, aber doch metabolisierbaren Elemente Schwefel (als Sulfat), Selen (als Selenit) und Arsen (als Arsenat) wurden mit einer NPK Düngergelösung zugefügt. Die Eluate von den Säulen wurden auf den Totalgehalt der darin gelösten Stoffe analysiert. Zur Bestimmung von Gesamtselen mußten Teile der Eluate mit Magnesiumnitrat verascht werden. In einem Vorlauf wurde das effektive Porenvolumen für jede Säule über das Durchlaufen von Chlorid, gegeben als KCl, bestimmt. Nach 1 Porenvolumen, traten steile Spitzen von gelöstem Schwefel in allen Eluaten auf, die 2–3 mal höher als die aufgegebene Menge waren, möglicherweise wegen Ionenaustausch und Schwefelmineralisation. Nur aus dem Paratschernosem trat auch etwas Selen bei einem Porenvolumen aus den Säulen aus, wie beim Schwefel. Selen wurde ansonsten stark zurückgehalten und konstant in einer nicht-vierwertigen Form ausgewaschen. Gesamt-Arsen begann mit dem Auswaschen nach 2 Porenvolumina und blieb in seiner Mobilität im Vergleich mit den Gesamtmengen in der Bodensäule auf konstant niedrigem Niveau. Nach einer Trocknungsperiode von 6 Wochen und Wiederbenetzen der Säulen, wurde die Schwefel-Freisetzung in allen Fällen beschleunigt, aber eine Freisetzung von Selen erfolgte nur aus der Feuchtschwarzerde. Innerhalb des Bodenprofils wurde das aufgegebene Selenit vorwiegend in den obersten Schichten sowohl im Königswasserextrakt, Oxalateextrakt und Natronlaugeextrakt erhalten, wobei es nach unten mit verschiedenen Geschwindigkeiten abhängig vom Bodentyp wanderte.

Im Hinblick auf Arsen führte das Zugabe-Auswasch-Experiment zu einem Anstieg von alkali-freisetzbarem Arsen aus dem Paratschernosem und der Feuchtschwarzerde. Bei der Feuchtschwarzerde trat außerdem ein Maximum an oxalat-löslichem Arsen in der Säulenmitte auf. Die Menge an zugefügtem Arsen schien geringer zu sein als der Wechsel der Bindungsformen während des Experiments.

Das signifikante Auswaschen von Schwefel, welches in allen Fällen stattfand, war in der NaOH-löslichen Fraktion nur beim tiefgründigen Tschernosem sichtbar, während die Freisetzung bei den anderen Proben offensichtlich aus anderen Bodenfraktionen erfolgte.

Schlagnworte: Selen, Arsen, Schwefel, Düngung, Auswaschung.

Summary

In Europe, Se occurrence in soils, crops and groundwater is rather low, but it may be enriched from fertilization with organic amendments or selenium containing mineral fertilizers. For reasons of comparison, Se was treated together with arsenic and sulfur, which may exert similar properties, and compete each other. In order to predict mobilities and possible losses to the groundwater, chernozem topsoils (haplic, gleyic, and calcic) from the East of Austria were packed into 4 columns each, in order to investigate the maximum mobility of Se, As and S, added as fertilizer components, due to elution with natural rainfall. The columns contained about 5 kg soil within 30 cm column length, and received the annual precipitation within 2 months. They were kept in the dark at room temperature without green plants and algae to achieve maximum vertical mobility. Potentially anionic but nevertheless metabolizable elements sulfur (as sulfate), selenium (as selenite) and arsenic (as arsenate) were added to an NPK fertilizer matrix. The eluates from the columns were analyzed for total contents of dissolved species. For total selenium, aliquots of the eluate had to be ashed with magnesium nitrate. Within a pre-run, the effective pore volume of each column was determined from the passage of chloride, added as KCl. After 1 pore volume, steep peaks of dissolved sulfur appeared in all eluates which were 2–3 times larger than the added amounts, possibly due to ion-exchange and sulfur mineralization. Only in the haplic chernozem, some selenium passed the columns at one pore volume, similar to sulfur. Selenium was strongly retarded and rather constantly eluted in a non-quadrivalent form. Total arsenic started to elute after 2 pore volumes and remained at constant low levels in amounts negligible with respect to the total contents in the column.

After a drying period of 6 weeks, and re-wetting the columns, sulfur release was enhanced in all cases, but selenium released only from the gleyic chernozem. Within the soil profile, the added selenite preferably was seen in the top layers, both in aqua regia, oxalate and NaOH leachable fractions, and migrated down at different speeds depending on the soil type.

With respect to arsenic, the addition-elution experiment led to an increase in NaOH-releasable arsenic from the haplic and gleyic samples. For the gleyic chernozem, a maximum of oxalate soluble As appeared in the middle of the columns. Speciation changes during the experiment seemed to be larger than the added amounts.

The significant washout of sulfur, which occurred in all cases, was clearly visible in the NaOH soluble fraction only for the calcic chernozem, whereas the release from the other samples derived from other soil fractions.

Key words: Selenium, arsenic, sulfur, fertilization, elution.

Ecological cycling of selenium, arsenic and sulfur shows a lot of parallels. In soils, these elements are bound in various oxidation states, they occur mainly in anionic forms, and can easily form covalent compounds with organics in the soil. They are introduced to the soil by precipitation and fertilization. Many transfer reactions can be promoted by microbial activities, including volatilization losses. Under reducing conditions, pyrite and other sulfides act as a sink.

Toxicity and essentiality have been widely discussed by many authors (e.g. SAGER, 1993).

1.1 Selenium

1.1.1 Occurrence and essentiality

Like in other parts of Central and Northern Europe, selenium background values (aqua regia) in air-dried agricul-

tural soils of Eastern Austria are rather low and independent from the geological unit (Table 1).

Besides the soil itself, groundwater and irrigation water contents influence the Se-level in edible crops.

In groundwaters of the Moldavian Basin, the Carpathian

Table 1: Occurrence of selenium in soils
Tabelle 1: Vorkommen von Selen in Böden

Geological unit	Sample number	Median mg/kg Se
Postglacial sediments	173	0,30
Glacial sediments	179	0,25
Loess	280	0,21
Molasse	78	0,26
Flysch	94	0,30
Limestone of Northern Alpine Zone	80	0,31
Schists and gneisses of Bohemian Crystalline	102	0,23
Granites of Bohemian Crystalline	113	0,16

Basin and the Fergana Basin total Se occurred largely within the range 0.1–1 µg/l. The contents of sulfidic waters were not significantly different, but increasing redox potential lowered soluble Se, presumably because of coprecipitation with Fe-hydroxide (KRAINOV et al., 1983). In Italian thermal waters, Se was in the range < 0.002–0.11 µg/l (median < 0.002), and in Italian river waters < 0.002–0.17 µg/l (median 0.02) (DALL'AGLIO et al., 1978). Contrary to this, Se in groundwater supplies in Southern Nigeria was found to be in the range 2,33–22,4 (mean 7,1) µg/l (ASUBIOJO et al., 1997).

1.1.2 Input to the soil by fertilization

In order to promote optimum growth and resistance to various illnesses, selenium as sodium selenite is added to commercial animal feedstuffs up to a total content of 0,5 µg/g. Excess of the selenium is excreted, and thus leads to enhanced selenium levels in manure and in sewage sludges. Organic amendments thus cover a wide and still unpredictable source of selenium enrichment for agricultural soils, and selenium speciation in these matrices is still an interesting subject of investigation. Table 2 shows some data obtained from investigations in our laboratory within the last 4 years.

Table 2: Selenium in organic amendments
Tabelle 2: Selen in organischen Düngemitteln

	Range mg/kg d.w.	Median mg/kg d.w.	Number of samples
Solid manure from pigs	1,08–7,7	3,09	25
Liquid manure from pigs	1,16–1,41	1,31	4
Poultry Dung	0,54–1,78	1,33	6
Liquid manure from fattening cattle	0,12–0,13	0,125	2
Liquid manure from dairy cows	0,804–0,864	0,825	2
Manure after biogas production	0,74	0,74	1
Sewage sludge airdried	0,33–10,8	1,25	16

The manure samples were dried in presence of $Mg(NO_3)_2$ and subsequently ashed in the muffle furnace. The sewage sludge samples were dried without additives, and decomposed with aqua regia.

The transfer of selenium to the edible parts of cereals seems to be independent from selenium contents of the sub-

strate at low levels, but increases in case selenium is added as selenate together with an NPK-fertilizer. The concentration of selenium in plants from selenate-treated pots was higher than for selenite treated pots (SINGH et al., 1981).

Organic Se from Se-accumulating plant material and inorganic Se were readily available for the uptake by many plants. Plants have been shown to actively absorb several amino acids, like methionine, and presumably Se-methionine. Competition between sulfate and selenate can reduce the selenate uptake (ABRAMS et al., 1990).

1.1.3 Batch experiment investigations on selenium mobility in soils

Selenite is strongly adsorbed on the soil matrix (ABRAMS et al., 1990). Na_2SeO_4 solution was purified from selenite traces by shaking with kaolinite 4h at pH 7,5 (ALEMI et al., 1991).

1.1.3.1 Adsorption studies

For **batch adsorption** experiments of selenite, 2 g of sandy loam topsoil sieved to grain sizes minor 1mm, containing 7 % clay size fraction and 0,64 % organic carbon, was shaken with 10 ml 0,05M NaCl for 48 hours. The adsorption could be fitted by Freundlich equations $S = K.C^n$, with $0,69 < n < 0,73$. Sterilization reduced selenite adsorption, and addition of gluten and manure increased adsorbed selenite concentration appreciably in the sterilized soil. The composted dairy manure had 28,9 % carbon and 3,2 % nitrogen, and was added at 2,4 %. The gluten was a purified protein of 51,2 % C and 14,7 % N, and was added at 0,05 % (GUO et al., 1999).

