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VERTICAL MIGRATIONS IN AN ALPINE GRASSLAND CAMBISOL AFTER LONG-TERM SEWAGE SLUDGE APPLICATION

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Abstract: Differences between vertical mobilities of nutrient and trace elements within a long-term sludge-treated and an adjacent untreated Alpine grassland cambisol were investigated by column experiments. The site had been intensely fertilized with urban sewage sludge for 10 years of 7.5 Mg/ha annually, whereas an adjacent site had been left untreated. A model column experiment was set up to investigate changes of permeabilities and trace element retentions at 0-20 cm and 20-60 cm layers thereof. Elution was performed with de-ionized water at amounts of expected rainfall at the sampling site (1000 mm), as well as with equal volume of manure after biogas production. Long-term sludge treatment increased organic carbon, formation of ammonium and nitrate, and increased vertical mobility of K, P, S, Cu, and Fe, but also slightly higher (below 10-fold) for Na, Sr, Ba, Ni and V. Additional application of manure was of minor effect, mainly upon nitrate formation, and upon leaching of Fe, Mn as well as Fe/Mn proportion. Prior addition of $FeCl_2$ to the manure in order to increase sulfide precipitation, mainly affected the output of ammonia, but hardly the cations or anions (e.g. P) investigated.

Keywords: sewage sludge deposition, vertical mobilities in soil, soil columns, phosphate, sulfate, nitrate, ammonium, copper, zinc, Fe-treatment of biogas residues

Introduction

Soil is the primary substrate for green plant growth and a filter for groundwater formation. After decades of mineral fertilization, soils have increasing needs to recycle organic carbon, nitrogen, phosphorus and sulfur to soils in order to maintain sufficient soil life as well as to save energy for ammonia synthesis from atmospheric nitrogen, and import of phosphates. Sewage sludge treatment plants as well as domestic animal farming produce a lot of organic wastes. Incineration removes pathogens and organic contaminants, and may solidify toxic metals in the bottom ash. High energy needs for drying beforehand are about equal to the energy gains from the combustion process. Because organic carbon and nitrogen get lost, bottom ash additions to soils do not contribute so much to soil life than the original sludge, however.

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As a source of organic carbon, nitrogen, phosphorus and sulfur, sludge addition should increase anaerobic soil life and increase fertility. After production of biogas, the need of utilization of solid residues still remains. Saturation of adsorbent sites of the original soil might lead to increased permeation of added material on top, and on the other hand, increase of the number of living microorganisms should increase the sorbent capacity. Manures and residues from biogas production usually contain more K, N, P, and S than soils, also more B and Mo, and some of them may be contaminated with Cu, Zn and Se [1, 2]. Methane formation in biogas facilities lowers the carbon content of the residues and thus the reproduction potential for humus, when applied as organic fertilizers to soils [3, 4].

After 30 years of sludge application to a sandy soil in Northern France, enrichment in heavy metals was more than 10-fold in the upper 40 cm, organic matter increased to 8% and carbonate was formed. Significant amounts of metals and organic carbon reached the lower sandy soil horizon, in spite of increased retention capability of organic carbon [5, 6].

Grass roots penetrate soils down to very deep layers if possible, whereas output by cutting seems comparable to arable crops, if grassland is supplied with sufficient nutrients [7], and just edible parts of crops are removed from arable soils. In case of metal contamination of applied sludges to grassland, there is no direct impact upon human nutrition, contrary to arable soils where staple foods are grown.

Input of manure to grassland is a common practice, particularly in Alpine areas. Effects of soil property changes induced by sludge additions on the migration of nutrients supplied via manures, has been hardly investigated in Alpine grassland soils.

Column experiments simulate vertical transports into the groundwater, usually from the sieved fine part of the soil, without plant cover and actions of the macrofauna (like earthworms). Contrary to batch extractions, soil life can be maintained during a period as long as crop plants are grown. Addition of water on top can be kept as low as the natural rainfall. Washout from top and reprecipitation in deeper soil layers caused by pH changes, redox changes or degradation of organic ligands, can be monitored [8]. Because chemical equilibrium, if any, differs from layer to layer, and because of various metabolism of archeo-bacteria and fungi, model calculations are difficult, however, thus necessitating appropriate experiments.

In anaerobic fermentation to produce biogas, prior to burning in a local electric power plant, or selling to natural gas suppliers, sulfur containing components (e.g. H_2S) in the biogas residues have to be kept at low levels, because the combustion product SO_2 is highly toxic and corrosive. Evolvation of corrosional H_2S can be substantially lowered by the addition of divalent Fe-compounds, to form Fe-S in the residue. Divalent Fe is contained in various hydrogenases and thus acts beneficial for methanogenic archaea [9, 10]. Whereas the amount of added Fe has been optimized with respect to the fermentation process, effects on fertilization in agriculture are lacking, particularly with respect to P fixation. This work should also investigate the effects of Fe-enriched biogas manure residues used as organic fertilizers upon mobility and washout of nutrients in grassland soils.

Biogas production and subsequent transformation to electricity is a promising source of future income for farmers in rural areas. Some sites in the grassland, however, have been intensely loaded with manure meanwhile. Therefore, this paper addresses long-term changes of an alpine grassland soil by sludge application with respect to chemical composition, changes of mobility, and retention of various items contained in manure residues after biogas production.

Material and methods

Choice and characteristics of the site

In order to address the problem of long-term changes of permanent grassland soils by long-time disposal of sewage sludge, two originally similar soils were sampled at 700 m above sea-level at 2 horizons from adjacent sites at the experimental station at Gumpenstein (Styria, Austria), which means 4 solid samples from 2 soils. They are of a non-carbonaceous cambisol type, consisting of an A-horizon of 20 cm and an AB-horizon 20-60 cm, which is quite common within the entire Ennstal alpine region, and makes 19% of the soils of the entire province of Styria. Average precipitation on site is 1035 mm, and average annual temperature is 6.9ºC. One permanent grassland-site had been fertilized with urban sewage sludge at 7.5 Mg/ha for 10 years, and therefore will be called the „high P" (P+ site), whereas the other had got no treatment and will be called „low P" (P– site). The P– site had still enough organic carbon (classified as medium humics level) to ensure adequate microbial life. Soils from the same site like used in this work have been filled into field lysimeters already in 1991, and used for the investigation of nutrient losses below bare land and grassland under field conditions, after manure application [11, 12]. The column experiment was run for more than 60 days, which should match the period of growing cereals at the experimental site.

The soils were investigated according to Austrian standard methods, as well as extractions by de-ionized water (saturation water extract termed as H_2O), 0.4M LiCl (= exchangeables; after [13]), HCl (= supplementaries), and aqua regia (= quasi total). Final determinations were done by ICP-OES and spectrophotometry (ammonium, nitrate). Further fundamental parameters were also done according to Austrian standard methods, like pH, lime contents, humics contents (= organic carbon · 1.72), total N, ammonium, nitrate, and cation exchange capacity (Table 1).

