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CHEMISTRY OF WOOD ASH LEACHATES AND THE FILTER EFFECT OF SOIL COLUMNS ON LEACHATE COMPOSITION

Master thesis
to obtain the academic degree of an
environmental engineer

submitted by

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Matrikelnummer 0440585

November 2012

Abstract

With the increasing energy production from biomass combustion, the interest in the reuse of its solid residue wood ash is also increasing. This master thesis focused on the leaching behavior of wood ash, in particular regarding metals and metalloids, in the context of the reuse of wood ash in forestry road construction. First, a leaching experiment with pure wood ash was performed; in a second experiment, this wood ash leachate was applied to soil columns to see how the leachate concentrations were affected by filtering through soil.

The first experiment showed that the leaching potential of wood ash in general decreases over time, though for some elements total leachate concentrations or even qualitative leaching trends differed between the experimental ashes. The most critical parameters concerning the compliance with legal thresholds were pH, electrical conductivity, B, Al, Cr, Fe, Ba, Pb and NO_2. The soil columns in the second experiment had a strong buffering effect on the wood ash leachate that was applied; most parameters complied with the drinking water thresholds after filtering through the soil columns.

Overall, from the ecological point of view, wood ash seems to be suitable for utilization in forestry road construction. As the composition of ashes can differ strongly in its element concentrations and speciation, it might be necessary to assess each particular ash before its application to forestry road.

Zusammenfassung

Die zunehmende Energiegewinnung aus Biomasseverbrennung bedingt ein steigendes Interesse an der Wiederverwertung des festen Verbrennungsrückstandes Holzasche. Die vorliegende Diplomarbeit behandelt das Auswaschungsverhalten von Holzasche, insbesondere der darin enthaltenen Metalle und Metalloide, in Hinblick auf den Einsatz von Holzasche im Forstwegebau. Zunächst wurde ein Sickerwasserversuch mit reiner Holzasche durchgeführt. In einem zweiten Versuch wurde das Sickerwasser der Holzasche auf Bodensäulen aufgebracht, um den Einfluss der Bodenpassage auf die Sickerwasserkonzentrationen zu untersuchen.

Der erste Versuch zeigte, dass das Auswaschungspotential von Holzasche im Allgemeinen über die Zeit abnimmt. Allerdings waren die Gesamtkonzentrationen oder sogar der Trend über die Zeit für manche Elemente in den verschiedenen Aschesickerwässern unterschiedlich. Die kritischsten Parameter hinsichtlich der Einhaltung von gesetzlichen Grenzwerte waren pH-Wert, elektrische Leitfähigkeit, B, Al, Cr, Fe, Ba, Pb und NO_2. Der zweite Versuch zeigte einen starken Puffereffekt der Bodensäulen auf das aufgebrachte Aschesickerwasser; die meisten Parameter lagen nach der Bodenpassage unter dem jeweiligen Trinkwassergrenzwert.

Insgesamt scheinen Holzaschen vom ökologischen Standpunkt her für den Einsatz im Forstwegebau geeignet zu sein. Da die Zusammensetzung der Aschen jedoch sowohl in der Konzentration als auch der Speziierung der Elemente stark variieren kann, muss möglicherweise jede Asche im Einzelnen auf ihre Eignung hin überprüft werden.

Danksagung

Mein Dank gilt als erstes meinen Betreuern Univ.Prof. Dipl.-Ing. Dr.nat.techn. Walter Wenzel und Dipl.-Ing. Dr. Alex Dellantonio für ihre Unterstützung während der Versuchsdurchführung und beim Verfassen der Arbeit selbst, sowie Dipl.-Ing. Dr. Eva Oburger für ihre Erklärungen und Ratschläge. Außerdem möchte ich auch allen anderen Mitgliedern der Arbeitsgruppe Rhizosphärenökologie für die ständige Hilfsbereitschaft und die freundliche Arbeitsatmosphäre danken.

Vielen Dank möchte ich auch meinen Eltern aussprechen, die mir dieses Studium ermöglicht haben, und meinen Freunden während der Studienzeit für die schönen gemeinsamen Momente und ihre Unterstützung. Ganz besonders möchte ich mich bei zwei wunderbaren Menschen, Jakob und Helene, für ihre unsagbar wertvolle Begleitung in den letzten zwei Jahren bedanken.

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1. Introduction

Interests in wood ash recycling

With the increasing energy production from biomass combustion, the generation of wood ash – the solid residue accruing from the thermal combustion of ligneous biomass not chemically treated after harvesting (Uckert, 2004; Knapp and Insam, 2011) – is also increasing, and along with it the interest in its reuse.

According to the Austrian Federal Waste Management Plan[1], about 149 000 tons of wood and straw ash were generated in Austria in 2008; about half of the amount (72 600 t) was landfilled. This number is expected to rise further, as the EU 20-20-20 targets stipulate an increase of the percentage of energy coming from renewable sources, in the case of Austria from 23.3 % in 2005 to 34 % in 2020. Thereof, in 2010, 40.5 % derived from biomass (Statistik Austria, 2011).

The interests in the reuse of wood ash are mainly economical ones, as landfilling in Austria costs between 70 and 300 €/t (Obernberger, 2011); but also ecological concerns to keep the plant nutrients that are contained in wood ash within the ecological cycle.

Ways of wood ash recycling

The possible ways of reuse of wood ash are determined by its three main physio-chemical properties:

Firstly, wood ash is highly alkaline (Demeyer, et al., 2001). The pH values of the ashes used in my experiment for example ranged between 11.7 and 13.2. For that reason, wood ash is being used as stabilizer for acidic soils.

Secondly, wood ash contains plant nutrients like Ca, Mg, K, P and Na in considerable concentrations. Obernberger (1997) reported mean values of 400 $g*kg^{-1}$ of dry matter for CaO and 2.6 $g*kg^{-1}$ of dry matter for P_2O_5 in bottom ashes from wood chips, sawdust and bark. This is why wood ash is broadly used as fertilizer or compost aggregate in agriculture and sylviculture.

Thirdly, wood ash has got puzzolanic properties (Tritthart, 2000), that means similar hardening properties as cement. Therefore, wood ash is used as a substitute of cement in building industry and road construction.

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[1] Österreichischer Bundes-Abfallwirtschaftsplan 2011, Bundesminister für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft.

Legal framework of wood ash recycling

Most of these ways of reuse have already been explored thoroughly and national legal frameworks have been established for their application.

The use of wood ash as compost aggregate, for example, is regulated by the Regulation on the Quality Requirements for Compost from Wastes[2], and for its use as fertilizer (wood as is excluded from the Regulation on Fertilizers[3]) a Plant Ash Directive[4] about the appropriate use of plant ash on agricultural and sylvicultural areas was released in January 2011.

The use of wood ash in forestry road construction, however, has not yet been included in the legal framework. In this case, according to the Austrian Federal Law on Waste Management[5] (§2 (1)), wood ash is considered waste material. Only if collected separately from other wastes in order to verifiably return it to a licit utilization (§4 (1)), wood ash – like any other waste material – turns into a potential recyclable that loses its status as waste material with the completion of a licit reuse process (§5 (1)).

Research objective

The contentious issue is that of a licit utilization. For a licit utilization, the ecological innocuousness as well as the benefit of the utilization needs to be proven. This master thesis forms part of a research project that explores both, the potential benefit and the ecological implication of the use of wood ash in forestry road construction.

Its aim is to assess whether wood ash can serve as a substitute for the primary resource lime. In forestry road construction, lime is used to render moist forestry roads trafficable for vehicles by binding the excessive water during the carbonation process and additionally increasing the bearing strength (University of Natural Resources and Life Sciences Vienna and Österreichische Bundesforste AG, 2011).

The potential benefit of this option is investigated by the Institute of Forest Engineering at the University of Natural Resources and Life Sciences Vienna. The

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[2] Österreichisches BGBl. II Nr. 292/2001, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Qualitätsanforderungen an Komposte aus Abfällen (Kompostverordnung).

[3] Österreichisches BGBl. II Nr. 100/2004, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, mit der Bestimmungen zur Durchführung des Düngemittelgesetzes 1994 erlassen werden (Düngemittelverordnung 2004).

[4] Österreichische Richtlinie für den sachgerechten Einsatz von Pflanzenaschen zur Verwertung auf land- und forstwirtschaftlich genutzten Flächen (Pflanzenascherichtlinie), Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, Fachbeirat für Bodenfruchtbarkeit und Bodenschutz, 2011.

[5] Österreichisches Bundesgesetz über eine nachhaltige Abfallwirtschaft (Abfallwirtschaftsgesetz), 2002.

ecological implications of this reuse possibility are explored by the Institute of Soil Research, together with project partners.

The laboratory experiments carried out in the course of this master thesis supplement the field experiments that are currently being conducted. This work focused on the leaching behavior of wood ash, in particular the leaching of metals and metalloids, as they have been reported to be the major threat to the environment, whereas organic pollutants in wood ash are usually negligible (Someshwar, 1996; Obernberger, 1997).

For this purpose, I conducted two experiments. The first one was a leaching experiment with pure wood ash, in order to obtain information about the leaching behavior of wood ash over time and the metal concentrations in the leachate. In the second experiment, the wood ash leachate from the first experiment was applied to soil columns, to see how the concentrations in the wood ash leachates would be affected by filtering through soil.

2. Materials and Methods

2.1 Wood Ash Leaching Experiment

To investigate the leaching potential of fresh wood ash over time, I conducted a leaching experiment with four different experimental ashes. In the experiment, well water was applied to pure wood ash in 20 steps and the leachates of each step were collected and analyzed.

Ashes

The four experimental ashes came from four different thermal combustion plants; each was used in three replicates:

1. The first experimental ash, in the following referred as “BH”, is a mixture of bottom ash and cyclone fly-ash from a grate furnace with granule burner, fired with wood chips and bark.
2. The second experimental ash, in the following referred to as “EG”, is bottom ash from a combined grate and injection firing system which was fed with wood chips, grinding dust and processed waste wood.
3. The third experimental ash, in the following referred to as “SIM”, is the fine fraction of bottom ash from a circulating fluidized bed furnace, fired with forest wood chips.
4. The forth experimental ash, in the following referred to as “SP”, is bottom ash of a grate furnace, fired with wood chips.

Before the start of the experiment, total element concentrations as well as water-extractable concentrations in the fresh ashes (Table 1) had been determined by the University of Natural Resources and Life Sciences Vienna and BIOS Bioenergiesysteme GmbH.

The analyses were done based on Austrian Norms on the characterization of waste. Total element concentrations were extracted with aqua regia, according to Austrian Norm EN 13657 on the characterization of waste – Digestion for subsequent determination of aqua regia soluble portion of elements[6]. Water-extractable concentrations were determined according to Austrian Norm S 2115 on the determination of the eluation capacity of waste with water[7] at a gravimetric ratio of ash to deionized water of 1:10, being shaken overhead for 24 hours.

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[6] ÖNORM EN 13657:2002, Charakterisierung von Abfällen – Aufschluss zur anschließenden Bestimmung des in Königswasser löslichen Anteils an Elementen in Abfällen, 2002.

[7] ÖNORM S 2115, Bestimmung der Eluierbarkeit von Abfällen mit Wasser, 1997.

Table 1: Total contents and water-extractable concentrations of the 4 experimental ashes

		BH		EG		SIM		SP	
		Total	W.-e.	Total	W.-e.	Total	W.-e.	Total	W.-e.
pH	[-]	13.2		13.2		11.7		12.6	
EC	[mS*cm^{-1}]	9.53		7.64		1.00		10.5	
TOC	[mg*kg^{-1}]	100000		<1000		94000		27000	
Na	[mg*kg^{-1}]	9600		18000		3010		2220	
Mg		27400		24900		5800		59600	
K		24200		23200		39300		39700	
Ca		203000		156000		43900		295000	
B	[mg*kg^{-1}]		0.265		0.000		<10		<10
Al		28700		35400		18700	20.7	19100	< 1
P		6290		5980		1990		6940	
V		41		38		10		32	
Cr		171	0.043	330	0.279	148	0.110	271	1.96
Cr(VI)							< 0.3		1.80
Mn		5490		2760		806		6170	
Fe		19800		36800		2620		11000	
Co		12	0.013	26	0.012	1	<0.3	7	<0.3
Ni		50.2	0.001	517	0.001	4.25	< 0.125	33.8	< 0.125
Cu		393	0.028	920	0.052	30.4	< 0.125	47.5	< 0.125
Zn		1780	2.542	3360	2.368	292	< 0.25	83.3	< 0.25
As		11	0.002	14	0.003	< 1	< 0.6	2	< 0.6
Mo		3		7		1		1	
Cd		6.19	0.00	3.60	0.00	0.10	< 0.025	0.51	< 0.025
Ba			46.0		28.6		1.7		27.8
Pb		284	0.018	939	0.309	10.3	< 0.6	8.16	< 0.6
NO$_2$-N	[mg*kg^{-1}]						<2		<2
NO$_3$-N							<2		<2
Cl		296		207		1.4	1.4	34	34
SO$_4$							370		190
PO$_4$							<2		<2

Experimental set-up

Barrels with an average diameter of 35 cm were filled with wood ash; 20 kg of wood ash were used for each replicate.

At the bottom, a 3-cm marble grit layer (grain size 4-8 mm) was installed for drainage. Then 20 kg of ash were placed in the barrel, separated from the gravel layer by a membrane to avoid translocation of material. On top of the wood ash, a 3 cm layer of silica sand (grain size 0.5-2.0 mm) for water distribution and reduction of evaporation was placed, again separated from the ash by a membrane. Additionally, a “ring” (d=28 cm) was placed on top to avoid bypassing of water between the ash body and the barrel (see Fig. 2).

The experimental ashes were installed with bulk densities of about 1.04 g*cm^{-3} for BH and EG, 1.22 g*cm^{-3} for SIM and 0.99 g*cm^{-3} for SP.

Fig. 1: Experimental set-up of the wood ash leaching experiment in barrels

Fig. 2: Ring for water distribution and top layer of silica sand

Water application

Well water with a pH around 7 was applied in 20 steps with a watering can. In each step I applied 5 L, summing up to a total of 100 L, or 1040 mm in relation to the surface. The total amount of water added corresponds approximately to the annual average precipitation in Austria (Hydrographischer Dienst Österreich, 2009).