Selenite adsorption upon L-, O-, and A-horizons of wood soils followed Freundlich equation. 2,5 g soil was shaken with 50 ml 0,003M $CaCl_2$ containing selenite, for 72 hours. Microbial life was stopped by addition of some drops of toluene. The intercept (of the equation in logarithmic form) as a measurement of sorption capacity correlated positively with pH and total nitrogen, and negatively with the C/N proportion. Correlation between actual and predicted selenite adsorption revealed no connection with organic substance and oxalate extractable Fe and Al. In parallel, 10 g of the same samples were percolated with 100 ml 0,003M $CaCl_2$ containing selenite, and microbial life was maintained. Much more Se was adsorbed on the soil, and no volatile selenium compounds were detected (WILKE, 1985).

Selenium sorption on kaolinite and montmorillonite decreased from pH 4 to pH 8. Hydroxyl ions were more effective in modifying the anions' adsorption capacity than competing with selenium on common adsorption sites. 0,4 g clay were shaken with 35 ml 0,005M CaCl₂ solution for 3 hours, the pH was adjusted, the sample was equilibrated for 24 hours, and finally selenium was added. After centrifugation, selenite and selenate were determined in the supernatant. At any pH, selenite adsorption exceeded that of selenate. Within pH 4,5-8, sorption almost linearly decreased. Selenite sorption on Ca-kaolinite at pH 6,2 and +390 mV was completed after 35 hours, and was 95 %. (BAR YOSEF and MEEK, 1987). Selenite adsorption on 5 alluvial soils from 0,05 M NaCl solution under N₂ decreased uniformly with increasing pH in the range 4-9, and was independent from the soil series at pH above 6 (NEAL et al., 1987).

Soil samples collected from 0-15 cm, pH range 7,6-10,1, organic carbon range 0,32-0,92 %, and clay range 8,8-18,4 %, were treated for 72 hours with selenite or selenate solutions. Adsorption decreased in the order high organic carbon soil > calcareous soil > normal soil > saline soil > alkali soil. Selenite sorption was much higher in all cases than selenate. The high organic carbon soil had the same clay content as the normal soil, but caused much higher adsorption. The saline soil had higher salts and similar cation exchange capacity, but showed lower adsorption. The alkaline soil showed lowest adsorption due to its high pH (SINGH et al., 1981).

1.1.3.2 Water soluble and ion exchangeable fractions

From soils, the "soluble" fraction was obtained by boiling 25 ml of soil in 100 ml of H₂O for 30 min. The extract was filtered, and ashed with magnesium nitrate (YLÄRANTA, 1982).

More than 98 % of soluble Se was Se(VI), except for the most leached site, at a site irrigated with low Se and low salinity water for 40 years (FIO and FUJII, 1990).

Soils were extracted for "soluble selenium compounds" by H₂O or Na₂SO₄ solution for 30 min at the boiling water bath. Na₂SO₄ solution may extract more selenium, depending on the soil type. Adsorbed selenite was not regained in the hot water extract. The dissolved selenium-species in the soil extracts were separated by gel permeation chromatography on Sephadex G25, due to their molecular weight. From an andosol, a high-molecular fraction of M = 3200 was identified, which was composed of 29 amino acids (YAMADA and HATTORI, 1989).

Desorption of selenite and selenate, freshly adsorbed at alkaline soils, was investigated in presence of 16 mg sulfate sulfur, or 15,5 mg phosphate phosphorus per gram of soil. Desorption by sulfate and phosphate was not completed in any case. Sulfate and phosphate were equally effective in normal, calcareous and alkali soils, but in organic soil, phosphate was more effective in displacing the sorbed selenite, whereas in saline soil, sulfate was more effective. Phosphate desorption was more effective for selenate than for sulfate in all soils (SINGH et al., 1981).

In alkalioxidized soils, Se(VI) has been reported as the dominant soluble form of Se, and adsorbed Se was mostly Se(IV) (FIO and FUJII, 1990). Se isolated by XAD-8 resin was associated with the hydrophobic organic matter, like Sep-Pak C18 Se species in soil saturation extracts. Negligible quantities of Se were measured in the XAD-8 and Sep-Pak C18 eluates (6 µg/l and 8 µg/l). The XAD-8 extract is associated with the humic acid fraction of DOC; XAD-8 recovered added hydrophobic organic Se, but no Se(IV) and Se(VI) (FIO and FUJII, 1990).

In interstitial water of anoxic sediments of San Francisco Bay, selenate and selenite were removed by a near-surface process unrelated to sulfate reduction. In the porewater profile, selenate was abundant in the surface waters but was undetectable at depths below 2 cm. Selenite was about 20-fold less abundant than selenate and disappeared below 10 cm. Sulfate was slowly reduced to half till 40 cm. Selenate reduction was more rapid with acetate and lactate, and was inhibited by O₂, nitrate, MnO₂ or autoclaving, but neither by sulfate nor FeOOH. A small quantity of the elemental selenium precipitated into sediments from solution could be resolubilized by oxidation with either nitrate or FeOOH, but not with MnO₂ (OREMLAND et al., 1989).

1.1.3.3 Alkaline solutions

In soils from an area high in naturally occurring selenium (> 1 mg/kg), a solution of 0,1M NaOH/0,1M Na₄P₂O₇ (alkaline pyrophosphate) extracted 12 % of total Se on the average (range 5-32 %), and more than half of it was organically bound. In the hydrophilic fulvate fraction, selenomethionine was identified by GC/MS. Pyrophosphate-extractable selenium represents a pool of potentially plant-available selenium.

From paddy soils, the greater part of soil selenium (43-73 % for the first run) could be extracted repeatedly by 0,1M NaOH solution, at 84° for 1 hour. Selenium in the alkali extract was parted into 5 fractions. At first, the alkali extract

was acidified to pH 1,5 with dilute H_2SO_4 and the humics precipitated. The solution was applied to a column packed with XAD-7 resin to adsorb the fulvic acid fraction. In the eluate, selenite, selenate and the seleno-amino-acids were determined (KANG et al., 1991).

From wet sewage sludge samples from Tarbes, total selenium was extractable with NaOH. Selenium in this eluate could be separated on anion exchange column of Amberlite CG 400 into organic and inorganic species, and finally determined by DPCSV. In the sewage sludges Se(IV) ranged from 30–40 % and Se(VI) ranged from 2–20 % of total selenium (HENINGER et al., 1998).

1.1.3.4 Oxidizing solutions

Organically bound selenium from natural waters and aqueous soil and sediment extracts could be oxidized to selenite with persulfate and MnO_2 as indicator substance, without affecting simultaneously present selenate. Soluble selenium in soils was found to be within the range 0,053–2,45 ng/g, including a fraction of 4,5–59 % organically bound. Selenate was the dominating species in pore waters of agricultural soils. Organically bound selenium was the main fraction in wetland soils (ZHANG et al., 1999).

Elemental selenium was determined as the $\text{Na}_2\text{S}_2\text{O}_3$ -extractable, and organic Se as the NaOCl-extractable fraction. The formation of seleno-organic compounds can be explained by a rapid incorporation into microorganisms which form amino acids and proteins (ZHANG and MOORE, 1997).

1.1.3.5 Sequential leaching

A sequential selective leaching procedure was developed in order to fractionate selenium in soils. "Soluble" Se was extracted with 0,25M KCl; from the residue, 0,1M KH_2PO_4 should release "ligand exchangeable" specifically adsorbed selenite. The residue of the leaching with phosphate solution was treated with 4M HCl to obtain the "acid extractable" fraction which is likely derived from dissolution of oxide minerals, carbonates, some sulfides, and hydrolyzable organics. "Oxidative acid decomposable" selenium was released after oxidation with KClO_3 in concentrated HCl, yielding the rest bound to sulfides and humified organic matter. The last fraction was obtained by digestion with $\text{HF}+\text{HNO}_3+\text{HClO}_4$ and termed as "strong mixed acid digestible" (CHAO and SANZOLONE, 1989). Great proportions of selenium were resistant to chemical

dissolution in soils developed through intensive leaching and weathering. Selenium can be easily extracted as mobile selenate from soils with high pH and low content of oxide minerals. Selenium associated with sulfide minerals may be detected by sequential extraction as an immobile fraction and an unavailable fraction. Soluble and exchangeable fractions were negligible in tropical soils from Hawaii. Main fractions appeared in HCl and in $\text{HF}/\text{HNO}_3/\text{HClO}_4$. In alkaline seleniferous soils from California, however, main fractions appeared in KCl and in HCl (CHAO and SANZOLONE, 1989).

In order to discriminate between soluble – adsorbed – carbonate – and soil organic matter bound selenium, sequential extraction was applied to the seleniferous slightly alkaline soils. The soils formed an old alluvial floodplain of the primary granitic parent material, and were drained with saline seleniferous drain water of the Na_2SO_4 -Cl type. Their clay content throughout the profile was 23 ± 4 %. Soluble amounts were defined as extractable with 0,25 M KCl for 2 hours as the first fraction. After this, "adsorbed" amounts were released with 0,1 M K_2HPO_4 pH = 8 within 20 h. 1 M acetate buffer pH = 5 yielded "carbonate-bound" selenium, and oxidation with NaOCl at pH 9,5, repeated 2 times for half an hour yielded the "organic-bound" fraction. Fractions reducible with hydroxylamine, assigned to Fe/Mn-oxides, were insignificant (TOKUNAGA et al., 1991). 75 % of the Se-load was concentrated in the upper 15 cm of the soil profile. Reducing conditions which developed during drain water ponding removed selenium from solution and formed selenite, elementary selenium and selenoorganic compounds (TOKUNAGA et al., 1991). Selenium in the soil solution in all these profiles occurred primarily as selenate, with selenite under 10 %. High selenium content in the soil solution did not reach a solubility limit to precipitate Ba/Ca/Mg/Sr-selenate. In the "adsorbed" and the "carbonate" fractions extracted, about 2/3 were found as selenite. Gypsum possibly co-precipitated selenate. Selenate and selenite both coprecipitated with calcite. NaOCl-extractable Fe/Al/Mn/Si was minimal, whereas for Se it was the main fraction (TOKUNAGA et al., 1991). In California agricultural surface soils, soil selenium derived from Se-bearing sulfidic minerals which yield a refractory inorganic pool for selenium. NaOCl-Se followed total Se sharply in the soil profile. A second maximum was found in 1m depth only in the NaOCl fraction (TOKUNAGA et al., 1991).