Table1

List of Austrian standard methods used for the analysis of the test soils (available at: www.austrian-standards.at)

OENORM L1080	Chemical analyses of soils - Determination of organic carbon by dry combustion with and without consideration of carbonates
OENORM L1082	Chemical analyses of soils - Determination of nitrogen according to Kjeldahl
OENORM L1083	Chemical analyses of soils - Determination of acidity (pH value)
OENORM L1084	Chemical analyses of soils - Determination of carbonate
OENORM L1085	Chemical analyses of soils - Extraction of elements with aqua regia or with a mixture of nitric- and perchloric-acid
OENORM L1086-1	Chemical analyses of soils - Extraction of the effective exchangeable cations Ca^{2+}, K^+, Mg^{2+}, Na^+, Al^{3+}, Fe^{3+}, Mn^{2+} and H^+ by bariumchloride solution and determination of the exchange capacity
OENORM L1092	Chemical analysis of soils - Methods for the extraction of water soluble elements and compounds
OENORM L1094-3	Chemical analyses of soils - Extraction of trace elements with a solution of lithium chloride

Manure after biogas-production

The test manure contained 95% of water. Quasi-total contents were determined from aqua regia digests of the dried sample. Total N was determined by Kjeldahl's method, and chloride from the water extract by ion chromatography [14] (Table 2).

Table 2

Composition of the biogas manure (in wet weight)

	Unit	**Manure**	**Manure + $FeCl_2$**
H_2O	[%]	95.1	95.1
pH (H_2O)	[-]	8.4	8.3
pH (KCl)	[-]	8.1	7.8
Org. subst.	[%]	2.0	1.9
Na	[mg/dm^3]	300	500
K	[mg/dm^3]	2900	3000
Mg	[mg/dm^3]	500	400
Ca	[mg/dm^3]	1100	1000
Fe	[mg/dm^3]	180	1240
Mn	[mg/dm^3]	13.2	11.8
Cu	[mg/dm^3]	4.6	4.8
N-Kjeldahl	[mg/dm^3]	3800	3800
P	[mg/dm^3]	620	550
S	[mg/dm^3]	200	300
Cl	[mg/dm^3]	2340	4990

The column experiment

For the column experiment presented in this work, plexiglass cylinders of 60 cm length and 12.6 cm diameter (125 cm^2) were mounted in plastic Buechner funnels and closed with a nylon gauze at the bottom. The soil samples were air-dried, homogenized, and sieved < 5 mm. The columns were filled with 22 cm soil from the AB-horizons, and then with 16.5 cm of the A-horizons, and wettened from top to bottom for 7 days to reach field capacity. After sacking, the column length before addition of the biogas residue was 35 cm.

The biogas manure had been produced from maize silage (25 Mg/d) and pig manure (20 m^3/d) by anaerobic fermentation in the dark for 60 days, and contained 95% H_2O. The amount of $FeCl_2$ added during the anaerobic fermentation biogas formation process was done to reach a level of 1000 mg Fe/dm^3, which has been regarded to be at optimum for CH_4 production.

After rewetting, 49 cm^3 of biogas residue slurry were added on top the soil columns, and mixed into the 2-3 cm surface layer, equivalent to 1½ livestock units. The controls got just the same amount of water. Then the columns were covered with quartz sand to homogenize the added water across the entire surface, and kept in a dark room at 19-21ºC. All column experiments were done in triplicate, which made 18 columns in total. 187 eluate solutions have been analyzed, taken within 49 days. Some parameters were measured till day 65.

120 cm^3 of de-ionized water were added 2 times a week on top, which resembles the average natural precipitation of 1000 mm on site (inner Alpine area), and the eluates sampled. The evaporation was 1.1-1.2 g per collection vessel. The water content inside the columns was measured by a TDR-probe. The column experiments were performed during 8 weeks to simulate an average growth period of pasture between cuts [14].

Results

Changes of the composition of permanent Alpine grassland soil by long-term sludge application, prior to manure addition

10 years of steady urban sewage sludge application on the investigated Alpine cambisol, increased the original grassland soil in concentrations of nutrients N (both nitrate and ammonium), P, and K, as well as (in alphabetical order) of Ba, Cr, Cu, Mn, Pb, V, and Zn, and depleted Ca, Mg and consequently lime, instead (Tables 3-5). But changes were not only found within the quasi-total contents of some elements, but also the proportion of mobile fractions obtained in batch. Details for mobile fraction selection have been given by Unterfrauner [14]. Whereas additional loads of K and Na moved to the exchangeables, Pb got enriched in the acid-extractables, and P-Cu-Zn-Cr increased in all fractions investigated. To the contrary, exchangeable Ca and Mg remained about the same, whereas HCl- and aqua-regia fractions of Ca and Mg got depleted.

Table 3

Fundamental parameters of permanent Alpine grassland soil used for the column experiments before and after by long-term sludge application

Parameter	A - horizon		AB - horizon		Trend
	grass	sludge	grass	sludge	
Water capacity [cm^3/100 g]	72	84.1	59.1	71.6	increase
pH (H_2O) [-]	7.4	7.5	7.7	7.4	
pH (KCl) [-]	6.6	6.3	7.3	6.2	decrease
$CaCO_3$ [%]	1.6	< 0.1	3.8	0.1	decrease
Electrical conductivity [mS/cm]	0.321	0.702	0.365	0.619	increase
Organic substance [%]	3.9	7.2	2.9	5.2	increase
KAKp [cmol/kg]	75	140	58	104	increase
Total nitrogen [%]	0.285	0.426	0.208	0.316	increase
NO_3-N (H_2O) [mg/kg]	8.4	26.7	7.3	21.4	increase
SO_4 (H_2O) [mg/kg]	5	22	5	17	increase
Cl (H_2O) [mg/kg]	2.9	41.2	1.4	40	increase
NH_4-N (H_2O) [mg/kg]	1.0	1.6	0.4	0.7	increase
NH_4-N (LiCl) [mg/kg]	20.3	21.1	11	13.7	

pH (H_2O) means the actual soil pH measured in the water extract, whereas pH(KCl) measured after extraction by a KCl-solution indicates a potential pH, which includes exchangeable H^+ versus other cations applied. A difference between pH (H_2O) and pH (KCl) more than one indicates a labile buffer system.