The time interval between the water applications was 3-4 days, the total duration of the experiment was 10 weeks. Before each subsequent step of water application, I collected the leachate samples for analysis.

Water extractions

Water-extractable concentrations were determined in the ashes also after the leaching experiment, in order to compare them to the water-extractable concentrations in fresh ashes, and to compare the water-extractable concentrations according to Austrian Norm to the concentrations actually leaching out from the ashes.

Water-extractable concentrations after the experiment were again determined based on Austrian Norm S 2115 on the determination of the eluation capacity of waste with water[8], being shaken for 24 hours at a gravimetric ash-to-deionized water ratio of 1:10, and were then filtered through folded paper filters (Munktell Folded Filters, diameter: 150 mm, 80 g*m², grade: 14/N).

In order to avoid changes in the chemistry of the ashes, the ash samples were not dried before the water extraction. Separate samples were dried at 105°C for 48 hours. The factor of wet-to-dry weight was calculated and included for correction of the element concentrations measured in the wet samples.

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[8] ÖNORM S 2115, Bestimmung der Eluierbarkeit von Abfällen mit Wasser, 1997.

2.2 Soil Column Experiment

The wood ash leaching experiment described previously did provide information about the leaching potential of wood ashes, but without considering the environmental context of their use in forestry road construction, where the wood ash leachate would filter through the soil underneath before reaching the groundwater. Therefore, I performed a second experiment to investigate the interaction of wood ash leachate with soil.

For that purpose, I applied a composite sample of the SIM ash leachates from the wood ash leaching experiment to 20-cm soil columns. For the composite sample, I mixed together 1L of each SIM replicate leachate of each sampling step during the whole duration of the wood ash leaching experiment. The leachate was applied in 26 steps and samples from each step were collected and analyzed.

Soil

One soil in three replicates was used in the experiment. The soil was characterized as Eutric Cambisol with a texture of loamy sand (508 $g*kg^{-1}$ sand, 417 $g*kg^{-1}$ silt, 75 $g*kg^{-1}$ clay). It had a pH of 6.26 in H_2O and a pH of 5.43 in $CaCl_2$. Its maximum water holding capacity was 42.5 %, which was determined by saturation of the soil in a filter over night and subsequent drying at 105°C.

Experimental set-up

In each column, I installed 2 kg of soil, with a bulk density of 1.27 $g*cm^{-3}$. At the bottom and top of each soil column, a 0.30-µm nylon membrane was placed to prevent translocation of soil material. On top, a 2-cm layer of polyethylene granulate (d= 0.3-0.4 cm) was placed to diminish evaporation.

The columns were made of polymethyl methacrylate and had a diameter of 10 cm and a bottom outlet diameter of 2 mm.

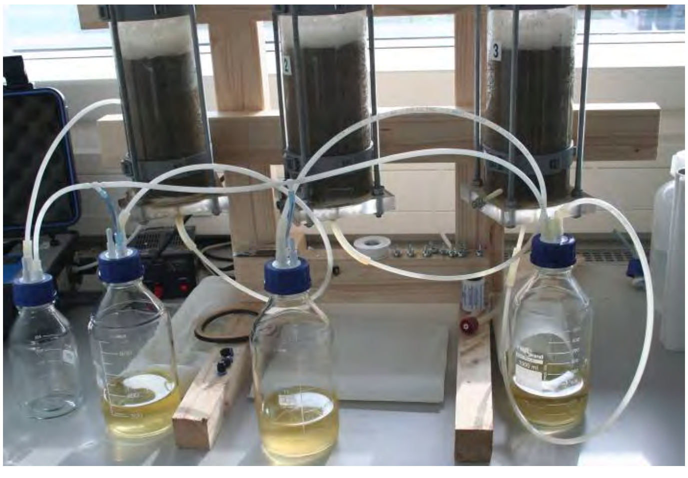

Fig. 3: Experimental set-up of the soil column experiment

Application of wood ash leachate

Initially, each soil column was saturated from the bottom with about 900 mL (850 mL corresponded to the maximum water holding capacity for 2 kg of the soil) of the SIM composite sample and left 6.5 hours for equilibration.

Then I re-saturated the columns in 25 steps from the top, applying 300 mL feed in each step, which summed up to a total of 955 mm in relation to the surface. The amount of 300 mL for re-saturation was chosen based on the amounts used by Mikovits (2012) in previous soil column experiments.

Leachate samples from the soil columns were collected before each step of re-saturation. A slightly negative pressure was applied with a suction pump which was activated after each re-saturation step for one minute, in order to prevent clogging of the soil. Time intervals between the re-saturation steps differed between 2.5 and 49 hours; the experiment lasted 2 weeks in total.

The exact time intervals between the steps were the following: 6.5 h (initial equilibration), 18 h, 4.5 h, 19.5 h, 3 h, 3 h, 19 h, 2.5 h, 2.5 h, 18 h, 49 h, 3 h, 21 h, 2.5 h, 2.5 h, 19 h, 2.5 h, 21.5 h, 2.5 h, 2.5 h, 19 h, 2.5 h, 2.5 h, 19 h, 2.5 h, 4 h.

2.3 Chemical Analysis

All samples (wood ash leachates, water extractions and soil column leachates) were filtered through a paper filter and stored at 4°C. Samples for the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were acidified with 1 mL of HNO_3 (65 %) added to 15 mL of sample before storage.

For all samples, pH and EC were measured directly in the filtered leachate samples. Element analysis was done on a PerkinElmer ICP-MS ELAN DRCe. Sodium, Mg, K, Ca, Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Ba and Pb concentrations were measured.

In the wood ash leachate samples, additionally the anions chloride, nitrite, nitrate, phosphate and sulfate were measured using ion chromatography (Dionex DX500).

Also the dissolved organic carbon (DOC) was determined in the wood ash leachate samples. It was estimated from the absorbance of light at 254 nm (UV), according to the correlation described by Brandstetter et al. (1996):

$$\text{DOC (mg*L}^{-1}\text{)} = 0.449 * A_{254\text{ nm}}\ (\text{m}^{-1}) + 1.0 \qquad (1)$$

The absorbance of light was measured on a Photometer Agilent 8453 UV-visible Spectrometer Spectroscopy System.

Measurements accuracy

All experiments were performed in three replicates. The standard errors (SE) are displayed in the graphs of the results section.

In the ICP-MS element analyses, reference materials and at least 3 instrumental blanks per measurement were measured along with the samples in order to monitor deviations from the calibration standards of the instrument. Along with the samples of the water extractions, additionally three experimental blanks of deionized water were measured, that had been shaken, filtered and acidified in the same way as the samples, in order to assess measurement accuracy. The instrumental limit of quantification (LOQ) was determined for all measurements. For the water extraction samples also the experimental LOQ was determined; the measured concentrations were compared to the relevant LOQ.

3. Results & Discussion

3.1 Wood Ash Leaching Experiment

The results of the wood ash leaching experiment are discussed in four different aspects:

Firstly, the leachate concentrations from the four experimental wood ashes are discussed as to their development over time and their absolute values.

Secondly, I compare the water-extractable concentrations according to Austrian Norm from the ashes before and after the experiment, to see how much of the initial water-extractable concentrations leached out during the experiment.

Thirdly, I compare the element concentrations in the wood ash leachate to the water-extractable concentrations according to Austrian Norm, to obtain information about the relation of the water-extractable concentrations to the concentrations that actually leached out.

Finally, I relate the wood ash leachate concentrations to legal threshold values to find out which parameters might be expected to pose a threat to the environment and/or human health.

3.1.1 Leaching behavior

Two main aspects related to the leaching behavior of wood ashes were investigated: On the one hand the general leaching behavior of wood ashes over time, on the other hand the concentrations and leaching potential of specific elements which might cause adverse effects on the environment.

For that reason, parameters that give an indication of the general leaching behavior, such as electrical conductivity (EC), pH, macroelements and anions were measured as well as trace metals and metalloids. First, I discuss the parameters indicating the general leaching behavior of wood ash, then the leaching of critical trace elements.

Electrical conductivity & pH

The following figures show the change of EC (Fig. 4) and pH values (Fig. 5) of the four ash leachates (EG, BH, SIM, SP) over the 20 water application steps of the experiment. The corresponding value of the input water at each step is displayed as well.

The first leachate from EG ash accrued after the first water application, but the first leachates from BH and SIM ash after the second water application and the first SP leachate not until the third application of water. This is the reason why the four graphs start at 5 L, 10 L and 15 L along the x-axis, respectively.

Wood ash in general has a very high EC, which indicates the presence of a high amount of mobile ions. In the wood ash leaching experiment, the leaching of ions, indicated by the EC (see Fig. 4), showed a general trend of decreasing concentrations over time and a strong initial leaching during the first few steps. The initial EC was 24 mS*cm^{-1} in BH, 28 mS*cm^{-1} in EG, 9.6 mS*cm^{-1} in SIM, and 106 mS*cm^{-1} in SP leachate. After the application of the first 30 L of water, it had dropped to values between 12 mS*cm^{-1} (SP) and 4.5 mS*cm^{-1} (SIM) and only decreased further to values between 9.7 and 0.8 mS*cm^{-1} during the remaining sampling steps. The water that was applied to the wood ash during the experiment had an EC of about 50 µS*cm^{-1}, which is 1-3 orders of magnitude below the EC of the wood ash leachates.

All four ash leachates showed similar qualitative EC changes, but differed in absolute values, owed to the different EC of the fresh ashes (cp. Table 1) but also to the different speciation of ions in the ashes as well as other ash characteristics.

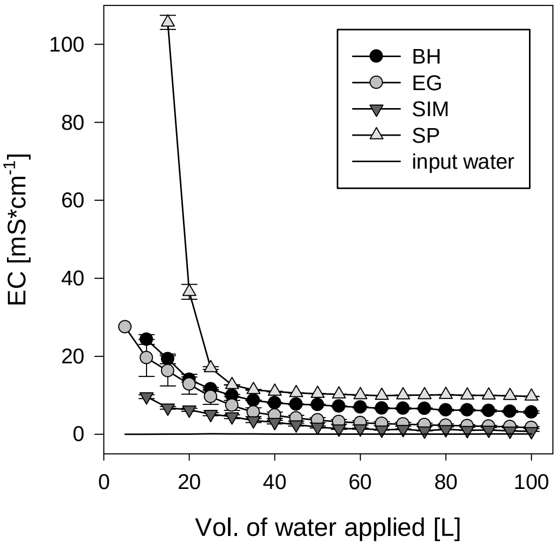

Fig. 4: Electrical conductivity and standard errors of the leachates of the 4 experimental ashes in the wood ash leaching experiment (n=3)

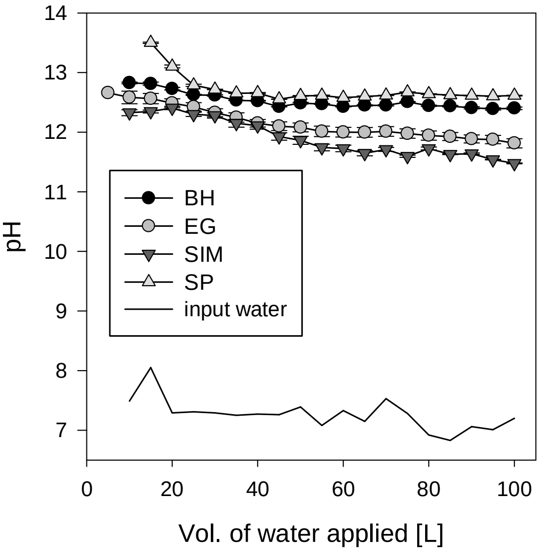

Fig. 5: pH values and standard errors of the leachates of the 4 experimental ashes during the wood ash leaching experiment (n=3)

Fig. 5 shows the change of pH values during the experiment. The input water that was applied to the ashes had a pH around 7. The pH values in the four ash leachates ranged from 12.3 to 13.5 at the beginning and decreased to values between 11.4 and 12.6 at the end of the experiment, indicating that the alkalinity in the ashes had decreased only little in response to the application of “one year’s precipitation”.

While pH stabilized in BH and SP leachate after about half of the total input water had been applied, it decreased continuously in EG and SIM ash leachate until the end of the experiment.

Macroelements

The elements Na, Mg, K and Ca belong to the major elements contained in wood ash (Demeyer, et al., 2001). Their concentrations in the leachates were measured primarily to gain information about the general leaching behavior of wood ash, not because of their adverse effects on the environment.

While up to 800 mg*L^{-1} of Ca and up to 2000 mg*L^{-1} of Na and K were detected in the leachates, Mg concentrations were below 1 mg*L^{-1}. (Potassium concentrations in BH leachate in the first sampling step, in EG leachate in the first three sampling steps and in SP leachate in the first two sampling steps were even higher than 2000 mg*L^{-1}, but exceeded the upper LOQ of the ICP-MS measurement device and could therefore not be quantified properly.) This coincides with the results of leaching tests performed by Steenari et al. (1999), who found Ca, Na and K to be the dominant cations present in wood ash leachates, whereas leaching rates for Mg and P were low. Therefore, only Ca, Na and K concentrations are discussed here.