1.1.4 Studies of vertical selenium transport

Reduction of added selenate was fast enough in columns filled with soil or soil-compost, soil-manure, soil-gluten admixtures to detect selenite in the eluate and to precipitate elementary selenium within the column during penetration time of 30 hours. Reduction was accelerated by an addition of organic substrates and by low oxygen concentration, resulting in increased retardation. Though selenate itself was hardly adsorbed on the solid, it was rapidly reduced to retarded species and thus accumulated in the top soil layers (GUO et al., 1999).

Soils of 7 % TOC, pH 7,7–8,0, and 28–36 % clay content were packed into columns and irrigated with synthetic irrigation water of the Na-Mg-Cl-type containing 200 µg/l selenium. In some cases dextrose was added to the irrigation water to serve as a microbial nutrient source. The first leachate fraction emerged after one pore volume. Dissection of the solid cores, however, revealed that soluble selenium leached with cold H₂O for 16 hours under N₂ was detectable only to the depth of 0,8 m; the total length of the soil columns was 1,5 m. Selenium peak obtained after one pore volume was assumed to derive from the native selenium leached from the original samples. Addition of dextrose to the irrigation solution resulted in a significant decrease in soluble Se above 0,4 m. The total soluble selenium in the aqueous extracts was mainly selenate, and in presence of dextrose, it was mainly organic selenium (NEAL and SPOSITO, 1991). Selenate was much more mobile than selenomethionine and selenite in columns filled with fine loamy calcareous soils equilibrated and leached with 0,05 M CaCl₂. Selenate was transformed to reduced and less mobile forms when the soil was C-enriched. Adsorption parameters obtained from batch experiments did not produce a satisfactory fit when used in simulation of real column studies but the transport model adequately simulated the respective selenium concentrations under sterilized conditions (ALEMI et al., 1991).

Within the soil profile of paddy soils (rice fields), Se was accumulated in the B horizons, and Se in the C horizons was higher than in A. The proportion of selenium compounds of low molecular weight increased in the lower horizons. Selenium in C horizons within mountain profiles was lower than in A. The distribution pattern of total selenium content in each profile closely resembled that of total Fe, total Al or clay content, but it differed from that of the total organic carbon. The water soluble selenium decreased from A to C horizons. Selenium in humic acid fraction decreased, and selenium in fulvic acid increased with depth. Inorganic sele-

nium was distinctly higher in the lower horizons. Low molecular organic selenium was generally low. Oxidation and reduction occur repeatedly in paddy soils, in the yearly cycle of drying and waterlogging. When Fe(III)hydroxides get reduced, occluded and sorbed selenium gets released, and Fe(II) moves down with percolating water. The greater part of soil selenium occurred organically bound, but no relation to TOC could be established (KANG et al., 1991).

1.1.5 Microbial actions

Redox reactions proceed much more favorably towards the direction of reduction, and the oxidation rate is very slow in soils. Large fractions of insoluble elemental selenium are often found under oxidizing conditions (GUO et al., 1999). Many microorganisms can reduce selenite but only a few of them selenate. The facultative anaerobic bacterium [*Enterobacter cloacae*] reduced selenite to elemental Se. During 2,5 h at 40°, 79 % of added selenite reacted. The microorganisms were fed with 1,4 mM glucose and nitrate. Selenite reduction was inhibited by nitrate, nitrite and sulfite, whereas sulfate was of no effect. Arabinose, xylose and sorbose as carbohydrate sources enhanced selenite reduction. Presence of elemental Se was confirmed by energy-dispersive spectrometry. The enzyme for selenite reduction may thus be a nitrate or nitrite reductase. *E. cloacae* can use selenate during aerobic respiration. Selenite reduction was not related to a sulfate reductive pathway. Selenite reduction was enhanced under conditions of limited O₂ availability. pH was optimal at 6,5, dropping to half speed at pH 7 or pH 4,5 (DUNCAN and FRANKENBERGER, 1998).

Strains of denitrifying bacteria from a sewage sludge treatment plant reduced selenite and selenate after an incubation time of 150 hours. During this lag time, nitrite and nitrate were consumed, and then nitrogen and selenium compounds were reduced in parallel. From selenate, only trace amounts of selenite were produced. With respect to the same biomass and substrate concentration, reduction of selenite was 4 times faster than reduction of selenate (REGE et al., 1999). A mixture of glucose/Na-acetate/Na-lactate/Na-succinate was added as a substrate for microorganisms. The gas phase was sampled for alkylated Se-gases. Selenite occurred in the unamended and the FeOOH-containing slurries but not in slurries containing nitrate or MnO₂. No significant levels of added ⁷⁵Se were detected in the gas phase of any of the slurries (OREMLAND et al., 1989).

In column experiments, sandy loam topsoil sieved less than 1mm, containing 7 % clay size fraction and 0,64 % organic carbon, was wetted from below with 0,05 M NaCl and preleached to remove any soluble selenium species, then drained for 2 weeks and resaturated. pH in the effluents was 6,6–6,9. The soils were mixed with either 2,4 % of composted dairy manure (28,9 % C, 3,2 % N), or 0,05 % of purified gluten (51,2 % C, 14,7 % N) prior to the filling of the columns. One pore volume of selenate (2 mg/l Se) together with bromide as a noninteractive tracer, was applied as a pulse to the columns, and elution was done with 0,05 M NaCl in the upflow mode. Sparging with O₂ through a porous bubbler could increase the concentration of dissolved oxygen from 6,9 mg/l to 32 mg/l. Break-through curves of bromide and selenate resembled closely. Selenite was formed during the mean residence time of 30 hours, which was retarded on column by a factor of 1,69–5,54. Half life of selenate was least in the unamended column leached with O₂-sparged influent solution with 115 hours, where 91 % of added selenate were recovered in the eluate. Selenate half life dropped to 10 hours in the gluten amended soil column without O₂ sparging, where 72 % of added selenium was retained, presumably as elemental selenium or selenide (GUO et al., 1999).

Added selenate remained in the top 2 cm in the soil profile, and only in case of limed clay soil it moved down to 6 cm. Selenite was retained in the top layers in the peat columns as well, but selenate moved down about 10 cm in the limed column. Alternate drying and wetting of the soil column caused a greater release of selenium (YLÄRANTA, 1982). Soils of 4,1 % clay and 1,8 % organic matter, as well as of 15,8 % clay and 1,5 % of organic matter were packed into the columns. Selenite equal to 125 or 500g Se/ha was placed on top after leaching and saturation with water. Each column received H₂O, equal to 700 mm of precipitation, and the eluates were collected. 88–95 % of the added selenite was retained within a distance of 2 cm from top. Addition of 2 % organic matter (ground wheat straw) decreased the movement of selenite through the column, leading to organically bound selenium. Addition of lime, however, increased movement and leaching of selenite in all samples, presumably due to the increase of pH (GISSEL-NIELSEN and HAMDY, 1977). In a field study on a calcareous chernozem with about 20 % clay developed on loess, with 3 % humics and 5 % CaCO₃, various amounts of Na₂SeO₃ were applied together with 100 kg/ha N/P₂O₅/K₂O. After growing corn, carrots or potatoes, 30 % of initially added selenium could be detected in the 2nd experimental year in the

0–20 cm plow layer, after extraction with ammonium acetate/EDTA at pH 4,8. Addition of 90 kg/ha slightly and 270 kg/ha significantly decreased the yields of corn, carrots, and potatoes; selenium got enriched in carrot roots (KADAR et al., 1994).

Selenate reduction occurs in surficial sediments while dissimilatory sulfate reduction occurs at greater depths. Potential dissimilatory selenate reduction did not correlate with chemical factors but was related to bacterial activity expressed as potential denitrification. Bacterial dissimilatory reduction of selenate to elemental selenium in sediments was investigated at pH 7,1–9,8 and salinities of 1–320 g/l. No reduction occurred at high salinity. There was no linear correlation between the potential rates of selenate and salinity, pH, total selenium content, porosity, or organic carbon. However, the potential selenate reduction correlated with the potential rate of denitrification at $r = 0,81$. No activity was evident in autoclaved sediment samples for each site, but selenium was extracted from autoclaved samples as selenite. Nitrate, nitrite, molybdate and tungstate inhibited selenate reduction to different extents, and sulfate partially inhibited activity in freshwater (STEINBERG and OREMLAND, 1991). The presence of elemental selenium in sediments was proved by extraction of labelled selenium (⁷⁵Se⁰) into CS₂ (STEINBERG and OREMLAND, 1991). The transfer of selenate to organic selenium compounds, reduction to selenite and elementary selenium are competitive reactions. 80 % of soluble selenate reacted with a wetland sediment within 72 hours at pH 7,6 to yield organic selenium (16 %), elemental selenium (11 %), adsorbed selenate (15 %), and selenite (3 %). Volatilization was only about 0,1 %, but it increased with concentration of the added selenate. Elemental selenium was determined as the Na₂S₂O₃-extractable, and organic Se as the NaOCl-extractable fraction. The formation of seleno-organic compounds can be explained by a rapid incorporation into micro-organisms, which form amino acids and proteins (ZHANG and MOORE, 1997).

1.1.6 Volatilization

Decomposition of organic matter can donate methyl donors directly producing dimethylselenide in the soil. Its solubility in water is rather high, = „24,4 g/l“, thus DMSe formed in the deeper layers would be trapped within the soil. 96 % of injected dimethylselenide was volatilized to the air from an air-dried soil but only 14 % from a water-saturated soil.

Dry-wet cycling of soil is an important factor affecting the removal of Se through volatilization. Microbial activity of a soil was much higher after rewetting a dry soil than when the soil was continuously maintained. Dimethylselenide could be caught in an activated C column and eluted again with an alkaline H_2O_2 solution (ZHANG and FRANKENBERGER, 1999).