Table 4

Change of mobilities by long-term sludge application, obtained by batch extraction utilizing saturation water extract, 0.4M LiCl, 2M HCl and aqua regia, for permanent Alpine grassland (A-horizon), given in [mg/kg dry weight] prior to manure addition

Element	H_2O		LiCl		HCl		Aqua regia		% HCl	
	grass	sludge	grass	sludge	grass	sludge	grass	sludge	grass	sludge
Ca	28.2	40.2	971	1077	6711	3975	8155	5090	82.3	78.1
Mg	9.1	12.7	194	222	2717	702	11660	9132	23.3	7.7
Ba	< 0.01	< 0.01	0.7	1.7	17.9	45.1	33.1	68.7	54.1	65.6
K	0.7	59.9	20.4	339	112	418	1058	1612	10.6	25.9
Na	1.2	7.4	8.0	14.9	21.3	20.5	101.4	92.9	21.0	22.1

Element	H_2O		LiCl		HCl		Aqua regia		% HCl	
	grass	sludge	grass	sludge	grass	sludge	grass	sludge	grass	sludge
P	**1.2**	**3.0**	**18.0**	**36.2**	**476**	**996**	**1137**	**2019**	41.9	49.3
Al	< 0.01	< 0.01	7.8	15.1	2499	3086	20540	21160	12.2	14.6
Fe	3.4	0.87	12.3	20.5	4538	5047	46770	45170	9.7	11.2
Mn	0.11	0.05	0.62	1.4	396	470	638	725	62.0	64.9
Cu	0.02	0.03	0.13	0.25	10.3	20.9	35.1	53.3	29.4	39.1
Zn	0.03	0.03	0.42	0.96	15.0	63.5	98.2	187	15.3	33.9
Co	< 0.01	< 0.01	< 0.02	< 0.02	5.47	6.47	17.9	17.5	30.6	37.0
Mo	< 0.01	< 0.01	< 0.05	< 0.05	0.09	0.08	1.04	1.48	8.7	5.4
Ni	< 0.01	< 0.01	< 0.03	< 0.04	6.4	8.3	42.6	47.1	15.0	17.6
Cr	< 0.01	< 0.01	0.07	0.13	4.5	8.2	39.8	58.4	11.3	14.0
Pb	< 0.01	< 0.01	< 0.01	< 0.14	0.24	40.3	29	58.9	0.8	68.4
Cd	< 0.01	< 0.01	< 0.01	0.03	0.24	0.43	0.55	0.75	43.6	57.3
V	< 0.01	< 0.01	0.02	0.06	9.31	11.9	38.6	45.0	24.1	26.4

Table 5

Change of mobilities by long-term sludge application, obtained by batch extraction utilizing saturation water extract, 0.4M LiCl, 2M HCl and aqua regia, for permanent Alpine grassland (AB-horizon), given in mg/kg dry weight, prior to manure addition

Element	H_2O		LiCl		HCl		Aqua regia		% HCl	
	grass	sludge	grass	sludge	grass	sludge	grass	sludge	grass	sludge
Ca	31	32.3	1001	875	10969	3775	13110	4638	83.7	81.4
Mg	6.2	8.2	107	148	4413	781	13290	9224	33.2	8.5
Ba	< 0.01	< 0.01	0.5	1.5	18.8	36.6	33.5	56.4	56.1	64.9
K	0.4	41.5	13.8	250	83.8	337	1023	1508	8.2	22.4
Na	0.9	6.9	6.6	14.7	22.4	21.6	107.5	113.1	20.8	19.1
P	**0.33**	**1.17**	**16.0**	**22.5**	**449**	**770**	**986**	**1562**	45.5	49.3
Al	< 0.01	< 0.01	6.9	9.5	2510	3030	20760	21180	12.1	14.3
Fe	0.55	1.38	7.95	13.3	4110	5428	46520	45530	8.8	11.9
Mn	0.01	0.09	0.33	0.94	403	519	656	756	61.5	68.6
Cu	0.02	0.03	0.2	0.21	9.7	18.4	33.9	48.5	28.6	38.0
Zn	< 0.01	0.03	0.27	0.63	14.0	42.1	92.3	147	15.1	28.7
Co	< 0.01	< 0.01	< 0.02	< 0.02	5.42	7.16	17.9	18.1	30.3	39.6
Mo	< 0.01	< 0.01	< 0.04	< 0.05	0.17	< 0.07	0.86	1.09	19.8	< 6.4
Ni	< 0.01	< 0.01	< 0.04	< 0.03	5.8	7.8	42.5	46	13.6	17.0
Cr	< 0.01	< 0.01	0.05	0.08	4.75	7.18	40.1	53.1	11.8	13.5
Pb	< 0.01	< 0.01	< 0.12	< 0.13	18.6	32.5	33.5	48	55.5	67.7
Cd	< 0.01	< 0.01	< 0.01	0.02	0.25	0.37	0.46	0.69	54.3	53.6
V	< 0.01	< 0.01	0.02	0.04	8.56	11.9	37.8	44.4	22.6	26.9

Effects of sludge pretreatment on transport to the leachates

Substantial differences between amounts found in the leachates due to vertical migration were found, which can be more smoothly expressed in diagrams of cumulative elutions versus time.

Explanation for Figures 1-9: NP … original grassland soil

P-Fe- … original grassland soil + biogas manure

P-Fe+ … original grassland soil + biogas manure + $FeCl_2$

NP+ … sludge treated soil

P+Fe- … sludge treated soil + biogas manure

P+Fe+ …sludge treated soil + biogas manure + $FeCl_2$

pH in the eluates

Within the first 40 days after manure addition, the pH (H_2O) in the eluates from the sludge-pretreated samples was higher (pH 8.0-8.7 versus pH 7.7-8.2), but after this period it approached the same range (pH 8.4-8.8). pH changes are usually due to nitrification and S-oxidation reactions (Fig. 1).