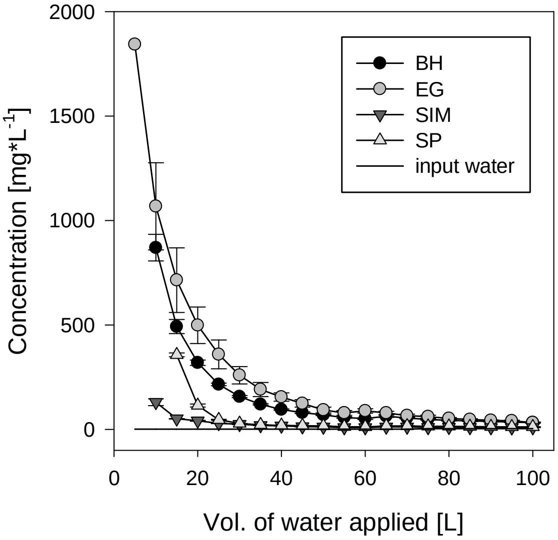

Fig. 6: Sodium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

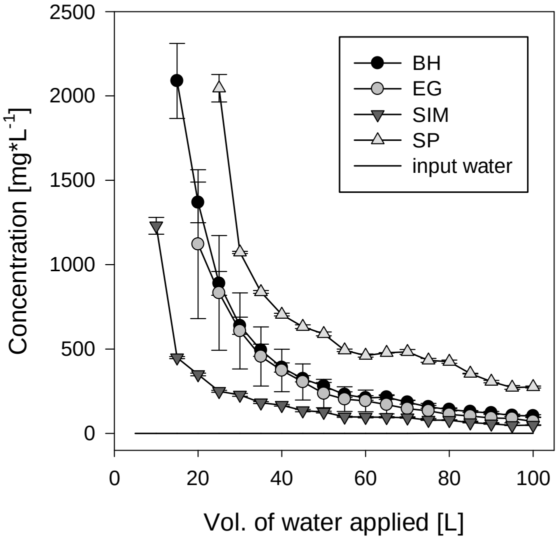

Fig. 7: Potassium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Sodium and K showed high initial leachate concentrations that decreased during the consecutive leaching steps, as a significant fraction of these alkali metals is present in form of highly soluble salts (Steenari, et al., 1999; Demeyer, et al., 2001).

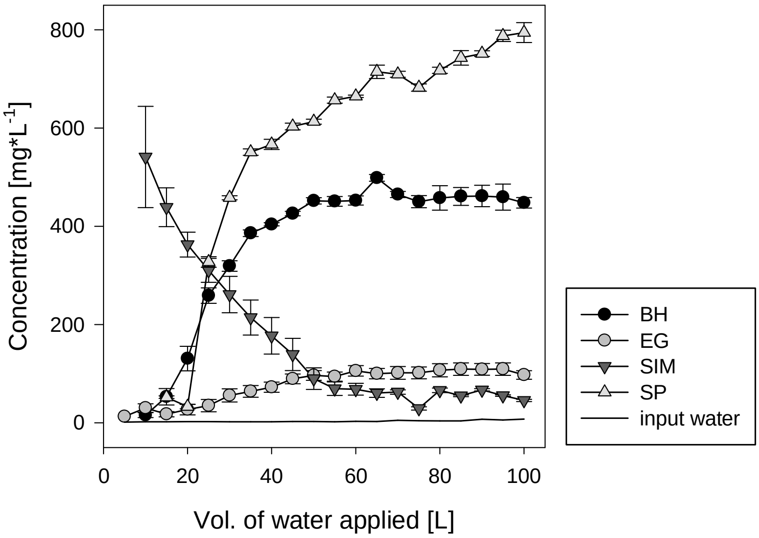

Fig. 8: Calcium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Ca showed a decrease in leachate concentrations only for SIM ash, whereas it was increasing in BH, EG and SP ash leachates.

The initial changes in element concentrations of BH and SP leachates (EG leachate concentrations were low in general, so it was hard to observe) resembled first order chemical reaction curves. Possibly, Ca was initially mainly present in form of oxides that first needed to be hydrated to calcium hydroxide.

Steenari and Lindqvist (1997) described the hydration of calcium oxide as the first step of carbonation:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

The carbonation process would go on as following in reaction with carbon dioxide from the air:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

This second step might have been inhibited in the experiment due to the partial saturation of the pores with water that occurred after the application of the first 15-20 liters, and due to the fact that carbonation occurs primarily in the surface layer, forming a $CaCO_3$ layer on the surface that is hindering the transport of CO_2 to the interior (Steenari, et al., 1999). During the experiment, I could visually observe the formation of such a “crust” on the surface of SIM and SP ash. With the lack of CO_2 and the continuous water application, $Ca(OH)_2$ might have dissolved in the water instead. I also observed the precipitation of $CaCO_3$ at the barrel outlets, where the dissolved $Ca(OH)_2$ had enough contact time with the CO_2 in the air to precipitate as $CaCO_3$.

The reason for the decrease of Ca concentrations in SIM ash leachate from the beginning on might be that Ca in SIM ash is already to a major part present as $Ca(OH)_2$ from the beginning. The speciation of alkaline earth metals in wood ash depends on characteristics of the combustion process, such as the combustion temperature (Obernberger, 1997; Demeyer, et al., 2001). The fact that SIM ash derives from a plant with a different combustion technology than the other three experimental ashes, namely from a circulating fluidized bed furnace, whereas the other ashes derive from grate furnaces, might explain the different speciation of Ca in SIM ash.

Another possible reason might be that SIM ash was “aged” or pre-treated in some way before its use in the experiment. In this case CaO might have been carbonated to $CaCO_3$ to a large extent during storage by being exposed to the air, and then the remaining Ca salts got washed out quickly in the wood ash experiment. This is, however, not likely, as the experiment was designed to be conducted with “fresh” ashes that hadn’t undergone an “aging” process before; the experimental ashes were therefore stored in closed barrels to avoid access of water and air during storage.

Anions

Anions like chloride, phosphate and sulfate are also contained in wood ashes in considerable concentrations and were therefore measured to gain information about the general leaching behavior of wood ashes. Nitrite and nitrate concentrations were determined as well because of their adverse effects on the environment, although they should not be present in high concentrations, as N in a complete combustion process is transformed into gaseous constituents (Demeyer, et al., 2001). Apart from the measured anions, OH^- ions are expected to be contained in high amounts (Steenari, et al., 1999).

Sulfate (Fig. 9) was present in the leachates in the highest concentrations, with initial concentrations of about 4100 mg*L^{-1} in EG, 2600 mg*L^{-1} in SP, 1300 mg*L^{-1} in SIM and 80 mg*L^{-1} in BH ash leachate. The major part of sulfate was washed out during the first few steps of the experiment. After the application of the first 30 L of water, leachate concentrations had decreased to values between 15 and 75 mg*L^{-1} in BH, SIM and SP leachates, and only a slow further reduction occurred during the application of the remaining 70 L, leading to final values between 5 and 15 mg*L^{-1} in BH, SIM and SP leachates. EG ash showed a slower release of sulfate; only after the application of 60 L of water no strong further reduction occurred.

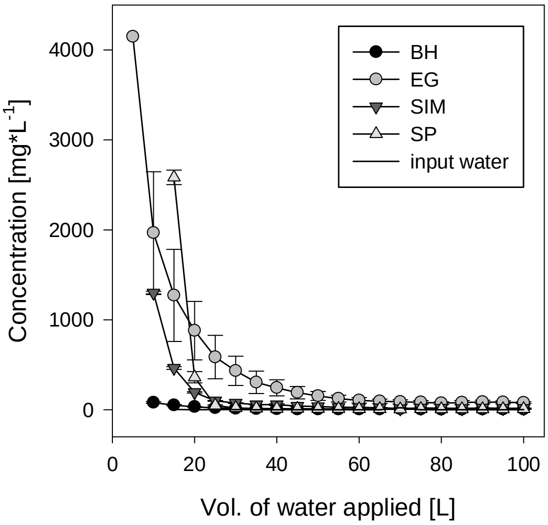

Fig. 9: Sulfate leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Fig. 10 displays the chloride leachate concentrations of the four experimental ashes. Initial chloride concentrations were by far the highest in EG ash leachate with about 500 mg*L^{-1}. The other three ash leachates contained initial concentrations of 90 mg*L^{-1} (SP), 65 mg*L^{-1} (BH) and 8 mg*L^{-1} (SIM). Similar to sulfate (cp. Fig. 9), the main reduction in leachate concentrations for BH, SIM and SP occurred during the first 30-40 L of water applied, falling to values below 10 mg*L^{-1} in BH and SP leachates and below 1 mg*L^{-1} in SIM leachate after the first 8 steps. Again, the rate of decrease was smaller in the EG leachate. After 60 L of water applied, EG leachate concentrations had fallen to 31 mg*L^{-1}; during the application of the remaining 40 L it only decreased further to 16 mg*L^{-1}.

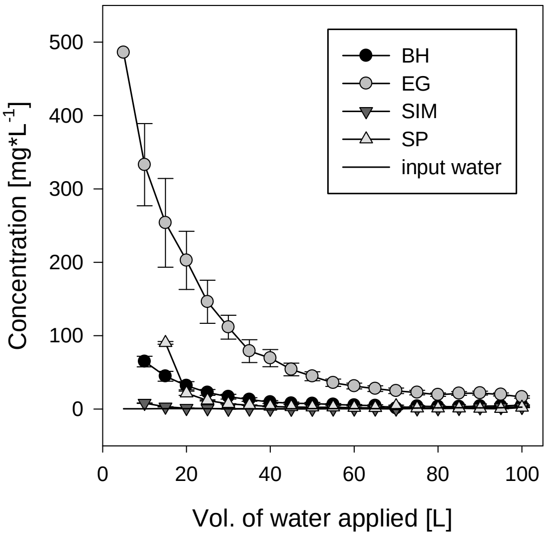

Fig. 10: Chloride leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

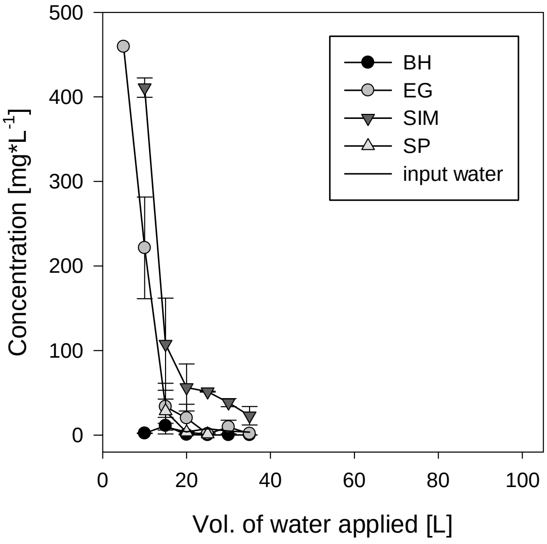

Fig. 11: Phosphate leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Phosphate leachate concentrations are displayed in Fig. 11. At the beginning, they were especially high for EG (460 mg*L^{-1}) and SIM (410 mg*L^{-1}) ashes; initial leachate concentrations of BH and SP ashes were 2 and 28 mg*L^{-1}, respectively. Phosphate leachate concentrations showed a pronounced decrease during the first few steps of the experiment and fell below the limit of detection after the application of the first 35 L of water in all four ash leachates.

Fig. 12 shows the development of nitrite leachate concentrations in the four experimental ashes. Initial leachate concentrations were especially high in SP leachate with 16 mg*L^{-1}, and decreased strongly during the application of the first 30 L of water to 0.5 mg*L^{-1}. In the other three ash leachates, initial nitrite concentrations were 8 mg*L^{-1} for EG, 4 mg*L^{-1} for BH and 0.7 mg*L^{-1} for SIM leachate. The main reductions in BH and SIM leachate concentrations occurred during the first 30-40 L. The “jump” in the concentrations at 25 L is likely to be an error of measurement.

Nitrite leachate concentrations in EG leachates decreased during the first 40 L, but increased during the following 25 L, before starting to decrease again. No explanation could be found for this increase.

Nitrite concentrations were below the limit of detection in the input water applied during the entire experiment.

For nitrate (Fig. 13), initial concentrations were also highest in SP leachate with about 32 mg*L^{-1} and decreased very strongly during the application of the first 30 L of water to 1.2 mg*L^{-1}. Initial nitrate leachate concentrations in the other three ash leachates were 8 mg*L^{-1} in EG, 4 mg*L^{-1} in BH and 3.2 mg*L^{-1} in SIM leachate. The main reductions also occurred during the first 30 L of water applied.

EG leachate concentrations again showed a slight increase during the last 20 L, which could not be explained.

Considering that N after a complete combustion should be found in the solid residues only in negligible concentrations, nitrite and nitrate concentrations in some ash leachates, especially from SP ash, seem surprisingly high and suggest further optimization of the incineration process.

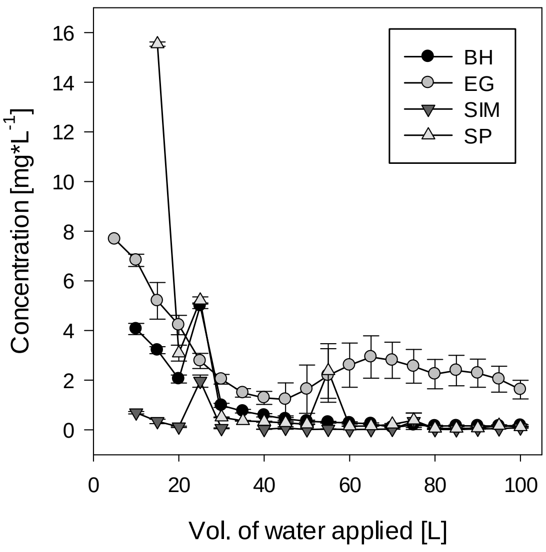

Fig. 12: Nitrite leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

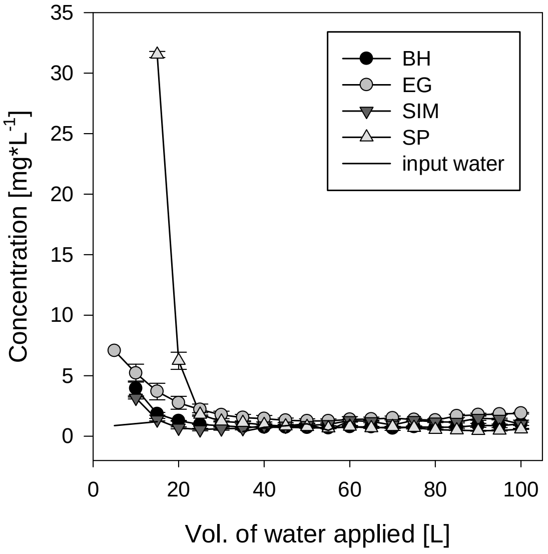

Fig. 13: Nitrate leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Dissolved Organic Carbon (DOC)

The DOC is a measure for the water soluble organic compounds contained in the leachates. As the total organic carbon contained in wood ash (Table 1) is a critical parameter for its deposition in landfills, it is of interest to know how much of it gets dissolved and washed out.