Formation of gaseous selenium compounds was studied by amending the upper 10 cm of an air-dried loam soil of pH = 7,4, 17,5 % clay, and 9 % organic matter, with ^{75}Se as sodium selenite. The samples were flushed with air twice a day for 1 hour and the evolved gases passed a trap with concentrated HNO_3 . No volatilization occurred from autoclaved soil or from air-dried soil. Maximum evolution of gaseous selenium compounds was achieved at 28 % water content which was about half the field capacity. The evolution of selenium from the soil and the decrease of the water-soluble selenium correlated, but there was a lag of several days between these two processes. More selenium could be volatilized from soil samples collected in March, than from the same soil samples collected in June or in September (ZIEVE and PETERSON, 1981).

From fine clay or sandy soils, no volatilization of added sodium selenite or selenate was observed during 96 days of incubation. Liming (= mixing with $Ca(OH)_2$ -powder) increased the soil pH by about 1,5 pH units, but it had no significant effect on the leaching of Se. From columns of Carex peat, however, more than 7 % of selenite, and 84 % of selenate were leached, and liming drastically reduced this leaching. In addition, between 2,1 and 4,6 % of added selenium was lost from Carex peat by volatilization (YLÄRANTA, 1982).

1.2 Arsenic

1.2.1 Occurrence in atmospheric deposition samples

Atmospheric deposition in the East of Austria in 1984/85 was determined by Bergerhoff-sampling at 36 locations (502 samples) as $0,7 \pm 0,5$ g/ha (SAGER, unpublished). The arsenic load by total atmospheric deposition in Austria was estimated from moss-monitoring to range between 0,31 g/ha in the Bohemian Crystalline, and 0,04 g/ha in the Southern Alps, establishing a clear trend of decline from North to South-East (ZECHMEISTER, 1991).

1.2.2 Occurrence in waters

Within the water monitoring program of the Austrian Environmental Agency, total arsenic in both ground and surface waters ranged from < 1–41 $\mu g/l$ and soluble arsenic from < 1–11 $\mu g/l$. The median values were 2 $\mu g/l$, and 1,6 $\mu g/l$, respectively (UMWELTBUNDESAMT WIEN, 2000); however, many samples were below the detection limit.

Arsenic is frequently at or below the detection limits in potable waters in Europe. In Italy, non-polluted river water contains just 0,1–0,2 $\mu g/l$ As, which may increase because of industrial pollution up to 1 $\mu g/l$. But arsenic is mobilized under hydrothermal conditions, and some thermal springs may contain up to 1000 $\mu g/l$ As. Arsenic in groundwater supplies in Southern Nigeria was found to be in the range 0,4–6,88 (mean 1,88) $\mu g/l$ (ASUBIOJO et al., 1997). Well waters from Bangla Desh may contain extraordinary high amounts of arsenite, which have caused serious health problems in the past (AKTHAR-AHMAD et al., 1997; DIPANKAR et al., 1996).

1.2.3 Occurrence, adsorption and mobility in soils and ediments

1.2.3.1 Occurrence and mobility

Soil pH, redox potential and water contents are the most important parameters for arsenic speciation in environmental samples. Weathering of arsenic minerals under oxic conditions yields arsenates primarily. At potentials lower than + 200 mV, slow reduction to arsenite takes place. Micro-organisms can methylate arsenite to methylarsonic acid and after further reduction again methylate to dimethyl arsenic acid. In trace amounts, As is mainly bound to hydroxides and less to humics and clay minerals. Adsorption on Fe(III)-hydroxides decreases in the order phosphate > dimethylarsinic acid > arsenate > methyl arsonic acid. Oxidative microbial destruction of organically bound arsenic leads to CO_2 + arsenate (IRGOLIC, 1994).

Environmental monitoring programs in Austria revealed spots of high arsenic contents in aqua regia extracts, mainly due to atmospheric deposition and special geological formations (sulfide ore deposits). Selective leaching procedures are available for discrimination of origin and ecological significance. Arsenic from purely geogenic sources (e.g. bound to pyrites) is clearly not soluble in citrate or oxalate extracts (SOMMERHUBER, 2000). In contaminated soils, however, about half of the arsenic was extractable with

ammonium oxalate, whereas amounts exchangeable with ammonium nitrate were low. Ammonium phosphate and ammonium sulphate extracts were slightly higher, and correlated with aqua regia (WENZEL et al., 1999).

In Tessier-type sequential extractions of sediments and soils, arsenic was preferably leached from Fe-hydroxide phases (oxalate extractable), but the fractions were all inter-correlated with each other. Decreasing particle size resulted in significant shifts towards more mobile fractions (SAGER et al., 1989). Sequential extractions revealed that after addition of both arsenite and dimethylarsinic acid to sewage sludges As was mainly found in the organic/sulfidic fraction. The second largest fraction was the soluble fraction at pH 8, and the hydroxide fraction at pH 4. Dimethylarsinic acid showed the same trend, but less pronounced (CARBONELL-BARRACHINA et al., 1999). Adsorption of soluble arsenic on sewage sludge resulted in partial enrichment of exchangeable fractions (SAGER et al., 1990).

In general, mobility in alkaline extracts was higher than in dilute hydrochloric acid (SAGER et al., 1989).

Reduction to arsenite released substantial proportions from a contaminated soil at alkaline pH or at an redox potential below 200 mV to the soil solution. At 0–100 mV, arsenic solubility was controlled by the dissolution of Fe-hydroxides, and soluble Fe reached a maximum (MASSCHELEYN et al., 1991).

Arsenic in mine soils from Montana occurred at 85 % as enargite CuAsS_4 , the rest was tennantite and arsenopyrite FeAsS . After leaching of mine soils for 2 hours with HCl at pH 1,3 at 37°, no alteration products were observed on the surface of the arsenic bearing phases by microanalytical techniques. Under stomach conditions (pH = 2,0 / Eh = 200 mV / 0,01 M Cl), solubility of enargite was 47 ng/l As (DAVIS et al., 1992).

1.2.3.2 Adsorption and As/P interactions

The adsorption of arsenate and molybdate in 3 different types of soil were significantly reduced in the presence of phosphate, which was attributed to competitive interactions. The adsorption of phosphate was not greatly suppressed by either arsenate or molybdate (ROY et al., 1986). Arsenate, molybdate and phosphate are adsorbed by the same mechanism, i.e. some type of ligand exchange reaction with singly coordinated OH or OH_2^+ groups associated with the edges of clay minerals and the surfaces of hydrous metal acids. The experiments were done in the batch mode for 48 hours, 1g in 50 ml, in order to achieve equilibrium.

Constant pH was maintained with dilute HCl or NaOH. The anion specific affinity was generally phosphate > arsenate > molybdate. The acid clay soil (58 % clay, mainly as kaolinite; pH H_2O = 4,5) adsorbed most of the anions, and the loam soil (23 % clay, mainly as illite; pH H_2O = 6,1) the least (ROY et al., 1986).

In sediment samples of the River Danube treated by a Tessier-like leaching sequence, the proportion As/Fe decreased from the mobile towards the less mobile fractions, like P/Fe also (SAGER, 1988).

Phosphate caused a reduction of the amount of arsenate adsorbed in all soils. Addition of molybdate suppressed the amount of arsenate adsorbed (range 10–100 mg/l As) in the acid soil (pH H_2O = 4,5) but not in the loam soil at pH 6,1. On the other hand, arsenate tended to reduce adsorbable molybdate (10–50 mg/l) in all soils. Competitive interactions could be expressed in Freundlich type competitive adsorption isotherm equations (ROY et al., 1986).

1.2.3.3 Contaminations

Atmospheric deposition can be regarded as the main source of arsenic input into soils. Input from fertilizers is generally low (SAGER, 1997) but contaminated products cannot be excluded a priori. Phosphate and arsenate are competitive adsorbents (see above).

Arsenate introduced into soils as a component of fly ash has been considerably mobilized at pH 8,4 in soil columns. Continuous leaching with sulfate solution led to a maximum eluate concentration within the first 2 pore volumes, explained as non-specifically adsorbed arsenate. Elution with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solution indicated a shoulder in the first 2 pore volumes, followed by a much larger and wider peak which is termed as “specifically sorbed” arsenic according to QAFOKU et al. (1999).

At some sites in Austria suffering from atmospheric pollution, arsenic could be easily mobilized from topsoil layers, and it migrated vertically down to mineral horizons, where it was fixed on hydroxides, but this fraction was still partially bioavailable (WENZEL et al., 1999).

1.2.4 Arsenic in fertilizers

Arsenic seems to come along with the phosphate components and organic compounds in fertilizers. Arsenic is enriched not only in sulfides, but also in soils and sediments (see table 3) with respect to the mean crust occurrence. As

Table 3: Occurrence of arsenic in fertilizers and soils
 Tabelle 3: Vorkommen von Arsen in Düngemitteln und Böden

	samples	Mean mg/kg d.w.	Median mg/kg d.w.	Range
Ammonium nitrate lime	6	0,15	0,09	0,08–0,40
NPK (inorganic)	10	12,2	11,5	2,5–17,8
Organic fertilizers	6	1,2	0,2	0,06–6,2
Trace element concentrates	5	0,64	0,4	0,07–0,82
Liquid fertilizers	13	1,4	0,04	0,02–7,4
Mean crust		1,5		
Mean sediment		7,7		
Mean soil		11,3		
East of Austria: calcic chernozems (0-20 cm)	154	9,4	9,1	4,6–13,9
East of Austria: Dystric Cambisols (0-20 cm) on granites	100	6,2	5,7	3,0–11,7
East of Austria: Dystric Cambisols (0-20 cm) on gneiss	81	4,3	3,4	1,4–11,4
East of Austria: Calcaric Cambisols (0-20 cm) on loess	46	9,0	8,5	3,5–14,2

Soil data after DANNEBERG (1995)

there has been no threshold value on arsenic in fertilizers in Austria, only a few data were done in fertilizer control samples (period 1986–1995).