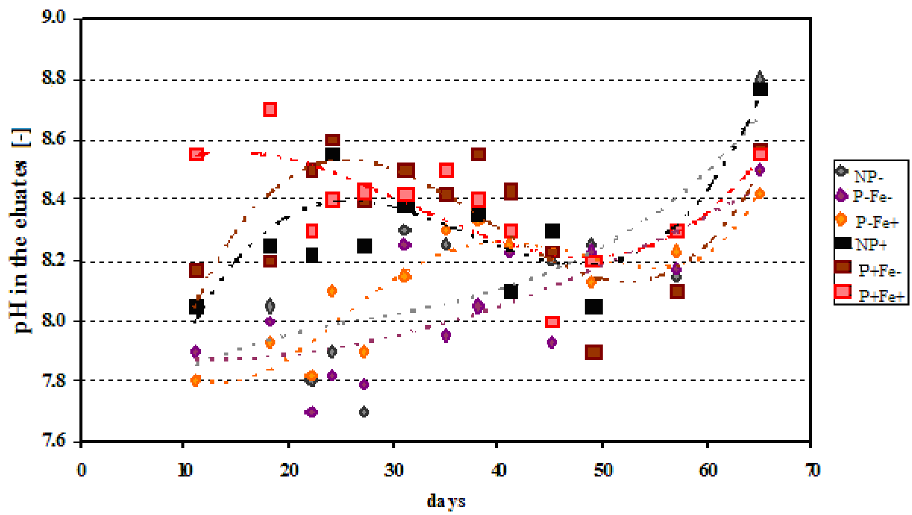

Fig. 1. pH (H_2O) in the eluates

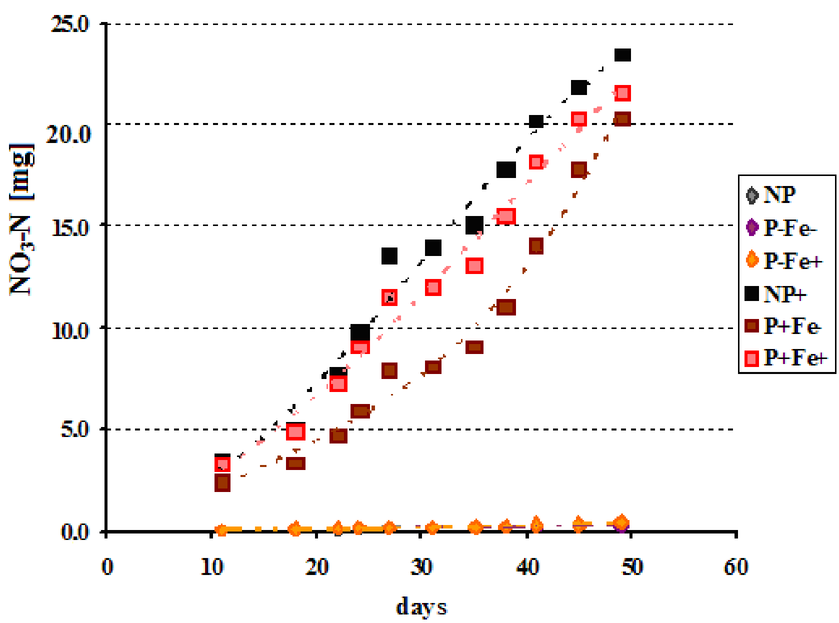

Fig. 2. Cumulative NO_3-N output (mg per column = 125 cm^2)

Nitrate and ammonium

Long-term sludge treatment significantly enhanced nitrate and ammonium release from the test soil columns to levels significantly above drinking water thresholds. The addition of manure instead of water decreased the cumulative output of nitrate from both soil column types, and enhanced losses of ammonia. With respect to the addition of untreated manure, Fe(II) addition increased nitrate release, but reduced the output of ammonium; the latter was the largest effect caused by Fe addition (Figs. 2 and 3).

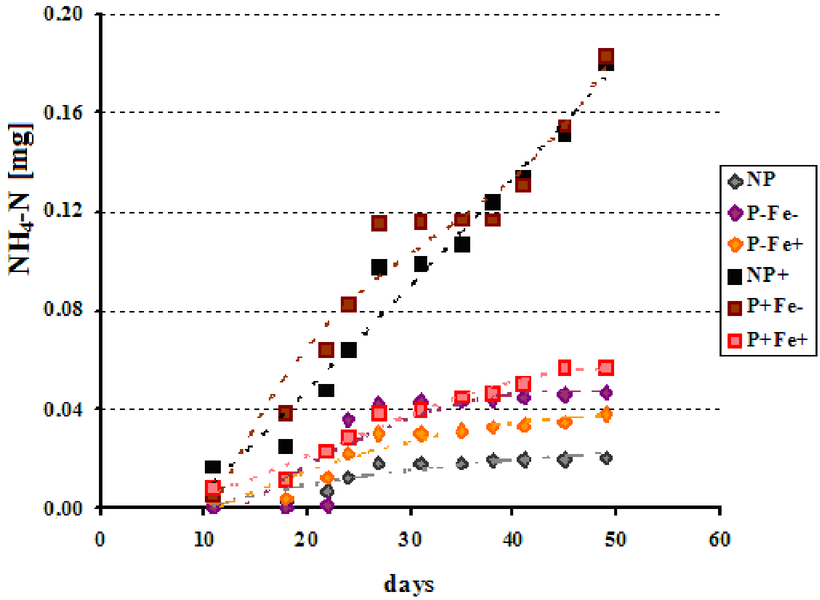

Fig. 3. Cumulative NH_4-N output [mg per column]

Phosphorus

Whereas there was steady and rather constant release of P from the sludge-treated soil columns, the release of P from the original soil was close to detection limits for a long time, and had a lag time of 50 days (Fig. 4). Fe-addition to the manure applied on top reduced P washout at the high release rate.

Sulfur

ICP-OES measurements cannot discriminate between sulfur species in the eluate. Elution of sulfur-compounds from the sludge-pretreated soil columns was significantly higher (Fig. 5).

Differences between leaching due to water or manure additions were marginal, in spite of S additions from the manure.

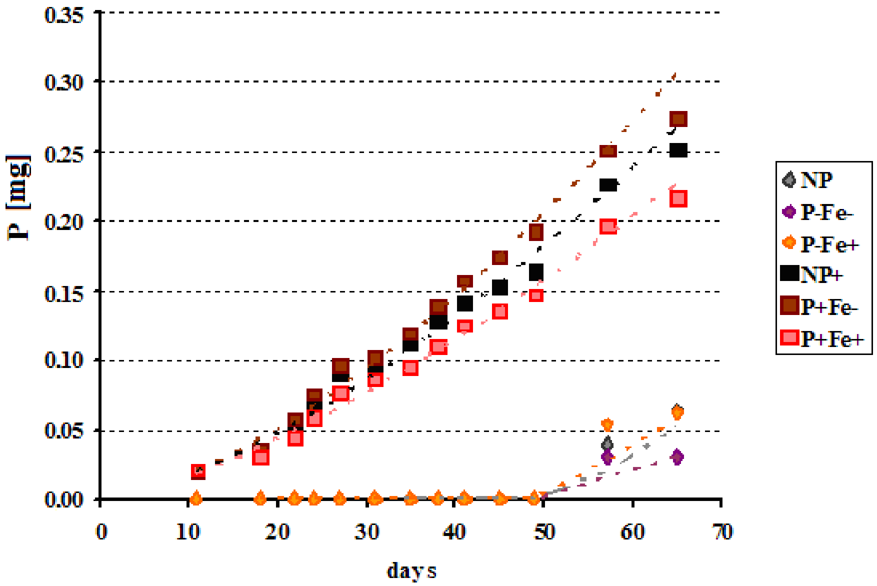

Fig. 4. Cumulative P-output [mg per column]

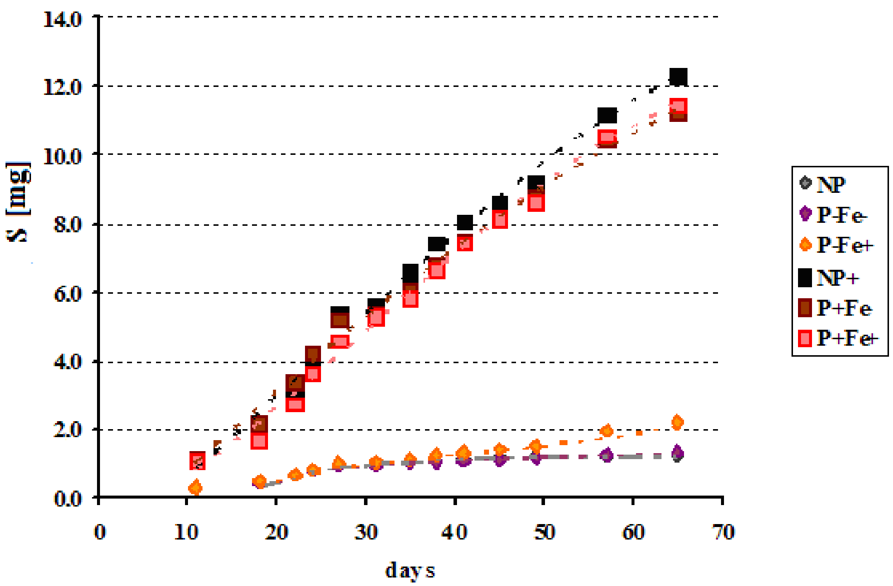

Fig. 5. Cumulative S-output [mg per column]