Initial DOC concentration was highest in SP leachate with 3.4 mg*L^{-1} and decreased rapidly during the first 30 L of water applied to 1.1 mg*L^{-1}. EG leachate initially contained 2.7 mg*L^{-1} of DOC, but showed a slower rate of reduction than SP leachate concentrations; after the application of the first 20 L it contained higher concentrations of DOC than the SP leachate. SIM and BH leachates initially both contained about 1.2 mg*L^{-1} DOC. At the end of the experiment, all four ash leachates contained about 1 mg*L^{-1} DOC.

Brandstetter et al. (1996) found that a small fraction of DOC does not absorb UV light, which probably corresponds to the saturated aliphatic compounds. That is why I also measured the absorbance at wavelength 400 nm (Fig. 15), which provides a qualitative indication of this fraction. SP ash leachate had the highest initial absorbance at 400 nm but the major part of non UV-absorbing DOC apparently was washed out in the first leaching step. Absorbance values decreased for all ash leachates during the experiment, though they didn't show a continuous decrease in the second half of the experiment in BH, EG and SP ash leachates. These variations, however, may be within the error of measurement.

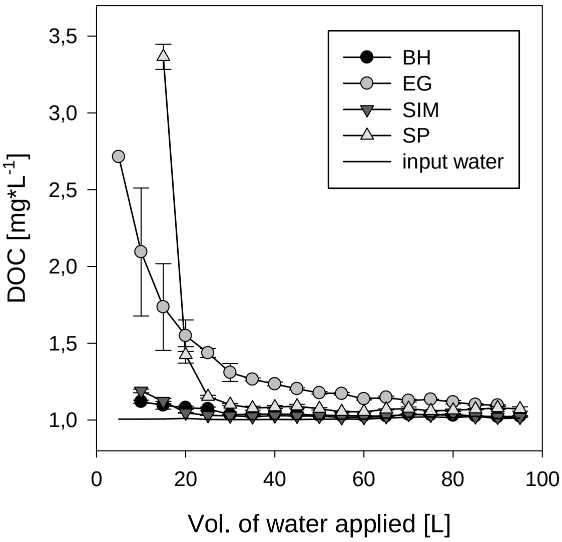

Fig. 14: Dissolved organic carbon leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

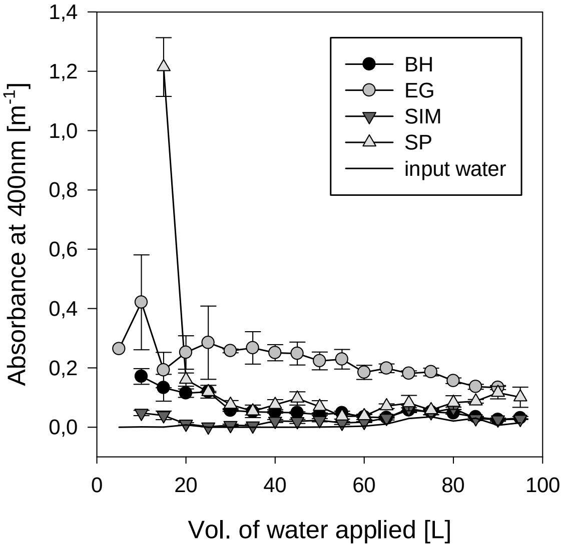

Fig. 15: Absorbance of light at 400 nm and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Trace elements

Molybdenum, Cadmium, Arsenic:

The figures below show the leachate concentrations of Mo, Cd and As during the experiment. All three elements followed the general trend of decreasing leachate concentrations over time.

Initial Mo leachate concentrations (Fig. 16) were around 1.1 mg*L^{-1} in EG, 0.7 mg*L^{-1} in SP, 0.4 mg*L^{-1} in SIM and 0.15 mg*L^{-1} in BH leachate. The main part of soluble Mo in BH, SIM and SP ashes was washed out with the first 30 L of water applied, reaching leachate concentrations below 0.04 mg*L^{-1} after the first six steps. Concentrations in EG leachate showed a lower initial reduction; after 30 L of water applied, the leachate concentration had only decreased to 0.2 mg*L^{-1} and reduced further to 0.02 mg*L^{-1} until the end of the experiment. Molybdenum concentrations were below the LOQ of 0.0016 mg*L^{-1} in the input water that was applied to the ashes.

Cadmium (Fig. 17) showed a very similar leaching behavior as Mo: Initial concentrations were highest in EG leachate with 0.008 mg*L^{-1}, followed by SP with 0.005 mg*L^{-1}, SIM with 0.003 mg*L^{-1} and BH with 0.001 mg*L^{-1}. BH, SIM and SP leachate concentrations decreased rapidly during the first steps of the experiment and fell below the LOQ (1.4*10^{-4} mg*L^{-1}) after the application of 30-40 L of water, whereas EG leachate concentrations decreased slower and fell below the LOQ after the application of 85 L of water. Cadmium concentrations in the input water were below the LOQ.

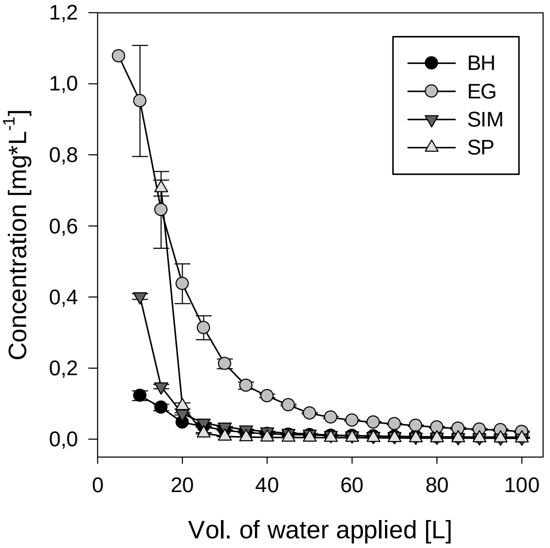

Fig. 16: Molybdenum leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

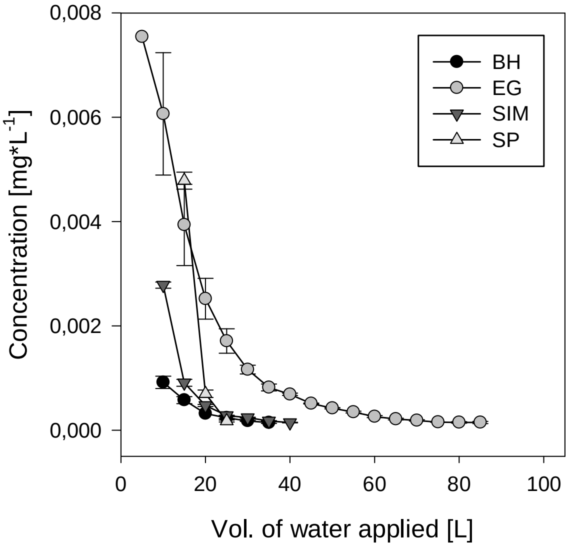

Fig. 17: Cadmium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Arsenic (Fig. 18) initial leachate concentrations lay around 0.02 mg*L^{-1} in EG leachate and around 0.01 mg*L^{-1} in BH and SP leachates. Arsenic showed a very strong reduction of leachate concentrations during the first few sampling steps. EG leachate concentrations fell below the LOQ (corresponding to 0.0018 mg*L^{-1}) after the first five sampling steps, BH and SP leachate concentrations after the first two steps. Arsenic concentrations were below the LOQ in SIM ash leachate and in the input water during the entire experiment.

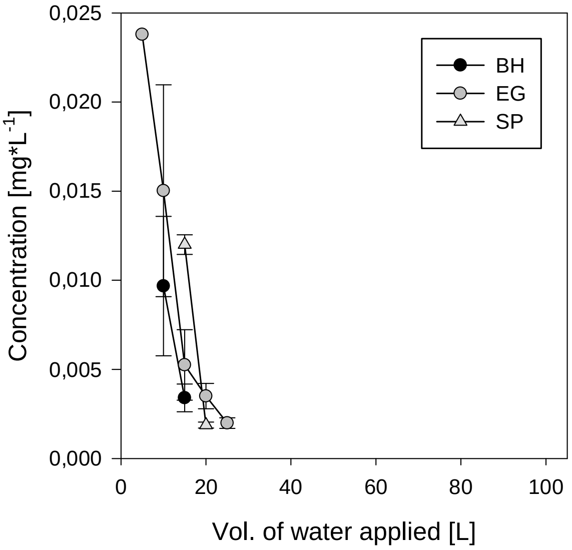

Fig. 18: Arsenic leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Chromium:

Fig. 19 displays the total Cr concentrations in the ash leachates. The initial Cr concentration was very high in SP ash leachate with 28 mg*L^{-1}. The initial leachate concentrations of the other three ashes, in comparison, were between 1.3 mg*L^{-1} (BH) and 0.08 mg*L^{-1} (SIM). Also, the water-extractable concentration of Cr in the fresh ashes was by a factor of 10 higher for SP ash (1.96 mg*kg^{-1} of dry matter; cp. Table 1) than for the other three ashes, though total contents were in the same range for all four ashes (170-330 mg*kg^{-1} of dry matter). This difference is explained by the fact that 1.80 mg*kg^{-1} of the total water-extractable Cr in SP ash were present as the most soluble species Cr(VI), which was washed out from the wood ash in high concentrations at the beginning of the experiment. The final Cr leachate concentrations ranged between 0.06 mg*L^{-1} (EG, SP) and 0.002 mg*L^{-1} (SIM).

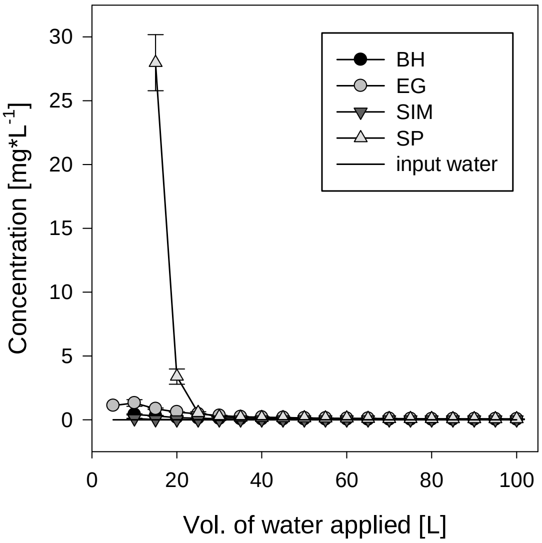

Fig. 19: Chromium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Manganese:

Manganese leachate concentrations displayed in Fig. 20 showed a high initial decrease from 0.012 mg*L^{-1} in SP leachate and 0.006 mg*L^{-1} in EG leachate to values below 0.002 mg*L^{-1} after the first two sampling steps. Manganese leachate concentrations in BH and SIM leachates were below 0.002 mg*L^{-1} from the beginning. After the application of the first 30-40 L, the concentrations mostly were below the LOQ in BH, EG and SIM leachates.

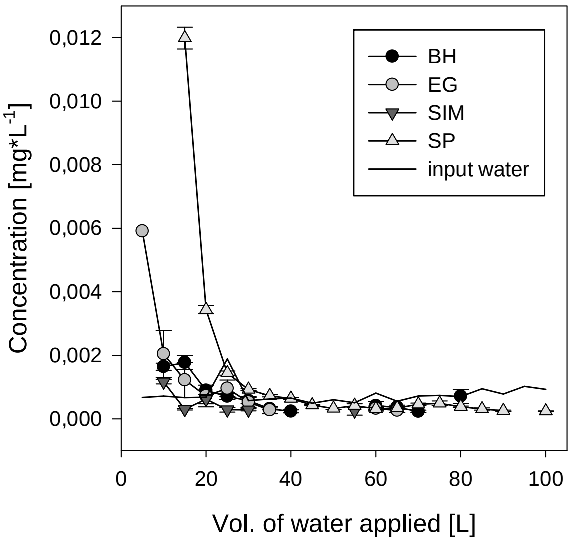

Fig. 20: Manganese leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Lithium, Boron, Copper, Lead, Zinc:

Lithium, B, Cu, Pb and Zn generally followed the trend of decreasing leachate concentrations over time, though these elements in some ashes reached their maximum leachate concentrations not until the second or third leaching step and only then decreased continuously.

Lithium (Fig. 21) reached its maximum leachate concentrations of 0.7 mg*L^{-1} in SP, 0.4 mg*L^{-1} in EG and 0.1 mg*L^{-1} in BH leachate in the second sampling step, in SIM leachate (0.1 mg*L^{-1}) in the third sampling step. Until the end of the experiment, leachate concentrations fell to values between 0.4 mg*L^{-1} (SP) and 0.006 mg*L^{-1} (SIM). The “drop” in concentrations between 60 and 65 L of water applied, especially visible in the development of SP leachate concentrations, resulted from the split-up of the ICP-MS element analysis in two measurement series at this point.

The B leachate concentration (Fig. 22) was highest in SP leachate in the first sampling step with around 13 mg*L^{-1}, followed by SIM leachate with around 7 mg*L^{-1} in the third sampling step, and EG and BH leachate with around 1 mg*L^{-1} in the second sampling step. Leachate concentrations decreased to values below 0.8 mg*L^{-1} at the end of the experiment in all four ash leachates; B concentrations in BH leachate dropped below the LOQ after 60 L of water applied. Boron concentrations in the input water were below the LOQ during the entire experiment. The “drop” in SIM and SP leachate concentrations between 60 and 65 L of water applied is again owed to the split-up of the ICP-MS analysis in two measurement series at this point.