Sewage sludges may frequently contain arsenic at higher levels. The maximum value permitted concentration in sludge disposable to arable land has been set to 75 mg/kg in the US (USEPA, 1999), and the maximum annual loading set to 2,0 kg/ha.y (CARBONELL-BARRACHINA et al., 1999).

1.3 Sulfate

1.3.1 Occurrence and essentiality

Sulfur is an essential element for all living plants, animals, and microorganisms. The sulfur-containing amino acids cysteine, cystine, and methionine are found in almost all proteins. Terrestrial plant tissues accumulate sulfur as sulfate esters or inorganic sulfate when soil sulfur is in excess. Proteins account for major proportions of soil organic N and S, because free amino acids are rapidly taken up by decomposers and autotrophs (HOWARTH and STEWART, 1992).

The soils of Central Europe contain 200–800 mg/kg of total sulfur, of which 60–90 % are organically bound. Soil micro-organisms (e.g. Mycorrhiza) steadily mineralize organically bound sulfur to yield sulfate, this process is faster during the warm than during the cold season. The proportion of mobile sulfate in soils significantly increases after the end of the vegetation period, because the consumption from higher plants ceases and there is additional input from the fallen leaves. This can lead to annual cycles of soluble sulfate concentrations in ground waters. Direct atmospheric input

as the source of sulfate in the ground water was excluded, because mobile sulfate was not correlated with dissolved CO₂ (MATTHESS and HAMANN, 1966). In soils of Oregon, contents of organically bound sulfur ranged from 77–765 mg/kg, and they were highly correlated with organic carbon and total nitrogen at the respective sites (HARWARD et al., 1962). In Eastern Canadian soils, total sulfur ranged from 80–2070 mg/kg, it was not linked to a geographical location nor utilization. The sulfur fraction extractable with Na-acetate pH 4,8 contained a significant and fairly constant proportion of non-sulfate sulfur. Na-acetate extracted 11–144 mg/kg S, highest values were found in the B horizons and in the calcareous C-horizons (MACKENZIE et al., 1967).

From cambisols and podsols, the fraction of “easily soluble sulfur” was obtained by extraction with 0,001M HCl, 1 + 9, for 2 hours. Humic sulfur was defined as a fraction extractable with 4 % aqueous ammonia. Organic sulfur was extracted with 0,5 M carbonate buffer pH 10, 1 + 19, at 90° for 16 hours (LOWE and DELONG, 1961).

In soils of Uttar Pradesh, taken from 0–23 cm and 23–46 cm depth, total sulfur ranged from 84–168 mg/kg, and the mean of the water-soluble fraction was 12,6 % of total sulfur (BHARDWAJ and PATHAK, 1969). In strongly acidic volcanic soils of Oniishi/Japan continuously exposed to H₂S, sulfur occurred as organic S, sulfate and pyrite, but no free H₂S or elemental sulfur were found (TAKAMATSU et al., 1992).

1.3.2 Adsorption of sulfate in soils

Sulfate enters the soil from precipitation or from fertilizers. Except for a few acid soils with high oxide contents, the

capacity of the soils to adsorb added sulfate is quite small. Soils with $\text{pH} > 6$ did not adsorb significant amounts of sulfate. Sulfate extractability increased sharply by adding NaCl or CaCl_2 in concentrations higher than 0,1 M. Water and KH_2PO_4 extracted similar amounts of sulfate for soils with $\text{pH} > 6$, but in acid soils, phosphate solutions extracted more (CURTIN and SYERS, 1990).

One hour equilibration time was sufficient to reach equilibrium of sulfate sorption on soils high in TOC, within a broad range of pH and texture. In some soils, a great difference in sulfate sorption between the air dried soils and other pretreatments appeared, because of recrystallisation of the Fe/Al-hydroxides (COMFORT et al., 1991).

With respect to migration in soils, the retardation of dissolved anions usually increases from chloride = nitrate to sulfate to phosphate. Sulfate forms complexes with Al, which can be measured as liberation of OH^- and thus a pH increase. The zero point of charge for alumina is at pH 9,1 – at higher pH there is no sulfate adsorption. Kaolin-type clay minerals retard sulfate more than montmorillonite type clay minerals (HARWARD and REISENAUER, 1966).

1.3.3 Transformation reactions

Mineralization occurs when microbes decompose organic molecules, respiring CO_2 and releasing sulfate. Mineralization of soil organic sulfur is measured as sulfate production (HOWARTH and STEWART, 1992). Mineralization rates are strongly related to the soil temperature. Sulfur mineralization is often higher in intermittently leached incubations than in closed systems where sulfate is allowed to accumulate. Sulfur mineralization exhibits a rapid flush of sulfate shortly after application of residues followed by a very slow linear phase of sulfate release. There may be a flush of soluble sulfate after drying of soil, apparently from the decomposition of microbial cells. The relationship between sulfur mineralization and sulfatase activity may be weak (JANZEN, 1998). Organic sulfur in soils and nitrogen are mineralized to yield extractable sulfate and nitrate, but not necessarily in the same ratio (MAYNARD et al., 1983).

Most of the sulfur in the surface horizon is usually present in organic combinations, typically more than 95 %. Significant amounts of sulfate may be also adsorbed to soil colloids in weathered and acidic soils. The majority of organic sulfur is present in a diversity of complex organic molecules. The microbial biomass has the highest turnover rate, but it accounts for less than 5 % of the organic sulfur, chiefly as

proteins. Various organisms, most notably fungi, can store excess sulfur in the form of organic sulfates (JANZEN, 1998).

3 soils from the Ap horizon of Canadian prairies with different C : N : S ratios, pH 6,3–6,8, were incubated for 17 weeks at $20 \pm 2^\circ \text{C}$, at moisture = 80 % field capacity. In the closed system, differences in extractable sulfate and nitrate were measured before and after incubation, in 0,01 M CaCl_2 -extract 1 : 5. There was either slight release, or slight fixation. In the open system, 50 g of soils were leached periodically in columns with 75 ml 0,01 M CaCl_2 followed by 25 ml nutrient Solution (Ca/P/K/Mg). There was rapid release of sulfate during the first week, followed by a slower release. The total amounts of mineralized N in the 2 procedures were not significantly different. The nitrate/sulfate ratio for both incubations modes was different to the $\text{N}_{\text{org}} : \text{S}_{\text{org}}$ ratio; it was narrower in the open, and wider in the closed system. Labelled extractable sulfur got immobilized (MAYNARD et al., 1983).

In surface soils, less than 10 % of total sulfur is usually present as sulfate, but the proportion of it increases towards deeper layers. Mobility of sulfate in aride soils is limited by the solubility of gypsum, which is independent from by soil colloids. Naturally precipitated calcium carbonates contain co-precipitated sulfate, resulting in higher total sulfur contents in carbonaceous soils (HARWARD and REISENAUER, 1966).

In anoxic environments, sulfate reduction is coupled to carbon oxidation and nutrient mineralization. Sulfate reduction is the major form of respiration in coastal marine sediments and in marine wetlands (HOWARTH and STEWART, 1992).

Drying of lacustrine sediments of pH 4,9 and high TOC contents at 60° or 100°C led to losses of sulfur within the range of 6–22 %, in some cases 0–86 %. During lyophilization and furnace drying in presence of HNO_3 , even higher losses occurred, presumably as volatile dimethylsulfide and methanediol. Ashing of the dried samples with magnesium nitrate and subsequent determination as BaSO_4 yielded results similar to the combustion method (AMARAL et al., 1989).

In acid volcanogenous regosols (pH KCl = 2,06–3,42), which have been continuously exposed to volcanic H_2S up to 2,3 mg S/cm².month, no other sulfur species than sulfate and organic sulfur could be detected in the soil, except FeS_2 . This suggested rapid H_2S -oxidation to sulfate, which was retained by poorly crystallized Fe oxides in the mineral layer, and regained by leaching with 0,2 M oxalate pH 3 (TAKAMATSU et al., 1992).

2. Material and Methods

2.1 Column design

A haplic chernozem, calcic chernozem, and gleyic chernozem sample was taken at depth 1–10 cm, 10–20 cm and 20–30 cm, from topsoils at Sierndorf/March, at the eastern border of Lower Austria. The air-dried soils were packed due to the succession of layers met in the field, to yield cylinders of 30 cm length, 12 cm diameter, and about 5 kg of dry mass. 4 replicate columns of each soil were made. The soils were characterized by aqua regia and water extracts, soil pH, clay size content and carbonate content (table 4). The effective pore volume of each column was determined experimentally in a pre-run, by fitting the peak of penetrating chloride, applied as KCl solution (for details, see SCHOISSENGEIER, 1999).

The soil columns were kept in a dark room in a cellar at constant temperature (21–24° C and variable humidity (55–90 %). Evaporation was fairly constant and about 10 %.

2.2 Addition and elution

2.2.1 Treating of the columns

The addition of a mineral fertilizer was simulated by adding 50 ml of a K/Ca/Mg/NH₄/NO₃/PO₄/SO₄-solution containing a cocktail of presumably anionic trace elements, i.e. B, As, Se, Mo, and V. An inorganic N-P-K fertilizer was selected as the matrix for the trace elements, with an application rate of 160 kg N/ha as NH₄NO₃, 320 kg P₂O₅/ha as Ca(H₂PO₄)₂·H₂O, and 200 kg K₂O/ha (from this 20 % given as K₂SO₄ 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, added in 50 ml of loading solution. This means in absolute terms per one column: 2,5 mg B and V, 1 mg Mo, and 0,5 mg As and Se, resp. 2g/ha, 0,8g/ha and 0,4g/ha (table 5).

Every day except the weekends, distilled water was added 3 times in 50 ml portions slowly via a pipette, to simulate natural rainfall, with intermediate periods of aeration. One addition was equal to about 1/10 of effective pore volume. Eluates were taken from the bottom of the columns due to natural flow. About 4–5 effective pore volumes were collected in 45 fractions each. The columns were left dry for 6 weeks after collection of 40 fractions in 2 months, and rewetted again with up to 5 portions of 150 ml, in order to estimate the effect of drying and aeration.