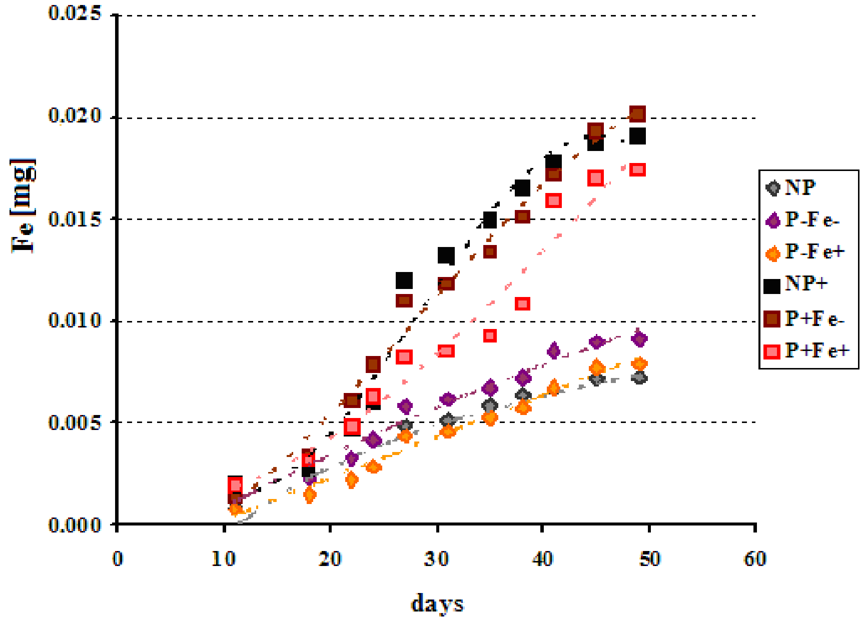

Fig. 6. Cumulative Fe-output [mg per column]

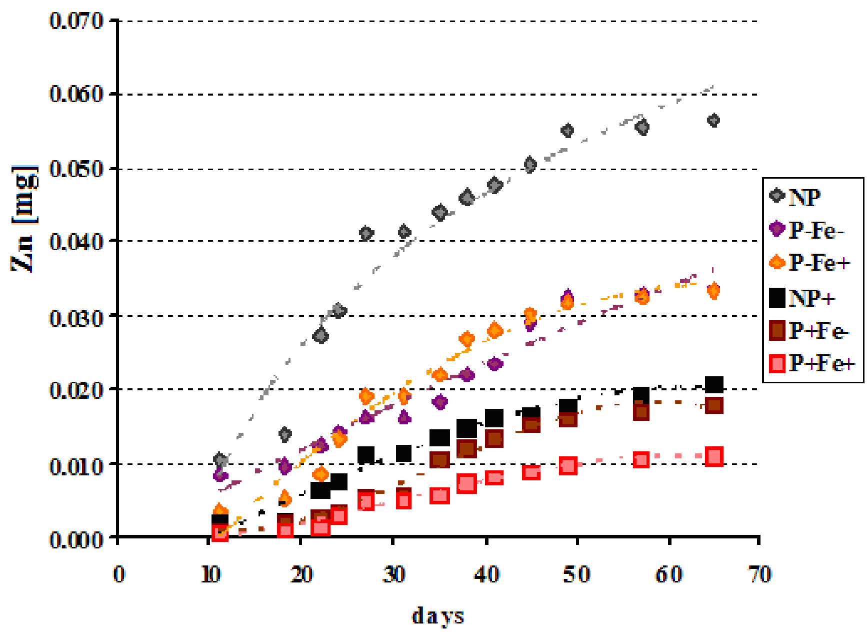

Fig. 7. Cumulative Zn-output [mg per column]

In spite of the high soil pH, some Fe was eluted from both soil column types, more from the sludge pretreated ones in spite of its higher pH. Manure addition slightly lowered the Fe-release, and Fe-treated manure surprisingly even more (Fig. 6).

Contaminant metals (Zn, Cu, Pb, Cd, Ni, V)

Zinc (and also Mg) were the only elements, of which the output from the original soil was more than from the sludge-treated one, though soils got enriched in Zn by sludge addition. Contrary to all other items investigated, addition of both manure and iron decreased Zn-mobility (Fig. 7).

Copper release from the sludge-treated soil was much more than from the original one. Additional manure application on top increased Cu-output from the columns (Fig. 8).

Leaching of Pb, Cd, Ni, and V was slightly higher from the sludge pre-treated columns (graphs not given), but some eluate-fractions of these were below detection limit of the ICP-OES.

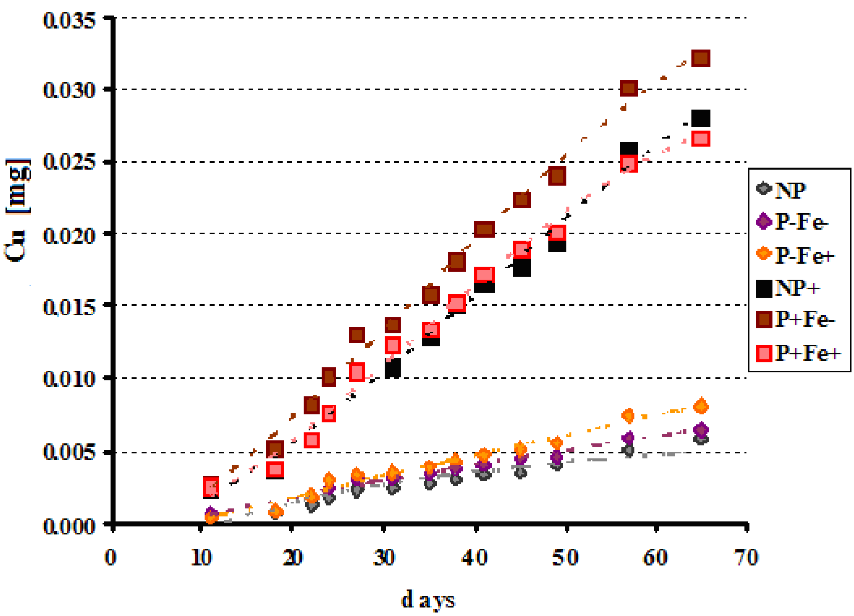

Fig. 8. Cumulative Cu-output [mg per column]

Others (B, Al, Mn, Na, Mg, Ca, Sr, Ba)

Whereas Ca and Al elution was in the same range from original and sludge-pretreated samples, Na, Sr, and Ba was slightly higher (below 10-fold), and Mg surprisingly lower from the sludge-treated samples.

Release of **Mn** was almost negligible within the first 55 days, and suddenly increased from the sludge-pretreated samples (Fig. 9).

The release of **boron** from the sludge-treated samples was slightly higher, and Fe addition decreased B elution in both cases, but due to very low levels encountered, some data were below detection limits (Fig. 10).