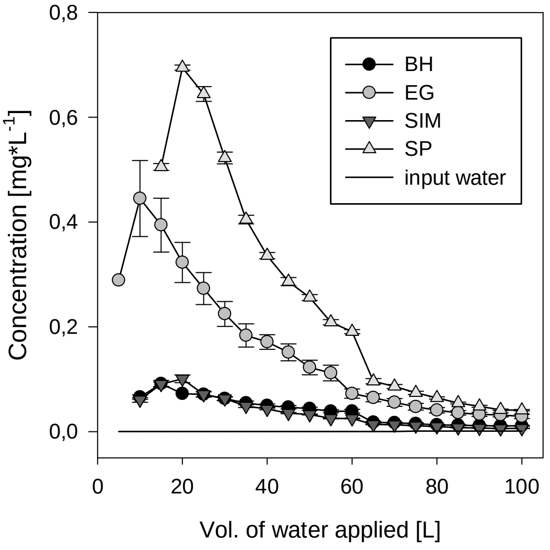

Fig. 21: Lithium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

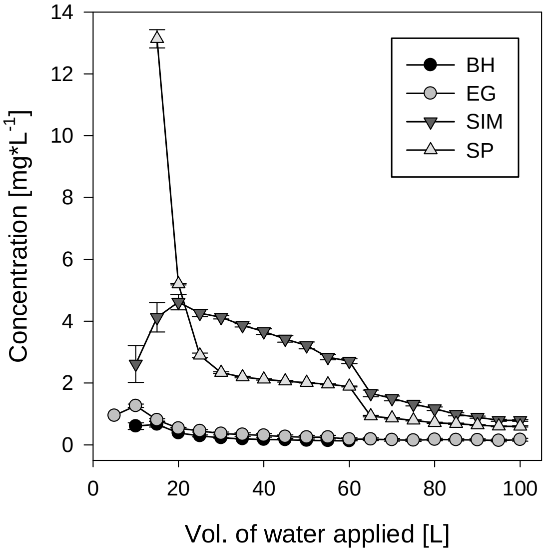

Fig. 22: Boron leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Copper leachate concentrations (Fig. 23) at the beginning of the experiment were about 0.23 mg*L^{-1} in SP leachate, 0.1 mg*L^{-1} in EG leachate (in the second sampling step) and 0.01 mg*L^{-1} in BH and SIM leachates. The main decrease of concentrations in BH, SIM and SP leachates occurred during the first 30-40 L of water applied, in EG leachate during the first 60 L. All leachate concentrations were below 0.001 mg*L^{-1} at the end of the experiment.

The highest Pb concentrations (Fig. 24) in EG leachates were observed in the second sampling step with 0.3 mg*L^{-1}; initial leachate concentrations in BH and SP leachate were 0.07 and 0.01 mg*L^{-1}, respectively. Lead concentrations lay below the LOQ in SIM ash leachate and the input water. After the application of 40 L, the concentrations were around 0.04 mg*L^{-1} in BH and EG leachates and a factor of 100 lower in SP leachate; final Pb concentrations in BH and EG leachates were 0.02 mg*L^{-1} and 0.01 mg*L^{-1}, respectively.

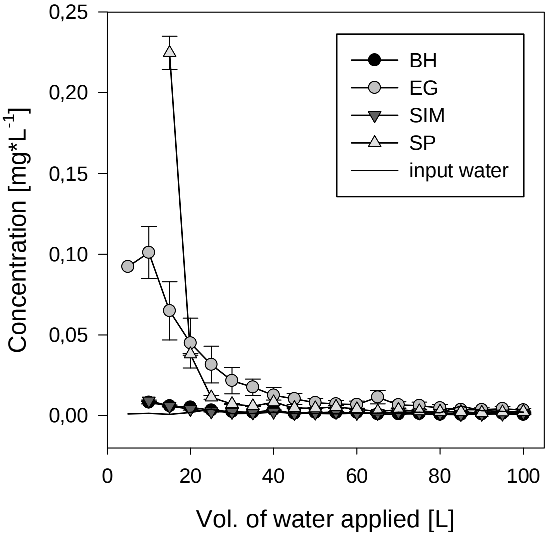

Fig. 23: Copper leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

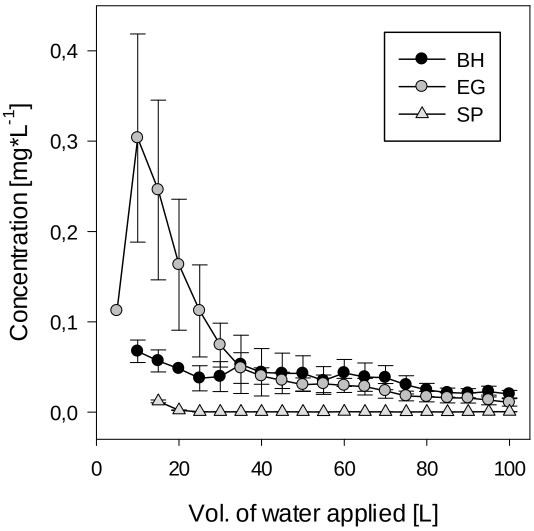

Fig. 24: Lead leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

The highest Zn leachate concentration (Fig. 25) was found in EG leachate in the second sampling step with 0.4 mg*L^{-1}; after the application of 40 L of water it fell below the LOQ. The initial Zn concentration in SP leachate was 0.1 mg*L^{-1} and decreased below the LOQ after the first two sampling steps. There was an outlying peek of > 0.1 mg*L^{-1} measured in SP leachate at 45 L, which might probably be attributed to an inaccuracy of measurement rather than an actual leaching peek. BH and SIM leachate concentrations were slightly above the LOQ of 0.003 mg*L^{-1} at the beginning of the experiment and dropped below the LOQ in most consecutive sampling steps.

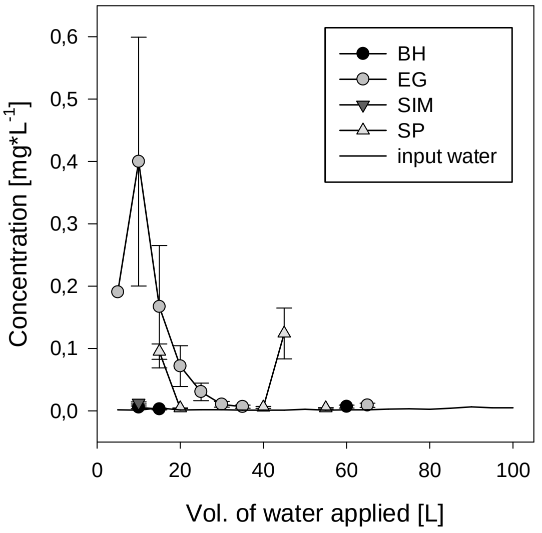

Fig. 25: Zinc leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Aluminum:

The initial Al leachate concentration (Fig. 26) was particularly high in EG ash leachate with almost 20 mg*L^{-1}. The initial concentration in SP leachate was around 3 mg*L^{-1}, in BH leachate around 2 mg*L^{-1} and in SIM leachate around 0.5 mg*L^{-1}. Aluminum concentrations showed a continuous decrease to 1.5 mg*L^{-1} in EG leachate, 0.15 mg*L^{-1} in BH leachate and 0.05 mg*L^{-1} in SP leachate at the end of the experiment, whereas they showed a slight increase in SIM leachate during the second half of the experiment to a maximum of 0.7 mg*L^{-1} after 80 L applied.

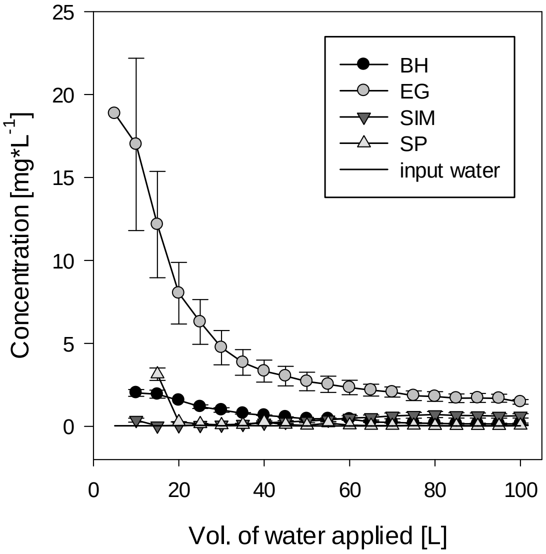

Fig. 26: Aluminum leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Vanadium, Nickel:

Initial V leachate concentrations (Fig. 27) were 0.11 mg*L^{-1} in EG leachate, 0.06 mg*L^{-1} in SP leachate and 0.03 mg*L^{-1} in BH leachate. They fell below the LOQ of 0.0008 mg*L^{-1} in BH and SP leachate within the first few sampling steps. In EG leachate, V concentrations also decreased during the application of the first 60 L to 0.004 mg*L^{-1}, then slightly increased again. In SIM leachate, the V concentration fell below the LOQ in the second sampling step but rose again above the LOQ after 70 L of water applied and then increased to 0.001 mg*L^{-1} at the end of the experiment. Vanadium concentrations in the input water were below the LOQ.

Nickel leachate concentrations (Fig. 28) showed a development similar to V concentrations. From initial Ni concentrations of 0.011 mg*L^{-1} in SP leachate, 0.004 mg*L^{-1} in SIM leachate and 0.001 mg*L^{-1} in EG leachate, the concentrations fell below the LOQ (0.0003 mg*L^{-1}) in SIM and EG leachates and below 0.001 mg*L^{-1} in SP leachate after the application of 30-40 L. SP leachate concentrations started to increase again after the application of 50 L of water and the concentrations in the other three leachates emerged above the LOQ after the application of about 60 L and increased slightly until the end of the experiment. Nickel concentrations in the input water were below the LOQ.

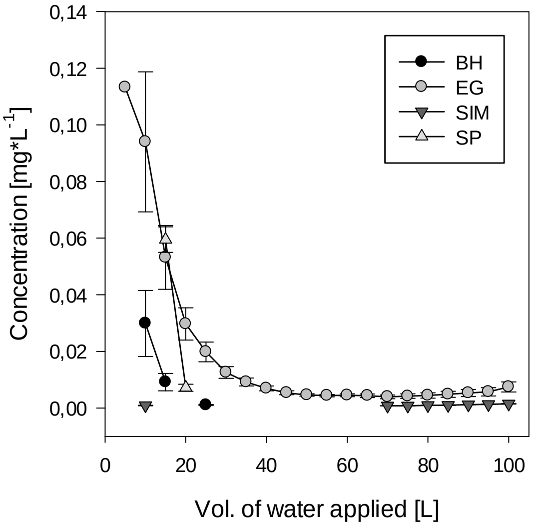

Fig. 27: Vanadium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

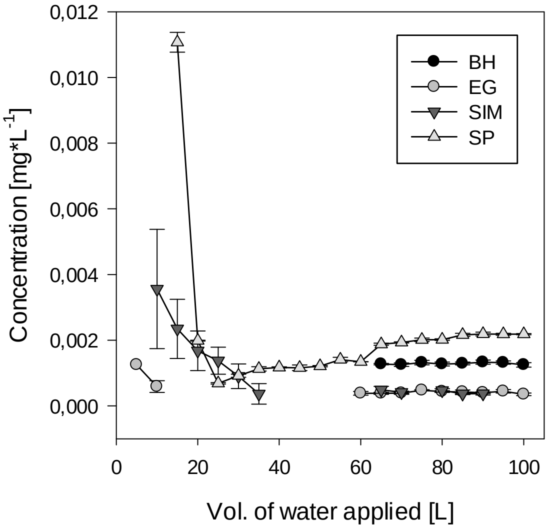

Fig. 28: Nickel leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Iron:

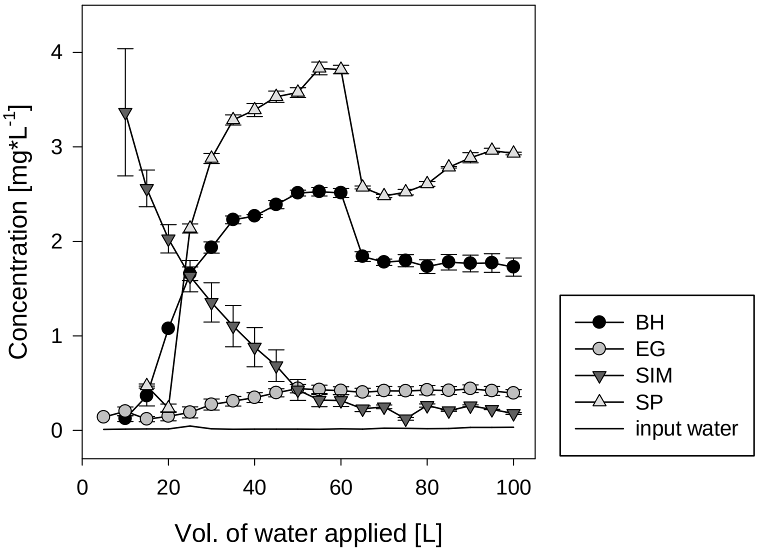

Fig. 29: Iron leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Fig. 29 displays the leachate concentrations of Fe, which showed a similar development over time as Ca leachate concentrations (cp. Fig. 8), rising for all ashes except SIM ash during the first half of the experiment. While SIM leachate concentrations decreased from 3.4 mg*L^{-1} in the beginning to 0.2 mg*L^{-1} at the end of the experiment, BH and SP leachate concentrations increased from 0.1 and 0.2 mg*L^{-1}, respectively, to around 2.5 and 3.8 mg*L^{-1}, in a development resembling a first order chemical reaction curve. (The offset in EG and SP concentrations between 60 and 65 L is again owed to the split-up of the ICP-MS measurement series at this point.)

This suggests that the different development of Fe leaching also occurred due to different speciation of Fe in the experimental ashes. Iron in wood ash is mostly present as oxides (Obernberger, 1997; Steenari, et al., 1999) which are only sparingly soluble. Thus, Fe oxides might have reacted to more soluble Fe salts (Fe(II)-/Fe(III)-Chloride, Fe(II)-Sulfate) during the first steps of the experiment as the conditions of water saturation and aeration were changing. Iron concentrations in SIM ash leachate were continuously decreasing, in contrary to the other three ash leachates, meaning that soluble compounds were present from the beginning in SIM ash. As for Ca, the presence of different Fe compounds at the end of the combustion process might be owed to the fact that SIM ash derived from a fluidized bad furnace, whereas the other three ashes were generated in grate furnaces, or, less likely, to a previous “aging” of SIM ash.