2.2.2 Treating the eluates

The eluates were weighed, pH was determined, and 1 ml HNO₃ 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 a check. Some samples at 1 effective pore volume had to be diluted 1 + 9. Checks of analysis were also done with flame- and graphite furnace AAS.

Arsenic was determined directly from the eluates by hydride AAS. For the analysis of total selenium in the eluates, 5 ml aliquots were mixed with 0,2 ml of 1 % KMnO₄-solution and 1 ml of 50 % Mg-nitrate-solution in 50 ml Erlenmeyer flasks, dried overnight at 105°C, and finally ashed in the muffle furnace for 4 hours at 560°C. The white residue was dissolved in 10 ml 1+1 HCl for 1/2 hour on a boiling water bath, and the whole sample was submitted to

Table 4: Some characteristics of the soils investigated
Tabelle 4: Einige Eigenschaften der untersuchten Böden

	depth	haplic chernozem [%]	gleyic chernozem [%]	calcic chernozem [%]
Carbonate	0–10 cm	0	0,9	1,3
	10–20 cm	0	1,1	1,1
	20–30 cm	0	0,7	1,2
Humics	0–10 cm	0,9	2,5	3,6
	10–20 cm	0,9	2,5	3,4
	20–30 cm	1,0	1,9	3,4
Clay size	0–10 cm	7	13	13
	10–20 cm	7	14	13
	20–30 cm	7	15	13

Table 5: Amounts added to each column

Tabelle 5: Aufgabemengen auf die Säulen

Nutrient salts per hectare			absolute amounts
160 kg/ha N	as NH_4NO_3		
320 kg/ha P_2O_5	as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	113 mg Ca	175 mg $\text{PO}_4\text{-P}$
200 kg/ha K_2O	as $\text{K}_2\text{SO}_4 + \text{KCl}$	208 mg K	20 mg $\text{SO}_4\text{-S}^*$
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

* Note: 17 mg $\text{SO}_4\text{-S}$ have been added in the form of nutrient salts; 20 mg are the measured value from the applied solution. As the V-solution was prepared in sulfuric acid, some additional sulfate was introduced.

Se-determination by hydride AAS (batch technique). Measuring of Se in the extracts without the pretreatment was tried only at the beginning, and led to much lower results.

Results for other main, nutrient and trace elements will be given by Sager in further papers on this subject.

After the pre-runs to test the mobility of KCl-solutions, nitrate formation within the soil columns was much higher than the nitrate input from the simulated fertilizer solution, which led us to exclude nitrate from further analyses.

It has to be noted that ICP-OES determination in the eluate reflects total dissolved sulfur, and not only sulfate.

2.2.3 Extraction of the soils

2.2.3.1 Water extracts

5 g of soil were shaken for 2 hours with 50 ml de-ionized water, filtered, acidified with 1 ml conc. HNO_3 , and submitted to ICP-OES multi-element determination, pure and 1 + 1 diluted with H_2O .

2.2.3.2 Aqua regia extracts

21 ml HCl conc. and 7 ml HNO_3 conc. were added to 2 g of soil 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. Sulfur and other elements were determined by ICP-OES after 1 + 1 and 1 + 9 dilution. Arsenic was directly determined by hydride AAS. 1 or 2 ml of sample solution were heated with 10 ml 1+1 HCl for 1 hour on the boiling water bath prior to the determination of selenium by hydride AAS in order to convert selenium to quadrivalent.

Addition of magnesium sulfate and methionine solutions to the soil prior to the dissolution procedure with aqua regia led to a recovery of the sulfur added of $84,2\% \pm 3,8\%$ for the sulfate, and $82,3 \pm 1,5\%$ for the sulfur from the methionine.

2.2.3.3 Oxalate extracts

2g of air-dried sample were shaken 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) (SAGER et al., 1990) for 4 hours at ambient temperature, and filtered. The extracts were analyzed by ICP-OES after dilution 1 + 1 and 1 + 9. As and Se were directly determined in these extracts. Ashing of the oxalate extracts with Mg-nitrate (see above) did not change the Se value. Se was stable less than 1 week in these oxalate extracts, however.

2.2.3.4 NaOH extracts

5 g of air dried sample were shaken in capped plastic vessels with 50 ml 1 M NaOH (40 g NaOH Merck p.a. Nr. 6498, in 1 l) for 4 hours at ambient temperature. The brown extracts were filtered into 250 ml glass beakers, and the residue was washed 2–3 times with water. The extracts were almost neutralized with 47 ml 1M HNO_3 (63 ml HNO_3 65 % Merck p.a. Nr 456, in 1000 ml). After adding 4 ml of 50 % Mg-nitrate-solution (50g Mg-nitrate Merck Nr. 5853 in 100 ml solution), the samples were evaporated to dryness overnight at 105°C and finally ashed in a muffle furnace for 4 hours at 560°C . Serious corrosions of the beakers occurred but blanks of many elements of interest were small. The white ash was finally dissolved with 30 ml 1 + 1 HCl (37 %, Merck p.a. Nr. 317) for 1 hour on a boiling water bath, and made up to 50 ml.

For ICP multi-element measurement, 1 + 4 dilutions of the ashed NaOH- extracts were measured versus calibration solutions of equal Mg concentrations to cope with various signal depression effects. The high concentration of Mg in the final solution restricts the available ICP lines to Ca/Cd/Cr/Cu/Fe/Mn/P/S/Zn because of signal distortion. The validity of the ICP measurement was checked in some samples by dilution 1 + 5 with H_2O , and in case of Cu and Zn by flame AAS versus calibration solutions of equal Mg + Na.

Mo was determined in the graphite furnace.

3. Results and Discussion

3.1 Elution curves

3.1.1 Total selenium (Fig. 1)

Selenium was retarded and steadily eluted in forms largely non-accessible to direct hydride AAS. Some selenium appeared together with sulfate in the haplic chernozem. Elution from the calcic chernozem was at a constant low level.

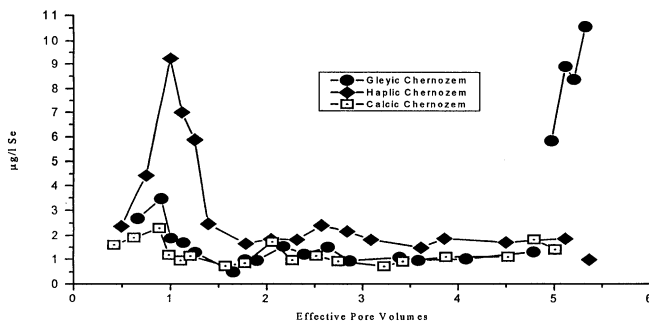


Figure 1: Selenium in the Eluates
Abbildung 1: Selen in den Eluaten

After permeation of about 5 pore volumes and the drying period, some selenium was released from the gleyic chernozem. Regarding the selenium present in the soil profile in all fractions investigated, no significant move of added selenium from the top to deeper layers took place. This selenium release parallels sulfur release after drying (see below). Similar release after drying was observed for sulfur from all columns.

3.1.2 Total Arsenic (Fig. 2)

Arsenic was detectable in the eluate after 2 pore volumes and remained at about constant level, similar to added

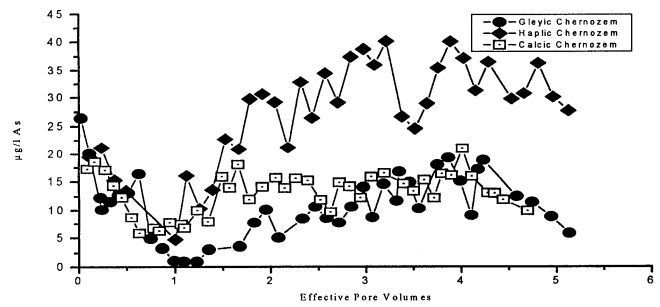


Figure 2: Arsenic in the Eluates
Abbildung 2: Arsen in den Eluaten

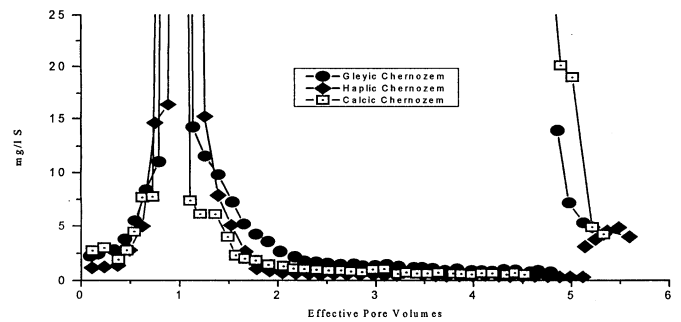


Figure 3: Sulfur in the Eluates
Abbildung 3: Schwefel in den Eluaten

phosphate, molybdate and vanadate. The gleyic chernozem strongly retained As, Mo and V. The elution of arsenic increased after the 6 weeks drying period (data not given).

3.1.3 Total sulfur (Fig. 3)

With respect to fertilizer components, 17 mg sulfate-sulfur were added on top of each column, but some sulfuric acid in the vanadium solution, which was part of the mixture, increased the added sulfate level to (measured) 20 mg.

The total dissolved sulfur (as measured by ICP-OES) was weakly retained in all soils investigated. In the eluates, sul-

Table 6: Sulfur load balances (means of 4 columns each)
Tabelle 6: Bilanz der Schwefelfrachten (Mittel von je 4 Säulen)

soil type	Aqua regia Original sample	Added	Sulfur peak at 0,5–1,5 PV	Sum of the eluates	Median – conc. after peak	H ₂ O-extract
	mg SO ₄ -S					
gleyic Ch.	117 ± 16	20	47,9 ± 3,5	58,9 ± 3,9	1,13 ± 0,32	0,77
haplic Ch.	98 ± 5	20	40,5 ± 1,4	45,6 ± 1,6	0,47 ± 0,02	0,50
calcic Ch.	148 ± 3	20	43,0 ± 9,4	63,0 ± 4,1	0,73 ± 0,08	1,09

* Note: Regain of sulfur in the aqua regia procedure was 84,2 ± 3,8 % for magnesium sulfate, and 82,3 ± 1,5 % for methionine (S-containing amino acid). The given values have not been corrected for incomplete recovery in aqua regia.

fur concentration had a steep peak along with the water front at exactly one effective pore volume, much narrower than the chloride in the pre-run. This peak contained much more sulfur than added, which can be interpreted due to anion exchange versus phosphate and other anions, as well as due to increased microbial sulfur mineralization because of the nutrient input. Prolonged continuous elution after this peak did not contribute much to losses of sulfur from the column; the sum of the eluates during the entire experiment was only slightly higher than the sulfur peak (table 6). The median sulfur concentrations found after the sulfur peak fairly well coincided with the sulfur concentrations found in the water extract. This indicates dissolution of a solid phase.