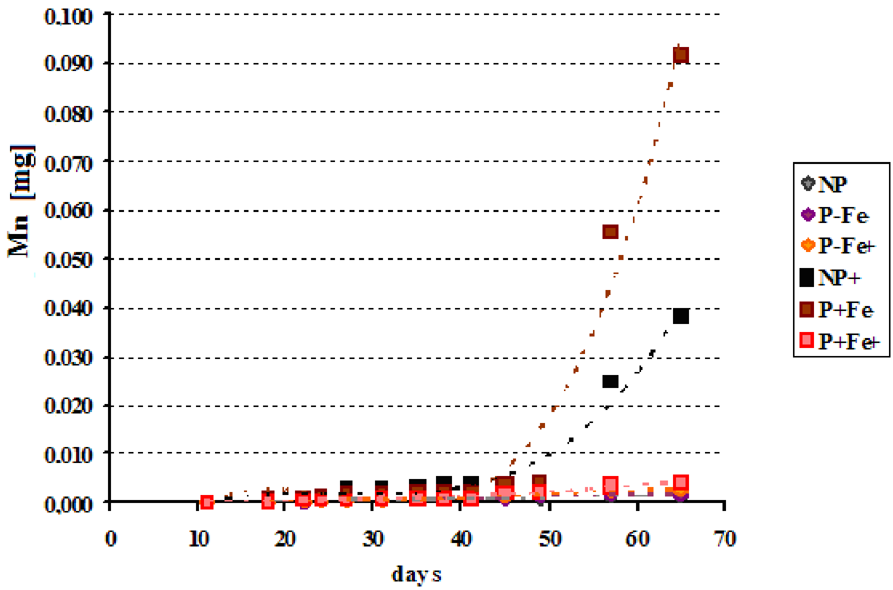

Fig. 9. Cumulative Mn-output [mg per column]

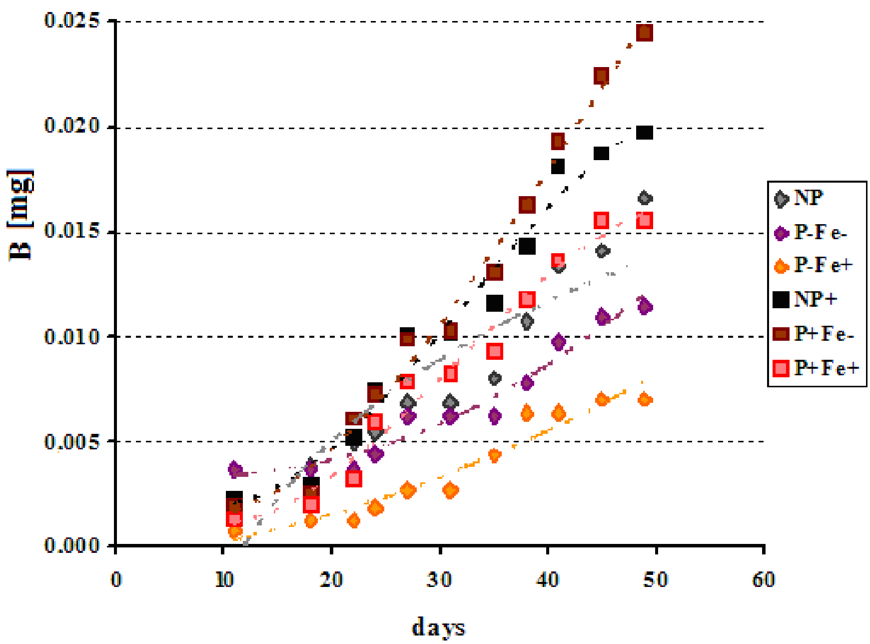

Fig 10. Cumulative B-output [mg per column]

Discussion

Effects on the N-cycle

Usually, most concern deals with the loss of nitrate and ammonia to deeper soil layers, because of nutrient losses and groundwater contamination. Though most of the N-input from sludge or manure is presumably ammonia or organic-bound nitrogen, the proportion of NO_3-N / NH_4-N, which might indicate the redox potential, did not show clear time trends and was about 20 times higher from the sludge-treated samples.

When sewage sludge applied on top of columns of sand or coal fly ash, nitrate in the leachates appeared on the second day from the sand, and on the fifth day from the fly ash. Ammonium retardation was 2 times the nitrate in the sand, and 1.5 times the nitrate in the fly ash [15, 16]. Excessive output of nitrate and ammonia from the sludge-pretreated sample columns in the current work, however, indicates intense nitrification processes.

The output of nitrate from previously high productive and currently bare soils had already caused some concerns with respect to high levels in potable waters. This led to recommendations to grow intermediate plant covers after the harvest of cereals and maize (e.g. [17]).

Effects on the P-cycle

At the pH given, P-release should be governed by Ca-Mg-phosphates, but low levels of Ca and Mg in the solid and high pH indicate vertical P-transport in organic or colloidal form. A look into references from the last years reveals that speciation of vertically transported P is greatly influenced by the actual soil life, and speeded up by conversion to metabolized forms.

When sewage sludge applied on top of columns of sand or coal fly ash, 95-98% of total P found in the effluents was ortho-phosphate [15]. But when columns of pasture soils of 11% clay were amended with poultry manure on top, water extractable and alkaline-EDTA-extractable P were highest after 4 weeks, and then decreased to a constant value. ^{31}P-NMR of alkaline EDTA extracts detected 68% of P as orthophosphate in the original soil, and 58% orthophosphate, 30% monoester phosphate and 10% diester phosphate in the poultry manure. The cumulative loss of leachate P from the columns was linear over 10 weeks of sampling, and filtration of the leachate removed just minor amounts of P [18]. Within the column, manure - P species were transformed, and diester-P accumulated in 10-15 cm depth, maybe due to the generation of microbe-derived phospholipids and nucleic acids. Leachates from P-saturated soil columns exerted a steady increase in the proportion of soluble reactive P, linked to phosphatase activities in respective batch experiments [18].

The capacity of soils of pH 5-6 and 4-6% organic carbon to adsorb additional phosphorus from poultry manures decreased with increasing duration of manure addition. The equilibrium concentration of total dissolved P increased linearly with greater amounts of total P in soil up to a threshold, above this the increase was much steeper. In high manured soils, Ca-phosphates were formed, and ^{31}P-NMR of respective alkaline soil extracts showed 51% P-monoesters and 11% diesters, and only few relevant differences between organic P-forms after short-term and long-term manure amendments [19].

In water-saturated soil columns, organic carbon addition stimulated microbial uptake of P, or at least chemical interactions between organic carbon and P reduced its solubility. In the leachates of manure amended soil columns, there was a strong relationship between cumulative total P and total organic C. Liquid and solid manures differed greatly in carbon speciation also. Liquid manures mainly consisted of carboxylic or phenolic compounds and aromatic ring structures, which are more resistant to aerobic oxidation, thus they moved to a greater depth in the soil profile [20].

It can be concluded that long-term sludge amendment at the test site significantly increased phosphate metabolic processes, which speeded up the washout.