Reduction processes as the possible cause were excluded, as no microbiological activity could have developed in the pure wood ashes and Mn leaching (cp. Fig. 20) did not show a similar pattern.

Barium:

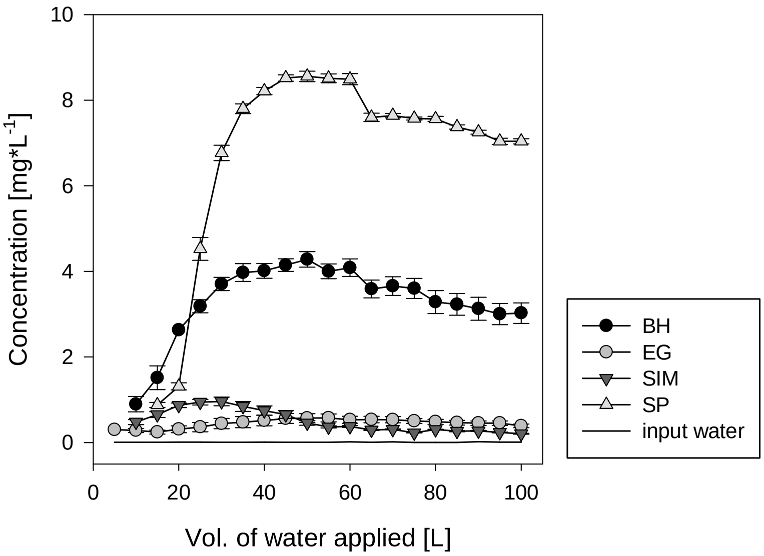

Fig. 30: Barium leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Barium leachate concentrations (Fig. 30) increased during the first half of the experiment in a development resembling a first order chemical reaction curve, before decreasing again. In contrary to the leaching of Ca and Fe, the increase of Ba concentrations occurred in all four ash leachates, including SIM leachate. No explanation for this increase was found.

Initial Ba concentrations were 0.9 mg*L^{-1} in BH and SP leachates, 0.5 mg*L^{-1} in SIM leachate and 0.3 mg*L^{-1} in EG leachate. In BH, EG and SP leachate they reached their maximum after the application of about 50 L with 4.3 mg*L^{-1}, 0.6 mg*L^{-1} and 8.6 mg*L^{-1}, respectively; in SIM leachate the maximum Ba concentration was found after the application of 30 L with 1 mg*L^{-1}.

Cobalt:

Cobalt leachate concentrations (Fig. 31) continuously decreased in EG and SIM leachates from initial 0.003 mg*L^{-1} and 0.0015 mg*L^{-1}, respectively, until they fell below the LOQ of 0.0002 mg*L^{-1} after the application of 60-70 L of water. Cobalt concentrations in the input water were below the LOQ. In SP leachate, the Co concentration fell from 0.004 mg*L^{-1} in the first sampling step to 0.001 mg*L^{-1} in the second sampling step and then started to increase again quite parallel with the Co concentration in BH leachate that increased from the beginning on. Concentrations rose to 0.0015 mg*L^{-1} in SP leachate and to 0.001 mg*L^{-1} in BH leachate at the end of the experiment. The offset between 60 and 65 L owed to the split-up of the measurement might falsify absolute concentrations but not the increasing trend of BH and SP leachate concentrations.

However, as total Co leaching was very low and the Co concentrations in all four ash leachates complied with the Austrian drinking water threshold at all sampling steps (cp. chapter 3.1.4), the possible reasons for the increase in BH and SP leachate concentrations were not further investigated.

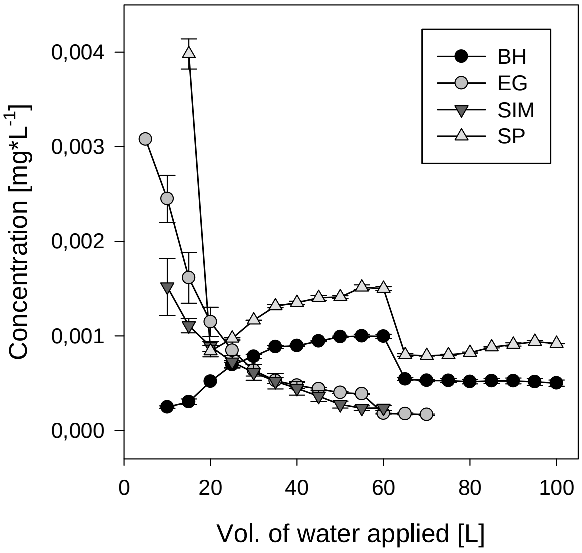

Fig. 31: Cobalt leachate concentrations and standard errors of the 4 experimental ashes in the wood ash leaching experiment (n=3)

Beryllium was also measured in the wood ash leachates, but the Be leachate concentrations lay below the LOQ for all ashes during the entire experiment.

3.1.2 Water-extractable concentrations

Water-extractable concentrations were measured in the fresh ashes (ashes before the wood ash leaching experiment) and in the ashes after the wood ash leaching experiment, so to say after having received “one year’s precipitation”, to compare how much of the original water-extractable concentrations had been washed out during the experiment.

Full data for the water-extractable concentrations of all four experimental ashes before and after the experiment were only available for the elements Cr, Co, Cu and Ba. That was because the water-extractable concentrations of the fresh ashes had not been determined for all elements, and because the water-extractable concentrations in the ashes after the experiment partly lay below the LOQ. Arsenic and Cd concentrations were below the LOQ in all four water extractions, Zn and Pb concentrations were below the LOQ in SIM and SP water extractions after the experiment.

Water-extractable concentrations decreased for all four compared elements (Cr, Co, Cu, Ba) during the wood ash leaching experiment. Particularly high reductions occurred for Cr concentrations in SIM ash (cp. Fig. 32), for Co concentrations in BH, EH and SIM ashes (cp. Fig. 33) and for Ba concentrations in BH and EG ashes (cp. Fig. 35).

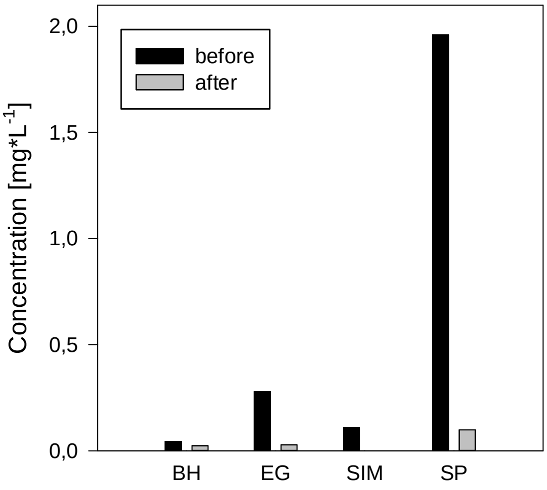

Fig. 32: Water-extractable concentrations of chromium in the 4 experimental ashes before and after the wood ash leaching experiment (n=3)

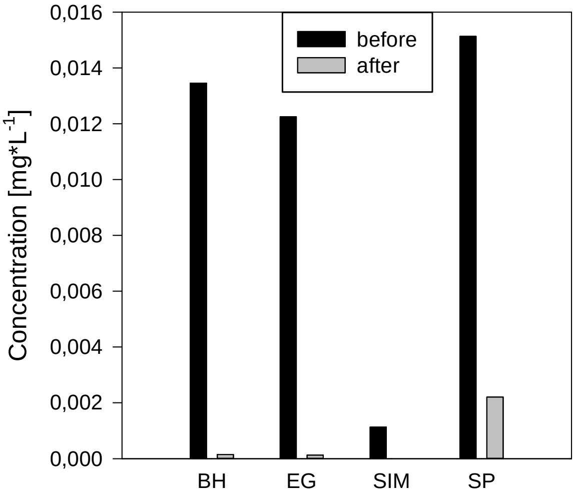

Fig. 33: Water-extractable concentrations of cobalt in the 4 experimental ashes before and after the wood ash leaching experiment (n=3)

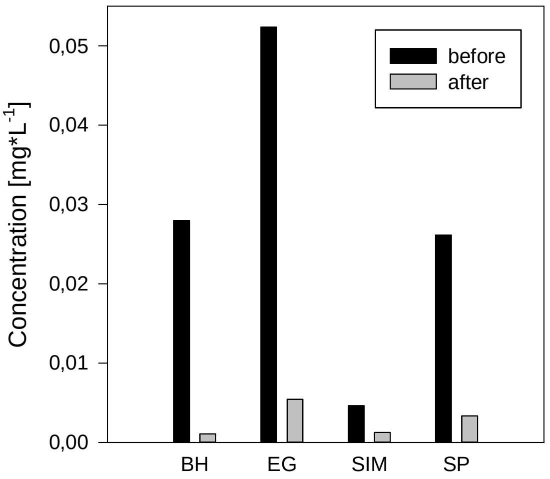

Fig. 34: Water-extractable concentrations of copper in the 4 experimental ashes before and after the wood ash leaching experiment (n=3)

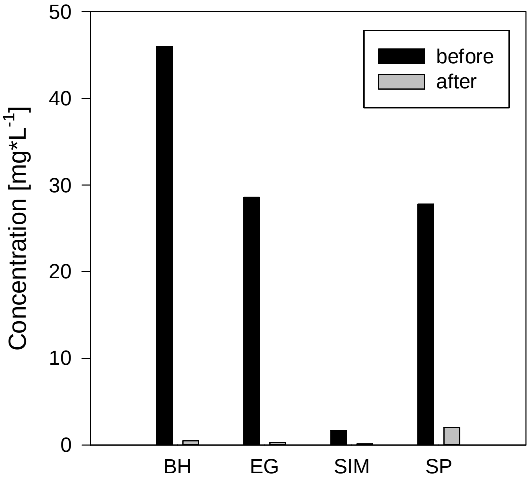

Fig. 35: Water-extractable concentrations of barium in the 4 experimental ashes before and after the wood ash leaching experiment (n=3)

Water-extractable Cr concentrations (Fig. 32) decreased in BH ash by a factor of 2 to 0.024 mg*L^{-1}, in EG ash by a factor of 10 to 0.028 mg*L^{-1}, in SIM ash by a factor of 100 to 8*10^{-4} mg*L^{-1} and in SP ash by a factor of 20 to 0.10 mg*L^{-1}.

Water-extractable Co concentrations (Fig. 33) decreased by a factor of 100 in BH, EG and SIM ashes to 1*10^{-4} mg*L^{-1}, 10^{-4} mg*L^{-1} and 10^{-5} mg*L^{-1}, respectively, and by a factor of 10 to 0.002 mg*L^{-1} in SP ash.

Water-extractable Cu concentrations (Fig. 34) decreased in BH ash by a factor of 30 to 0.001 mg*L^{-1}, in EG ash by a factor of 10 to 0.005 mg*L^{-1}, in SIM ash by a factor of 5 to 0.001 mg*L^{-1} and in SP ash by a factor of 10 to 0.003 mg*L^{-1}.

Water-extractable Ba concentrations (Fig. 35) decreased by a factor of 100 in BH and EG ashes to 0.48 mg*L^{-1} and 0.27 mg*L^{-1}, respectively, and by a factor of 10 in SIM and SP ashes to 0.12 mg*L^{-1} and 2.03 mg*L^{-1}, respectively.

3.1.3 Comparison leachate concentrations – water-extractable concentrations

Water-extractable concentrations according to Austrian Norm are, in addition to total contents, the basis of waste classification according to the Austrian Directive on Landfills[9]. They are meant to give an indication about how elutable the totally contained compounds are, but do not give information about the actual leachate concentrations. In order to obtain information about whether and how the water-extractable concentrations according to Austrian Norm relate to the concentrations that actually leached out from the wood ashes, the water-extractable concentrations were compared to the concentrations in the wood ash leachates.

The water extractions of the fresh ashes (ashes before the wood ash leaching experiment) were compared to the leachate concentrations from the first sampling step. The water extractions of the ashes after the experiment were compared to the leachate concentrations of the last sampling step.

The comparison showed that the leachate concentrations were often higher than the water-extractable concentrations, up to a factor of 35 for Pb in BH ash. Hottenroth et al. (2004) also found leachate concentrations up to factor of 40 higher than water-extractable concentrations in a leaching experiment with a similar set-up, and attributed this fact to the different ratios of liquid-to-solid matter. In addition, the agitation during extraction of the water-extractable concentrations and kinetic limitations of element mobilization and concentration gradients in the wood ashes might have an influence as well.

The relation of leachate to water-extractable concentrations differed for the different elements and ashes; no general pattern could be found for it.

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[9] Österreichisches BGBl. II Nr. 39/2008, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Deponien (Deponieverordnung 2008).

3.1.4 Comparison with legal thresholds

Some elements leaching from wood ash, mainly metals and metalloids, can pose a threat to the environment and/or human health. Therefore, their maximum allowed concentrations are regulated for different occasions by the legal framework. As there is no “direct” framework for the use of wood ash in forestry road construction, I compared the leachate concentrations to the thresholds of the Austrian Drinking Water Ordinance[10] and the Austrian Wastewater Directive on landfill leachates[11]. In this case, using the thresholds of the Austrian Drinking Water Directive is a very conservative approach, as the water leaching out of a forestry road will not be required to comply with drinking water standards, whereas using the thresholds for the emission of landfill leachate is a far less conservative approach. The elements complying with drinking water thresholds can be expected to not pose a risk at all.

For the purpose of providing an overview of the element leachate concentrations in relation to legal threshold concentrations, I used an extended traffic light logic, as shown in Fig. 36. In case there were no thresholds indicated by the Austrian Drinking Water Ordinance and the Austrian Wastewater Directive on landfill leachates, I resorted to the WHO Drinking Water Guideline[12] and the Austrian General Wastewater Directive[13].