After about 6 weeks of drying period, however, elution significantly increased for the first eluates, but differences among the 3 soil types were noted. This can be interpreted as sulfur mineralization to yield soluble sulfate, during the aerobic dry period. This sulfur mineralization was highest in the gleyic, medium in the calcic, and least in the haplic chernozem sample (table 7). This reflected rather Cation Exchange Capacity (CEC; conventionally determined with BaCl_2 -solution) than humics contents (for details see SCHOISSENGEIER, 1999).

3.1.4 Precipitates in the run-off

A brown residue was noted in the space between the lower end of the column and the eluate vessels after demounting of the columns. This was collected, dissolved in hydrochloric acid and analyzed. This precipitate 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 from the analysis of main chemical components. 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.

The amount of arsenic caught in this residue was in the same range than the amount found in the eluates (table 8), but it was small with respect to arsenic originally present. This coincides with the observation that mobilized arsenic can be scavenged by hydroxide subsurface layers.

Eluted amounts of selenium were small with respect to those originally present and added, but significantly larger than those caught in the residue after leaving the soil columns. Selenium leaving the column was thus not co-precipitated with Fe/Mn oxides or carbonates formed after aeration of the eluates. Organically bound selenium seems to prevail in the eluates and will be subject to further studies.

Table 7: Sulfur release after drying
Tabelle 7: Schwefelfreisetzung nach dem Trocknen

Soil type	Median – conc. after peak mg/l $\text{SO}_4\text{-S}$	H_2O -extract mg/l $\text{SO}_4\text{-S}$	mean eluate concentrations after the drying period						humics	CEC
			I	II	III	IV	V	VI	%	cmol/kg
gleyic	1,13 ± 0,32	0,77	2,23	13,89	7,18	5,29	4,87	4,21	2,3	21
haplic	0,47 ± 0,02	0,50	3,10	3,76	4,52	4,85	4,0	–	0,9	2,3
calcic	0,73 ± 0,08	1,09	4,45	86,4	51,0	30,2	20,1	19,0	3,5	22

Table 8: Arsenic loads in the eluates and in the run-off precipitate
Tabelle 8: Arsenfrachten in den Eluaten und im Niederschlag beim Auslauf

Soil type	Originally present $\mu\text{g As}$	Added $\mu\text{g As}$	Eluted $\mu\text{g As}$	Residue $\mu\text{g As}$
gleyic ch.	22000 ± 446	500	32 ± 14	31 ± 9
haplic ch.	11220 ± 108	500	136 ± 17	91 ± 32
calcic ch.	37810 ± 272	500	70 ± 10	100 ± 10

Table 9: Selenium loads in the eluates and in the run-off precipitate

Soil type	Originally present $\mu\text{g Se}$	Added $\mu\text{g Se}$	Eluted peak at 1 PV, $\mu\text{g Se}$	Total eluted $\mu\text{g Se}$	Residue $\mu\text{g Se}$
gleyic ch.	619 ± 13	500	2,3 ± 1,0	11,6 ± 3	0,14 ± 0,08
haplic ch.	360 ± 4	500	5,7 ± 0,5	13,8 ± 0,8	0,19 ± 0,07
calcic ch.	1058 ± 8	500	1,9 ± 0,5	7,0 ± 1,0	0,13 ± 0,03

At about 1 effective pore volume (PV), a peak of eluted Se occurred together with the huge sulfur peak in the haplic chernozem samples (Fig. 1).

Sulfur in the run-off precipitate was not measured. Reduced forms would be lost during dissolution in HCl; smell of H₂S, however, was not noticeable.

3.2 Soil profile

3.2.1 Aqua regia extracts

Differences between aqua regia extractable selenium in the soil profiles before and after the column experiments clearly showed the added selenium to be trapped in the top 5–10 cm (fig. 4). Downward migration was highest in the gleyic sample. There was some washout from the lower layers of the calcic chernozem.

With respect to arsenic within the depth profile, aqua regia soluble arsenic remained constant in the haplic chernozem and declined towards deeper layers in the calcic and gleyic chernozems (fig. 5).

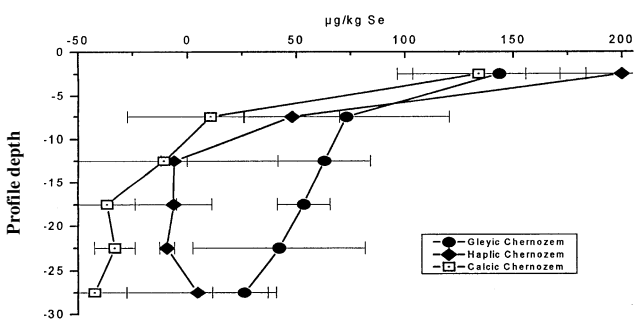


Figure 4: Differences between aqua regia extractable selenium in the soil profiles before and after the column experiment
Abbildung 4: Unterschiede bei Königswasser-löslichem Selen zwischen den Bodenprofilen vor und nach dem Säulenversuch

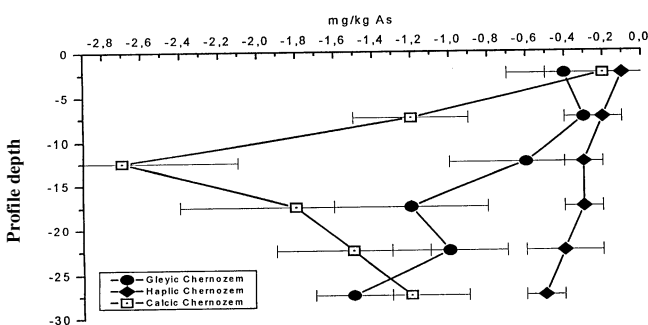


Figure 5: Differences between aqua regia extractable arsenic in the soil profiles before and after the column experiment
Abbildung 4: Unterschiede bei Königswasser-löslichem Arsen zwischen den Bodenprofilen vor und nach dem Säulenversuch

The initial arsenic load was not visible in any of soil profiles. Arsenic was generally lower after the elution experiment. May be that the added amount was too small to produce significant effects in the soils. Losses from the middle of the core appeared in the calcic chernozem.

Sulfur was not determined in aqua regia after the experiment.

3.2.2 Oxalate extracts

In all 3 soil types investigated, oxalate extractable Se was very low compared with aqua regia.

Differences between oxalate extractable selenium in the soil profiles before and after the column experiments clearly showed the added selenium to be trapped in the top 5–10 cm, similar to conclusions from the aqua regia extracts (fig. 6). From the calcic chernozem there was also some washout from the lower layers. Selenium in oxalate might indicate the same than aqua regia for practical applications, and it is easier to measure by hydride AAS – no conversion to Se(IV) is necessary. However, selenium in the oxalate extracts is stable just for a few days, and then declines steadily.

The proportion of oxalate-soluble Se/Fe rapidly decreased down the profile, irrespective of new formation of oxalate-soluble Fe. Thus, the migrating fraction did not seem to be influenced by newly formed oxalate-soluble Fe.

Oxalate-extractable arsenic (fig. 7) was about constant in case of the haplic chernozem soil profile, whereas in the deepest layer it got enriched in the calcic chernozem. In the gleyic sample, from which elution was lowest, oxalate extractable arsenic got enriched in the middle of the profile, which was not detectable in aqua regia. Contrary to this, the

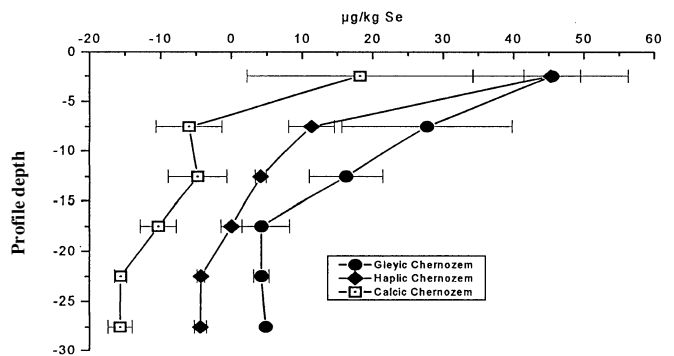


Figure 6: Differences of oxalate leachable selenium in the soil profiles before and after the column experiment
Abbildung 6: Unterschiede bei oxalatlöslichem Selen zwischen den Bodenprofilen vor und nach dem Säulenversuch

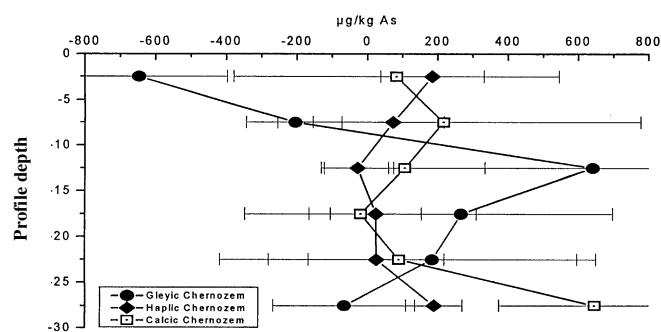


Figure 7: Differences of oxalate extractable arsenic in the soil profiles before and after the column experiment

Abbildung 7: Unterschiede bei oxalatlöslichem Arsen zwischen den Bodenprofilen vor und nach dem Säulenversuch

As-minimum in the aqua regia at the calcic chernozem could not be traced in oxalate as well.