Effects on the S-cycle

Sulfur elution was substantially higher from the sludge-pretreated sample columns, but effects of manure additions instead of water were marginal, as well as the impact of Fe-additions to precipitate FeS_2. S had not been determined in the test manure, but biogas residues are expected to contain 0.24-1.08% S in dry mass [1]. In our case, the utilized manure had 95% water, which means max. 0.5 g S per litre, and this should completely react with 1 g of Fe(II) per litre to yield insoluble FeS_2.

Iron and metals

Because of alkaline and fluctuating pH, in the absence of organic ligands, Fe and many metals should be retained in the columns mainly as hydroxides or carbonates. In fact, in this work, output of Mn as well as of Ni, Cr and V was low, but the mobility of Fe, Cu and Zn was much higher than expectable from hydroxide or carbonate solubilities. When sewage sludge applied on top of columns of sand or coal fly ash, which are presumably dead substrates, the release of Cd, Cr, Cu, Ni, Pb and Zn was below 2% and stabilized at low levels [15]. But it had been shown that in sewage sludge amended soils, increased presence of N- and S-containing groups enhances the complexation of metals. Whereas the hydrophobic fraction adsorbs onto various soil mineral phases, dissolved organic matter may also extract previously adsorbed metals, particularly Cu. Cu might be precipitated as Cu-sulfide, Cu-phosphate, taken by microbial biomass, and forms the strongest complexes with soil humics. Cu complexation with soluble low-molecular organic matter obtained from sewage sludge, occurred between pH 4 and pH 7.5 and peaked at pH 6.5. Addition of soluble organic matter from liquid sewage sludge, resulted in the release of soil adsorbed Cu from a contaminated soil of 527 mg Cu/kg [21].

In irrigated soils incubated with anaerobic sewage sludge, polluting trace metals may be immobilized, or mobilized through organic matter mobilization. Sludge added on top of soil columns at 69 Mg/ha (dry weight equivalent) led to an increase of soil pH and exchangeable Ca+Mg, and formation of Al-hydroxide precipitates. Water addition on top resulted in downward transport of Cr, Cu, Pb and Zn, and precipitation in deeper horizons, thus less than 2% of added loads were collected in the eluates. Fe particles enriched with Cr were identified [22].

Agricultural soils from Tuscany (Italy) treated with sewage sludge 10 years ago, treated recently, as well as controls, were packed into columns and loaded on top. Metal sorption applied as nitrates at pH = 2 or pH = 4 decreased in the order Pb>Cu>Zn>Ni>Mn. The sludge-pretreated soils had a higher retention capacity for all metals applied, indicating that the added organic matter was responsible for metal sorption. Grain size effects were most pronounced for Cu [23].

But the situation for Zn in this work is surprisingly reverse, which might be due to the amount of loads. Zn might be retained as ZnS, Zn-phosphates, or increased uptake by microbial biomass. At moderate loads of sludge (10 Mg/ha as dry weight; in the current work, load was 7.5 Mg/ha d.w.) added to neutral low carbon soils to increase organic matter at 3 g/kg, the retention of zinc applied to soil columns was reduced, but increased at high loads. Colloid concentrations in the leachates, which were measured by absorbance at 500 nm, were significantly associated with Zn elution. During incubation, substantial Zn moved to a non-soluble soil pool. Effects of sludge-induced changes were more pronounced in soil samples of low soil organic carbon, low clay and high sand contents [24]. Similarly, addition of composted sewage sludge to soil columns retarded the elution of added metals by simulated acid rain. Exchangeable and weak acid soluble fractions were readily transported through the column profile, leaving less mobile fractions untouched. In the combined profile, added metals were transported from the compost layer to deeper soil layers and retained there [25].

The effect of Fe-treatment on the mobility of manure added to the top of the soil columns was surprisingly low. $FeCl_2$ added during the anaerobic fermentation biogas formation process at a level of 1000 mg Fe/dm^3 had been regarded to be at optimum for CH_4 production. The re-oxidation of iron sulfides under aerobic conditions might immobilize P, which explains the lower release from the sludge-treated columns [18].

Element proportions

Proportions of elements with similar properties may tell something redox changes, depletion of phases and the like. Sludge pretreatment significantly enhanced the proportion of K/Na in the eluates, or in other words, the washout of K increased about 5 times more than of Na. At this rather low level of alkaline earths, Ca/Mg steadily decreased in eluates from the original soil, but remained about constant from the sludge-treated soil. The output of Mn was generally low, but increased sharply after 2 months from the sludge-pretreated material.

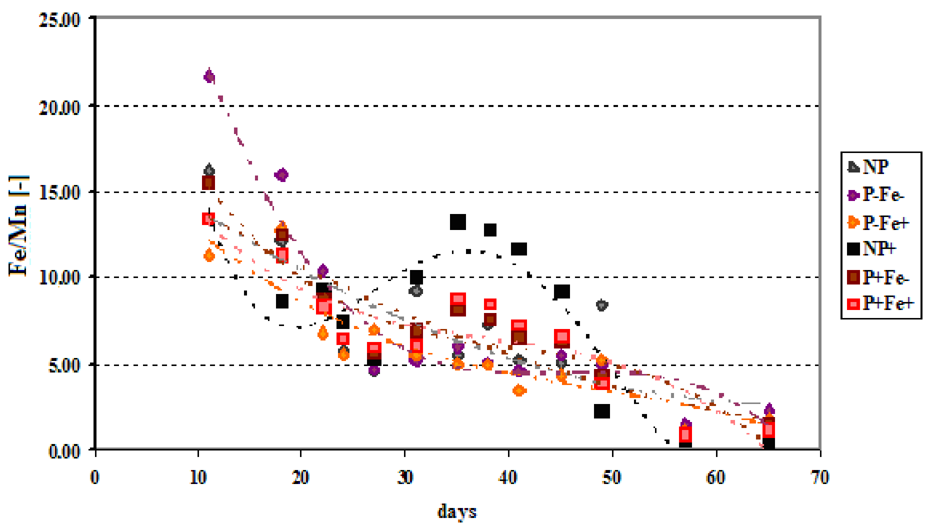

Fig. 11. Proportion of Fe/Mn in the eluates

Fe/Mn in the eluates might reflect the redox potential in the columns, it was about the same and decreased steadily, but in case of sludge-treated samples, an intermediate maximum appeared after about 35 days, which was the only case of all parameters investigated. This maximum was smaller, when manure was applied on top of the columns instead of water (Fig. 11).

Conclusions

Effects of sludge pretreatment on transport to the leachates

Sludge-pretreatment significantly lowered the retention capacity in the soil column, except for Zn. Because of high pH in the leachates, transport was presumably mediated by soluble or colloidal organic compounds. The leachate-output from sludge-pretreated columns was significantly higher for ammonium, nitrate, K, P, S, Cu, and Fe, but also slightly higher (below 10-fold) for Na, Sr, Ba, Ni and V. For Ni and V, however, as well as for Cd and Pb, some element concentrations in the eluates were below detection limit of the ICP-OES. Ca and Al elution was in the same range from original and sludge-pretreated samples, and Mg and Zn elution was even more from the columns of the original sample, though soils got enriched in Zn by sludge addition. This might indicate enrichment in increasingly formed biomass. Though the mobility of boron in soils is generally high, boron release was generally low, and slightly more from sludge-pretreated samples.