	'Traffic light' scale:
🟩	< threshold Austrian Drinking Water Ordinance / Austrian Wastewater Directive on landfill leachates
🟨	1-3* threshold Austrian Drinking Water Ordinance
🟧	> 3*threshold Austrian Drinking Water Ordinance
🟥	1-3* threshold Austrian Wastewater Directive on landfill leachates
🟫	> 3*threshold Austrian Wastewater Directive on landfill leachates
⬜	no data / no threshold

	pH:	EC [µS*cm^{-1}]:
🟩	< 9.5	<2500
🟨	9.5-10	2500-5000
🟧	10-11	5000-7500
🟥	11-12	7500-10000
🟫	>12	>10000
⬜	no data / no threshold	

Fig. 36: Extended traffic light logic for the comparison of the wood ash leachate concentrations with legal threshold values

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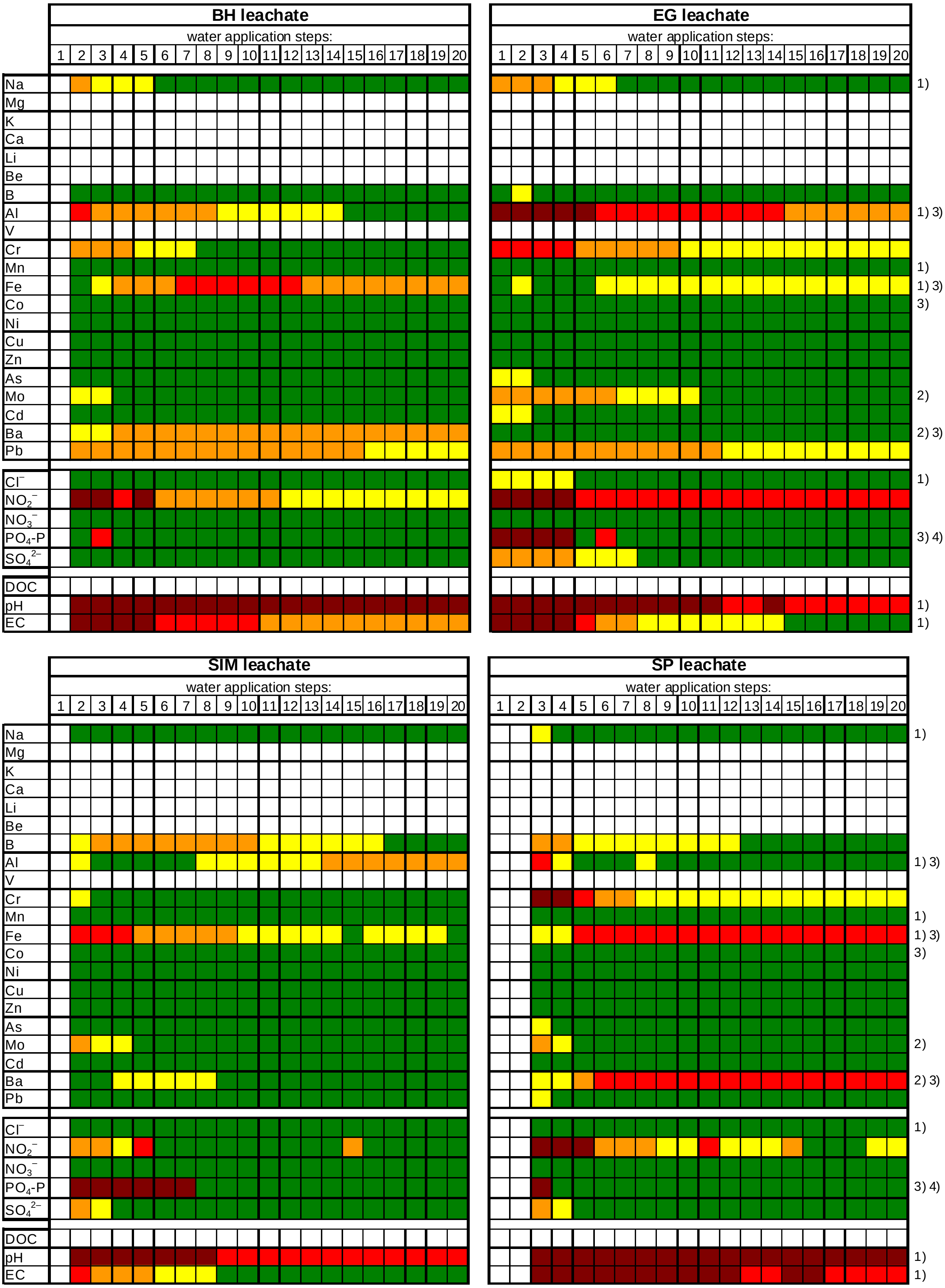
[10] Österreichisches BGBl. II Nr. 304/2001, Verordnung des Bundesministers für soziale Sicherheit und Generationen über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung), 2001.

[11] Österreichisches BGBl. II Nr. 263/2003, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Sickerwasseremissionen aus Abfalldeponien (AEV Deponiesickerwasser), 2003.

[12] World Health Organization (WHO) Guidelines for Drinking-water Quality, 3rd edition, 2008.

[13] Österreichisches BGBl. Nr. 186/1996, Verordnung des Bundesministers für Land- und Forstwirtschaft über die allgemeine Begrenzung von Abwasseremissionen in Fließgewässer und öffentliche Kanalisationen (AAEV), 1996.

Table 2: Comparison of the 4 ash leachates to legal thresholds using an extended traffic light logic (n=3)



	BH leachate																			
	water application steps:																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Na	⬜	🟧	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mg	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
K	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Ca	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Li	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Be	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
B	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Al	⬜	🟥	🟧	🟧	🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩
V	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Cr	⬜	🟧	🟧	🟧	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mn	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Fe	⬜	🟩	🟨	🟧	🟧	🟧	🟥	🟥	🟥	🟥	🟥	🟥	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
Co	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Ni	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Cu	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Zn	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
As	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mo	⬜	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Cd	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Ba	⬜	🟨	🟨	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
Pb	⬜	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟨	🟨
Cl^-	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
NO_2^-	⬜	🟫	🟫	🟥	🟫	🟧	🟧	🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
NO_3^-	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
PO_4-P	⬜	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
SO_4^{2-}	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
DOC	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
pH	⬜	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫
EC	⬜	🟫	🟫	🟫	🟫	🟥	🟥	🟥	🟥	🟥	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧

EG leachate																				
water application steps:																				
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🟧	🟧	🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	2)
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🟫	🟫	🟫	🟫	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	
🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
🟫	🟫	🟫	🟫	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	3) 4)
🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟥	🟥	🟫	🟥	🟥	🟥	🟥	🟥	🟥	1)
🟫	🟫	🟫	🟫	🟥	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	1)

	SIM leachate																			
	water application steps:																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Na	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mg	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
K	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Ca	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Li	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Be	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
B	⬜	🟨	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩
Al	⬜	🟨	🟩	🟩	🟩	🟩	🟩	🟨	🟨	🟨	🟨	🟨	🟨	🟧	🟧	🟧	🟧	🟧	🟧	🟧
V	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
Cr	⬜	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mn	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Fe	⬜	🟥	🟥	🟥	🟧	🟧	🟧	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟩	🟨	🟨	🟨	🟨	🟩
Co	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Ni	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Cu	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Zn	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
As	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Mo	⬜	🟧	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Cd	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Ba	⬜	🟩	🟩	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Pb	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Cl^-	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
NO_2^-	⬜	🟧	🟧	🟨	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟧	🟩	🟩	🟩	🟩	🟩
NO_3^-	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
PO_4-P	⬜	🟫	🟫	🟫	🟫	🟫	🟫	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
SO_4^{2-}	⬜	🟧	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
DOC	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
pH	⬜	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
EC	⬜	🟥	🟧	🟧	🟧	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

SP leachate																				
water application steps:																				
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⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	🟥	🟨	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	1) 3)
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	🟫	🟫	🟥	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	1)
⬜	⬜	🟨	🟨	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	1) 3)
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	3)
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
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⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	🟨	🟨	🟧	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	2) 3)
⬜	⬜	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	1)
⬜	⬜	🟫	🟫	🟫	🟧	🟧	🟧	🟨	🟨	🟥	🟨	🟨	🟨	🟧	🟩	🟩	🟩	🟨	🟨	
⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	🟫	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	3) 4)
⬜	⬜	🟧	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
⬜	⬜	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	1)
⬜	⬜	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟫	🟥	🟥	🟫	🟫	🟥	🟥	🟥	🟥	🟥	🟥	1)

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1) *Drinking water: trigger value*

2) *Drinking water threshold from WHO Drinking Water Guideline*

3) *Wastewater threshold from Austrian General Wastewater Directive*

4) *Compared to threshold for* P_{tot}

Even though the compliance of element concentrations with the legal thresholds differed between the four experimental ashes, some characteristics showed elevated levels (Table 2); pH, EC, B, Al, Cr, Fe, Ba, Pb and NO_2.

The pH was above 11 in all ashes during the entire experiment and did only slightly decrease during the experiment, while the maximum pH allowed for both, drinking water and landfill leachate, is 9.5. The pH, however, is expected to be well buffered by the soil (cp. chapter 3.2.1). The EC initially exceeded the threshold for landfill leachates in all four ashes. It showed a strong initial decrease and fell below the trigger value for drinking water in EG and SIM ash leachate in the course of the experiment. EC was particularly high in SP ash where it was still above 7500 $\mu S*cm^{-1}$ at the end of the experiment. EC is also expected to be buffered to a large extent by the soil.

Boron concentrations exceeded the drinking water threshold by a factor of up to 4 in SIM ash leachate and up to 13 in SP ash leachate, but fell below the threshold after the application of 80 L and 60 L of leachate, respectively. Boron concentrations didn’t exceed the drinking water threshold in BH and EG ash leachates. Boron can be harmful to human health when consumed in high concentrations. It may adversely affect animal growth, survival and reproduction, and in excess is phytotoxic. Boron is not bioaccumulative (Eisler, 1990).

Aluminum concentrations exceeded both, the drinking water trigger value and the wastewater threshold value in all four ash leachates during several sampling steps and were especially high in EG ash leachate. While Al concentrations were decreasing in BH, EG and SP leachate, they showed an increasing trend in SIM ash leachate. Aluminum can lead to several health effects on humans, such as the development of dementia in dialysis patients. It is toxic to water organisms and can be accumulated in animals and plants (Alloway and Ayres, 1997).

Initial Cr concentrations did not comply with the threshold for landfill leachate in BH, EG and SP ash leachates; in SIM ash leachate only the drinking water threshold was exceeded in the first sampling step. Concentrations decreased during the experiment and fell below the threshold for landfill leachate in BH, EG and SP leachate after three, nine and five sampling steps, respectively. Chromium concentrations exceeded the drinking water threshold in EG and SP leachates until the end of the experiment. Chromium is a micronutrient; its toxicity depends on its speciation. In general the hexavalent form Cr(IV) is more toxic than the trivalent Cr(III). Chromium(IV) is carcinogenic and toxic to most organisms in the environment; Cr(III) can also be phytotoxic and toxic to fish (Alloway and Ayres, 1997).

Iron concentrations in SIM ash leachate initially exceeded the threshold for landfill leachate but decreased during the experiment and dropped below the trigger value for drinking water by the end of the experiment. They were, however, increasing in the other three leachates, probably due to different Fe speciation in the ashes, as discussed in chapter 3.1.1. At the end of the experiment, Fe concentrations exceeded the drinking water threshold in EG leachate and even lay above the threshold for landfill leachate in BH and SP ash leachates. Iron is essential to humans, although it might cause adverse effects when taken up in excessive concentrations. The trigger value for Fe in drinking water is owed mainly to esthetic reasons, such as turbidity and taste of the water, and technical considerations, such as Fe precipitation in the pipes (Amt der Oberösterreichischen Landesregierung, 2011).

Barium concentrations were high in BH and SP ash leachates, exceeding the threshold for landfill leachate during most sampling steps. They complied with the drinking water threshold in SIM leachate in most sampling steps and in EG leachate during the entire experiment. Barium concentrations reached their maximum approximately at the half of the experiment and then decreased again. Barium can cause gastrointestinal disturbances and muscular weakness in humans. Especially water-soluble Ba compounds comprise adverse effects on humans and animals. In the environment, however, Ba usually forms insoluble compounds with other common components of the environment, such as carbonate and sulfate. Barium can be accumulated by fish and other aquatic organisms (U.S. Department of Health and Human Services, 2007).

Lead concentrations initially exceeded both threshold values in BH and EG leachate; the drinking water threshold by a factor of 7 and a factor of 30, respectively. They decreased to concentrations slightly above the drinking water threshold in the course of the experiment in those two ash leachates. In SIM and SP ash leachate, Pb concentrations were complying with the drinking water threshold during the entire experiment. An elevated Pb uptake by humans can lead to the inhibition of hematosis and a damage of the central nervous system and the kidneys. Lead is bioaccumulative and toxic to water and soil organisms. Therefore an exceedance of thresholds is problematic to both, humans and the environment (Alloway and Ayres, 1997).

The NO_2 drinking water threshold initially was exceeded in all four ash leachates. The NO_2 concentrations in BH, EG and SP leachates also surpassed the threshold for direct landfill discharge (in SP ash leachate by a factor of up to 15). The NO_2 concentration only fell below the drinking water threshold in SIM ash leachate, after the first four sampling steps. In EG leachate, it remained above the threshold for direct landfill discharge during the entire experiment. Nitrite is toxic to fish. In humans it can inhibit the oxygen transport of hemoglobin and lead to methemoglobinemia. Under the presence of oxygen, it however will be further oxidized to nitrate. (U.S. Environmental Protection Agency, 2007)

Chloride, PO_4 and SO_4 also exceeded both thresholds in some ashes in the first few sampling steps. They showed high initial leaching rates and fell below the respective drinking water threshold latest after the first 7 sampling steps.

The Mn, Co, Ni, Cu, Zn and NO_3 concentrations lay below the threshold for drinking water in all four ash leachates during all sampling steps.

There are no thresholds indicated by the legal framework for Mg, K, Ca, Li, V and DOC.

3.2 Soil Column Experiment

The results of the soil column experiment are discussed in two main aspects:

Firstly, the soil column leachate concentrations are regarded as to their absolute values over time. They are furthermore compared to the concentrations in the input water that was applied to the soil columns, to assess how the element concentrations were affected by the soil passage.