The oxalate mobile As/Fe proportion decreased in haplic and calcic chernozems, because of additional formation of oxalate extractable Fe, which apparently did not influence oxalate extractable As.

Sulfur was not determined in the oxalate extracts.

3.2.3 NaOH extracts

Sulfur leachable with 1M NaOH remained rather constant through the soil profile in case of gleyic and haplic chernozems. Some washout was noticed from the top layers of the calcic chernozem (fig. 8). The levels of NaOH leachable sulfur were 4–7 mg/kg. No connections between sulfur in the eluates and NaOH-leachable sulfur in the profiles were found.

The column experiment made alkali-mobile arsenic to increase significantly towards the bottom of the column for both the haplic and the calcic chernozem samples. Thus, transformation reactions took place leading to quite different pictures depending on the method (figs. 5, 7, 9). Added arsenic might be seen above all in the NaOH leaches. Relations to arsenic in the eluates and the core profiles, were not found.

Like in the case of aqua regia and oxalate, added selenium distinctly appeared in the NaOH extractable fraction in the top 10 cm, and migration in the gleyic chernozem was fastest (fig. 10). In absolute terms, NaOH extractable Se nearly approached the aqua regia, whereas oxalate extractable Se was much less. The aqua regia and NaOH extracts reflect all soluble Se species, because the eluates were ashed with Mg-nitrate. The oxalate extracts were submitted directly to hydride-AAS, and therefore reflect Se(IV).

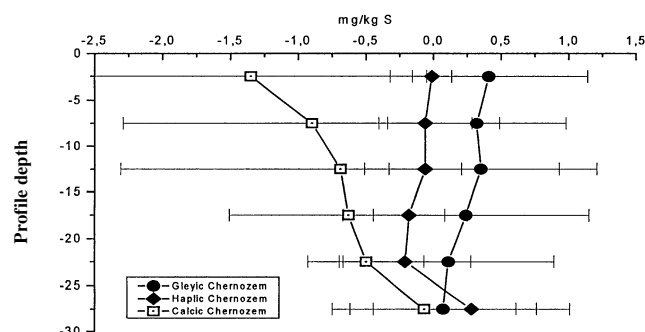


Figure 8: Differences of NaOH-leachable sulfur in the soil profiles before and after the column experiment

Abbildung 8: Unterschiede bei NaOH-löslichem Schwefel zwischen den Bodenprofilen vor und nach dem Säulenversuch

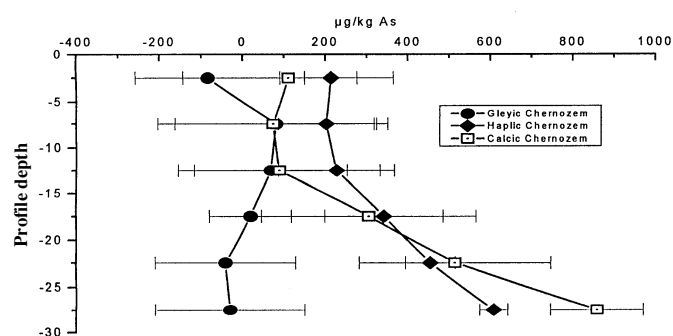


Figure 9: Differences between 1 M NaOH extractable arsenic in the soil profiles before and after the column experiment

Abbildung 9: Unterschiede bei 1 M NaOH-löslichem Arsen zwischen den Bodenprofilen vor und nach dem Säulenversuch

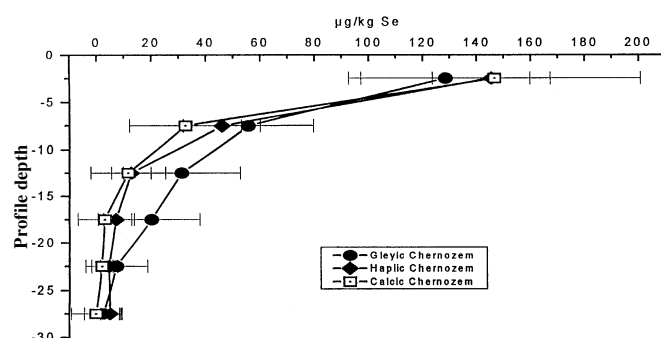


Figure 10: Differences between 1 M NaOH extractable selenium in the soil profiles before and after the column experiment

Abbildung 10: Unterschiede bei 1 M NaOH-löslichem Selen zwischen den Bodenprofilen vor und nach dem Säulenversuch

3.2 Conclusions

From the review given within this paper, much can be concluded about mobility and vertical transport of sulfur, selenium, arsenic and other elements occurring in anionic

forms, in arable soils. Referring to agricultural practice, sulfate is frequently added to mineral fertilizers, and selenate addition is in discussion. Arsenic may occur in phosphates as an impurity. No paper, however, has been found so far to treat arable soils from Central Europe with a mixture of sulfate, selenite, and arsenite in a matrix of a typical mineral fertilizer. This should simulate the situation before germination of higher plants in early springtime. From the given review, contradictory conclusions about trace and nutrient element mobilities in natural soils may be drawn.

Selenium

In the column experiments of this work, selenium was strongly retained in all chernozem topsoils, which was also predictable from the review. There was also slight and steady release of selenium from the columns in non-selenite forms (not directly accessible to hydride-AAS), which was also found in leachates from Japanese paddy soils. Contrary to expectations, release from the acid soil (haplic chernozem) was highest. Humics, cation exchange capacity and clay size fraction indicate that the 2 alkaline soils have a higher active surface and thus microbial activity, which has a much stronger effect than the pH of adsorption. Excess of phosphate and sulfate should prevent selenite adsorption by competition, but in an intact soil, they also increase microbial activity, which clearly overturns adsorption effects. Thus, the peak of selenium in the eluate along with sulfate at one pore volume occurred just in the acid and least retaining soil (haplic chernozem).

Selective dissolution may reveal the form of adsorption on the solid. Regarding selenium speciation in solids, it is reasonable to discriminate soluble, exchangeable, Fe-hydroxide-bound, organic, sulfidic, and elementary fractions, by sequential leaching (see review). Alkali-mobile (= operationally defined organic) selenium may range from 12 % in high Se-soils to total in sewage sludges. In all column experiments of this work, added selenium was recovered with 1 M NaOH. Another important mechanism of selenium retention in soils is scavenging on Fe-hydroxides, which may lead to Se enrichment in the B-horizon. But acid oxalate (= operationally defined Fe-hydroxide) extracts of the solids before and after the column experiments showed much less net adsorption, and even a washout from lower layers. As a conclusion, within our 3 chernozem soils, the organic components (and possibly the microbial life) are of primary importance for selenium.

Arsenic

In Austria, input of arsenic to the soil surface is usually much more from fertilizers than from atmospheric deposition. In case of simultaneous input of P and As on top of the soil columns, competitive adsorption can be expected, and this should increase arsenic mobility. On the other hand, increase of soil life because of nutrient supply may have the opposite effect. Therefore, As has been applied together with a large excess of P.

In the eluates of the non-contaminated chernozem soils treated in this study, significantly more arsenic was found in the eluates than expected from the mean of the groundwater monitoring program, in spite of the fact that half of the mobilized arsenic was scavenged in the ochre at the column outlet. In wells, ochre formation thus seems to be a major sink of arsenic.

Like in case of selenium, higher humics, clay size fraction and cation exchange capacity of the calcic and gleyic chernozem samples were more relevant for arsenic retention than the mere pH effect, which should favour the retention of arsenic in the more acid soil.

In selective leaching, most of the arsenic was released by oxalate (= operationally defined hydroxide bound) or alkali (= operationally defined organic bound). In the column experiment, alkali mobile arsenic clearly increased from top to bottom in the haplic and calcic chernozems, whereas in the gleyic chernozems the oxalate mobile arsenic clearly moved from the top to the middle of the column. As a conclusion, arsenic was transferred from less mobile forms to organic or hydroxide bound fractions during the experiment (one growing season).

Sulfur

Like for selenium and arsenic, there was constant steady release of sulfur to the eluates, probably from mineralization of soil organic sulfur. Parts of added sulfur were not retained and moved along the water front like chloride as predicted. The drying-wetting cycle led to increased washout of sulfur as predicted. According to the review, much of the sulfur in arable soils should be immobilized in organics. In spite of intact microbial life, however, there were no shifts in alkali-soluble sulfur in the gleyic and haplic chernozem samples during the experiment along the entire profile. From the calcic chernozem columns, there was significant washout of alkali-soluble sulfur from the top layers.

There was no indication of sulfate reduction to H₂S within the columns, which is usual for wetlands. This would

lead to sulfur losses within the experimental time, and to intense smell. As a conclusion, the chosen procedure of periodical wetting of soil columns with intermittent free access of air did not provoke wetland-soil formation, and thus yield realistic experimental conditions.

List of Abbreviations

AAS	atomic absorption spectrometry
CEC	cation exchange capacity
DOC	dissolved organic carbon
DPCSV	differential pulse cathodic stripping voltametry
d.w.	dry weight
Eh	redox potential
GC/MS	gas chromatography / mass spectrometry
ha	hectare
ICP-OES	inductively coupled plasma – optical emission spectrometry
mV	milli volt
M	molecular mass
N _{org}	organically bound nitrogen
NPK	multi-nutrient fertilizer containing nitrogen, phosphorus and potassium
pH KCl	pH determined in KCl extracts
pV	pore volume
S _{org}	organically bound sulfur
TOC	total organic carbon
USEPA	United States Environmental Protection Agency

Danksagung

an Frau Martina Schoissengeier für die praktische Betreuung der Säulenversuche;

an Herrn HR Doz. Dr. O. Danneberg für die fachliche Mitbetreuung der Diplomarbeit von Frau Schoissengeier, insbesondere für Beratungen und Diskussionen;

an Herrn HR Dr. W. Schneider für Beratung und Mit-hilfe bei der Probennahme im Feld.

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Eingelangt am 19. September 2000
Angenommen am 3. Jänner 2002