Vertical losses of nitrate and ammonium are of some concern to groundwater quality.

Increasing mobility also means increasing availability to green plants on site. The experimental conditions within this context represent bare soil without plant cover, and thus the worst case of vertical migration. Thus, keeping bare soil at sludge-treated sites should be avoided in order to protect local groundwater.

Effects of biogas manure applied on top of the columns

The manure applied on top of the soil columns contained in dry weight more N, K, P, Na, Ca and Cu than the soils, about the same level of Mg, and less Fe and Mn, in spite of Fe-spiking. Other elements had not been determined in the manure. In general, its influence on the leaching behaviour was much lower than the differences caused by long-term sludge treatment. Manure addition slightly increased leaching of P, K, Ba, Al, Ni, V just in sludge-pre-treated samples, and increased release of Mg and Ba from the original soil. Due to scattering, differences were insignificant for pH as well as K/Na and Ca/Mg proportions.

B leaching got less from the original soil, and Fe addition decreased B elution in both cases.

Manure addition increased Mn leaching after a time-lag of 55 days, but just from the sludge-pre-treated soil. The intermediate maximum of Fe/Mn, which appeared after 35 days just from the sludge-treated samples, got lower after manure addition

Effects of Fe(II) addition to the biogas manure applied on top of the columns

Beneath Fe-contents, Fe(II) addition did not change much of the composition of the biogas manure applied on top the soil columns, except slight enhancement of N, K, B, Cu and Zn, as well as some decrease of P.

Fe-addition to the manure should fix sulfide by pyrite formation, but differences between application of manure and Fe-added manure were small; the largest effect was the decrease of the output of ammonia from the sludge-pretreated samples. In addition, cumulative elution over the 60 days period got slightly lowered for K, P, B, Mg, Ba, Fe, Cu, Zn, Mn and NH_4 just from the sludge-treated soil columns, as well as B and Fe from the original. Fe-addition to the manure enhanced elution for NO_3 from the sludge-pre-treated columns, as well as Mg and Cu from the original. It resulted in no significant differences for pH, S, Na, Ca, Sr, V.

Lowering of Fe-washout by Fe addition to the applied manure was certainly surprising.

Final conclusions

Long-term sludge treatment changes grassland soils significantly. In this case, vertical migration was much more affected than changes in quasi-total concentrations (aqua regia). In spite of alkaline pH in the eluates, there was substantial leach from the columns, which means groundwater infiltration in the open field. Application of manure instead of infiltration water was of minor effect. Addition of Fe(II) to get a fixation of sulfides mainly affected the output of ammonia, but hardly the cations or anions (e.g. P) investigated.

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References

[1] Sager M. Soil Biol Biochem. 2007;39:1383-1390. DOI: 10.1016/j.soilbio.2006.12.015.
[2] Sager M. Int J Agric Sci. 2011;1(7):403-428.
[3] Zimmer J. Humuswirtschaft und Kompost aktuell. 2009;11:4-6. www.kompost.de/publikationen/hk-aktuell/.
[4] Thelen-Juengling M. Humuswirtschaft und Kompost aktuell 2011;5:1-3. www.kompost.de/publikationen/hk-aktuell/.
[5] Greffard J, Sarcia C, Bourg A. Hydrogeology. 1985;1:55-64.
[6] Legret M, Divet L, Juste C. Water Research. 1988;22(8):953-959. DOI: 10.1016/0043-1354(88)90141-8.
[7] Diepolder M, Raschbacher S, Heinz S, Kuhn G. VDLUFA Schriftenreihe 68, Kongreßband 2012 Passau, 299-306. http://www.vdlufa.de/de/index.php/veranstaltungen/124-vdlufa-kongress.
[8] Sager M. Die Bodenkultur. 2004;55(4):165-182. http://www.boku.ac.at/fos/themen/die-bodenkultur/.
[9] Hoban DJ, van den Berg L. J Appl Bacteriol. 1979;47:153-159. DOI: 10.1111/j.1365-2672.1979.tb01179.x.
[10] Deppenmeier U, Mueller V, Gottschalk G. Arch Microbiol. 1996;165:149-163 DOI: 10.1007/BF01692856.
[11] Eder G. 7. Gumpensteiner Lysimetertagung 1997:125-128.
[12] Eder G. 9. Gumpensteiner Lysimetertagung 1999: 61-66. https://www.raumberg-gumpenstein.at/cm4/de/forschung/publikationen/downloadsveranstaltungen/viewdownload/66-lysimetertagung-1999/582-stickstoffaustraege-eder.html.
[13] Husz G. J Plant Nutr Soil Sci. 2001;164:71-75. DOI: 10.1002/1522-2624(200102)164:1<71::AID-JPLN71>3.0.CO;2-1.
[14] Unterfrauner H. Model investigation of the Fe-P antagonism in soil columns with respect to fertilization with residue from anaerobic digestion. Report of the Research Project No.100372 (BMLFUW-LE. 1.3.2/0125-II/1/2008), June 2009. www.bowasan.at/organische-duengung.
[15] Łuckiewicz A. Polish J Environ Stud. 2006;15(6):869-876. http://www.pjoes.com/pdf/15.6/869-876.pdf.
[16] Łuckiewicz A, Quant B. Polish J Environ Stud. 2007;16(4):587-593. http://www.pjoes.com/pdf/16.4/587-593.pdf.
[17] Stauffer W. Schweiz Landw Forsch. 1993;32(1/2):229-234.
[18] Giles CD, Cade-Menun BJ, Liu CW, Hill JE. Geoderma. 2014;257-258:134-141. DOI: 10.1016/j.geoderma.2014.08.007.

[19] Lehmann J, Lan Z, Hyland C, Sata S, Solomon D, Ketterings QM. Environ Sci Technol. 2005;39:6672-6680. DOI: 10.1021/es047997g.
[20] Tarkalson DD, Leytem AB. Soil Sci. 2009;174(2):73-80. http://www.extension.uidaho.edu/nutrient/soilproperties/PDF/ARS1288.pdf.
[21] Ashworth DJ, Alloway BJ. Water Air Soil Pollut. 2007;182:187-196. DOI: 10.1007/s11270-006-9331-7.
[22] Egiarte G, Corti G, Pinto M, Arostegui J, Macias F, Ruiz Romero E, et al. Water Air Soil Pollut. 2009;198:133-148. DOI: 10.1007/s11270-008-9832-7.
[23] Pietrantonio M, Liberatori A, Petronio BM, Pietroletti M. Water Air Soil Pollut. 2001;132:141-151. DOI: 10.1023/A:1012044202829.
[24] Antoniadis V. Water Air Soil Pollut. 2008;190:35-43. DOI: 10.1007/s11270-007-9577-8.
[25] Kowalkowski T, Buszewski B. J Environ Sci Health A. 2009;44:522-527. DOI: 10.1080/10934520902720066.