Secondly, I relate the soil column leachate concentrations to the legal thresholds to find out which parameters might be expected to pose a threat to the environment and/or human health.

3.2.1 Leaching behavior

When applying wood ash in forestry road construction, the water leaching from a forestry road would further leach through the soil before reaching the groundwater. Therefore, in the soil column experiment, the SIM ash leachate obtained from the wood ash leaching experiment was applied to soil columns. This experiment was mainly intended to provide an order of magnitude of the buffering effect of soil on the wood ash leachate, as the experiment was performed with only one soil and one ash leachate.

The following graphs display on the left vertical axis the total output concentrations after filtering through the 20-cm soil columns. On the right vertical axis, the relation of element output concentrations to element input concentrations is displayed, to illustrate in which ratio element concentrations are buffered by or mobilized from the soil.

Electrical conductivity & pH

Fig. 37 shows the change of EC in the soil column leachate over the 26 steps of the experiment. The EC of the input wood ash leachate was 3460 $\mu S*cm^{-1}$; the EC of the saturation extract of the soil was 242 $\mu S*cm^{-1}$. After filtering through the soil columns, the EC in the soil leachate reached a maximum of about 1000 $\mu S*cm^{-1}$ in the third sampling step, then decreased again and stabilized around 700 $\mu S*cm^{-1}$ after the application of 5 L of input wood ash leachate. This reduction in EC illustrates that a major part of the mobile ions was retained by the soil and not found in the leachate anymore.

Also for pH (Fig. 38), the soil showed a very high buffering capacity: The pH value of the input wood ash leachate was 12.1; the pH of the experimental soil was 6.26 (in H_2O). The initial pH of the soil leachate was around 10 in the first sampling step and dropped to 7.5 in the second step. The pH values ranged between 7.3 and 8 during the rest of the experiment with a slightly decreasing tendency.

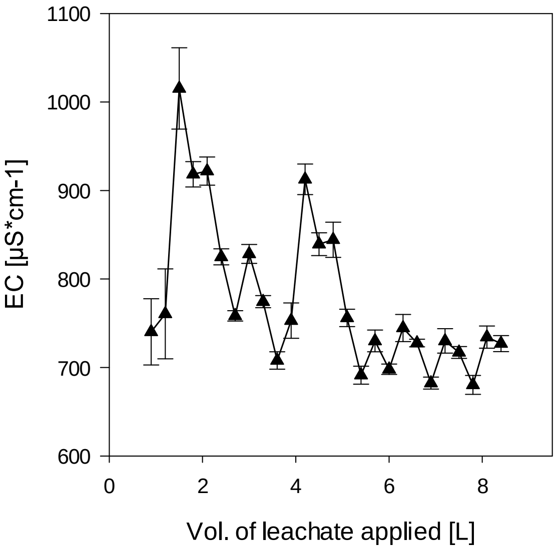

Fig. 37: Electrical conductivity and standard errors of the soil leachate during the soil column experiment (n=3)

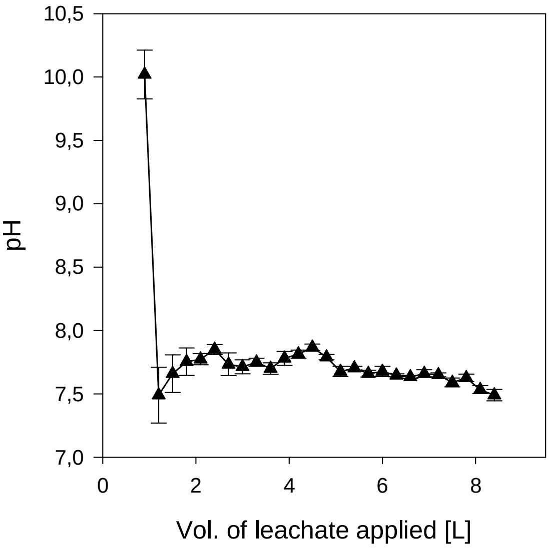

Fig. 38: pH values and standard errors of the soil leachate during the soil column experiment (n=3)

Macroelements

The figures below show the total output concentrations of the macroelements Na, K and Ca in the soil column leachates, as well as the ratio of output concentrations (c) to input concentrations (c_0).

The Na concentration in the soil leachate (Fig. 39) decreased during the first four sampling steps from 27 mg*L^{-1} to 19 mg*L^{-1} and then increased again during the eight consecutive steps until stabilizing around 31 mg*L^{-1} during the second half of the experiment. In relation to the input concentration, the output concentration amounted to 60 % after the first four sampling steps and then rose to about 90 % of the input concentration during the second half of the experiment.

The K concentration in the soil leachate (Fig. 40) fell from initial 120 mg*L^{-1} to 40 mg*L^{-1} after the application of 3.6 L. Then it increased again up to 100 mg*L^{-1} at the end of the experiment, after a total of 8.4 L of wood ash leachate had been applied. In the first sampling step, about 40 % of the K input concentration leached out. This ratio decreased to about 15 % after the application of 3.6 L and then increased again to 35 % at the end of the experiment.

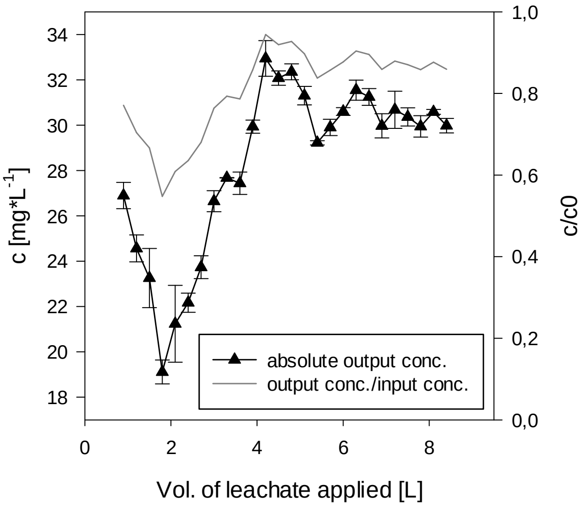

Fig. 39: Sodium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

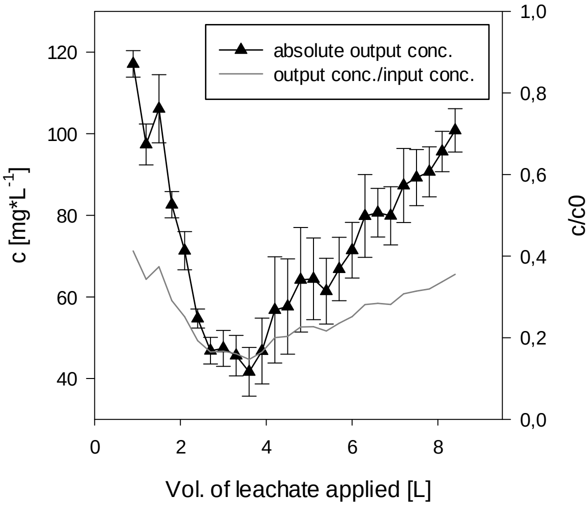

Fig. 40: Potassium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

The Ca concentration in the soil leachate (Fig. 41) rose from initial 50 mg*L^{-1} to 140 mg*L^{-1} during the first five sampling steps, then decreased to 40 mg*L^{-1} at the end of the experiment. At its maximum after the first five steps, around 60 % of the input concentration leached through the soil, at the end of the experiment only 20 % of the input concentration was found in the soil leachate.

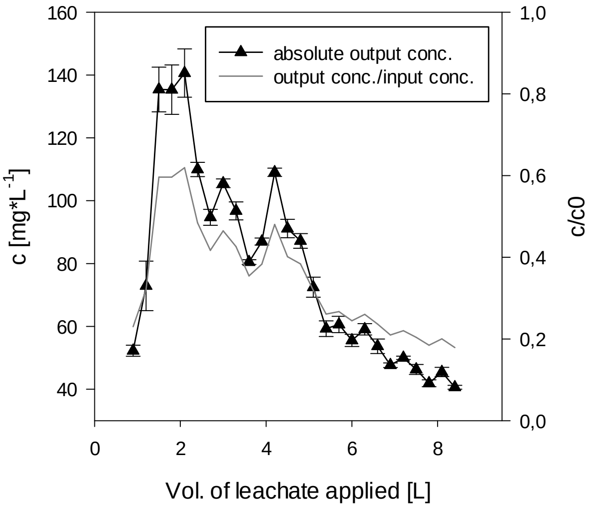

Fig. 41: Calcium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Total Na output concentrations reached their minimum after four sampling steps, K output concentrations after ten sampling steps, then both rose again, whereas Ca concentrations continued to decrease until the end of the experiment. This is probably owed to the different binding affinity of these three elements, being the lowest for Na and the highest for Ca. With the increasing loading of the cation adsorbing surfaces, the elements Na and K with lower binding affinity get adsorbed in lower proportion. Around 90 % of the Na contained in the applied leachate was found in the soil output leachate during the second half of the experiment and was therefore not adsorbed to the soil particles anymore. For K and Ca, the percentage of input concentration found in the output leachate at the end of the experiment amounted to 40 % and 20 %, respectively.

Trace elements

Iron, Manganese, Aluminum:

Fig. 42 shows the Fe concentrations in the soil leachate, as well as the ratio of output to input concentration. The Fe output concentration was around 0.5 mg*L^{-1} during the application of the first 4 L and then increased to 3 mg*L^{-1} until the end of the experiment. The input Fe concentration was 0.9 mg*L^{-1}. At the end of the experiment, over 300 % of the input concentration was detected in the output leachate.

Manganese output concentrations (Fig. 43) also increased during the experiment from initial 0.04 mg*L^{-1} to around 12 mg*L^{-1} at the end of the experiment. They showed a slightly decreasing trend during the second half of the experiment. The ratio of output to input concentration could not be indicated since Mn lay below the LOQ in the wood ash leachate applied. The LOQ corresponded to 1.9*10^{-3} mg*L^{-1}, meaning that Mn was at least 4 orders of magnitude higher in the output leachate compared to the input concentration.

This means that Fe and Mn contained in the experimental soil (in a concentration of 16000 mg*kg^{-1} and 769 mg*kg^{-1}, respectively) were mobilized and leached out from the soil columns.

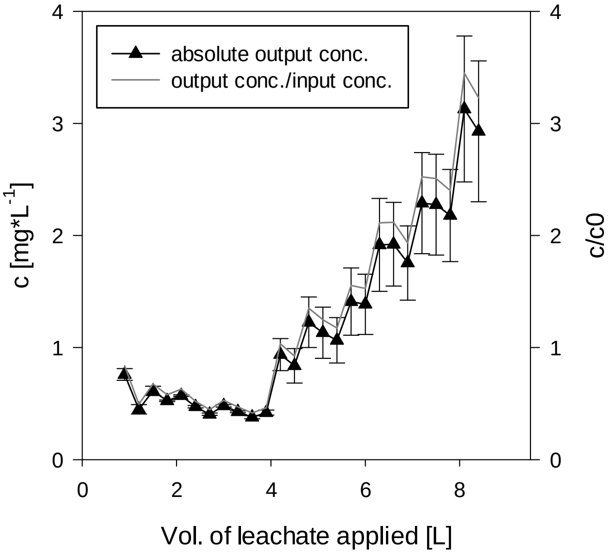

Fig. 42: Iron concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

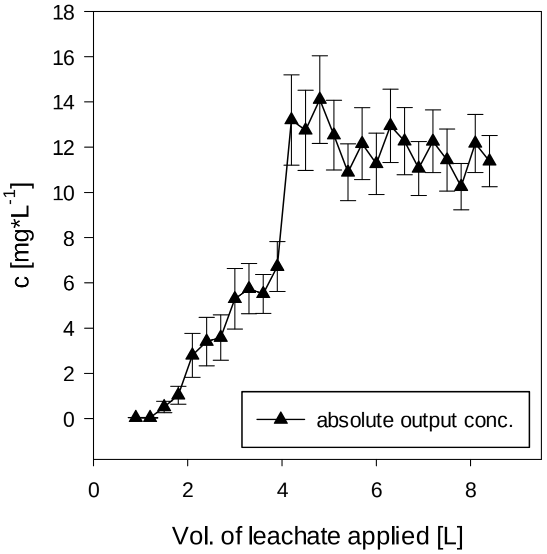

Fig. 43: Manganese concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Aluminum concentrations (Fig. 44) decreased from initial 3.5 mg*L^{-1} to about 0.1 mg*L^{-1} during the application of the first 2 L and started to increase again during the last five sampling steps up to a concentration of 0.6 mg*L^{-1} at the end of the experiment.

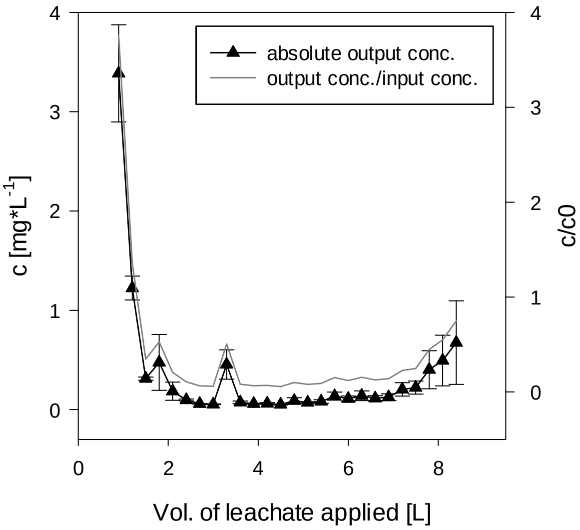

Fig. 44: Aluminum concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

The oxides of Fe, Mn and Al play an important role in the chemical behavior of soils as they are adsorbing a number of anions and cations which are released in case of dissolution of the oxides (Alloway and Ayres, 1997).

Fe and Mn oxides are strongly affected by changes in the redox conditions of the soil. Reducing conditions lead to the destruction of Fe and Mn oxides and the ions adsorbed to them get released (Alloway (Ed.), 1999). As the soil columns were almost permanently water saturated during the experiment, Fe and Mn oxides were mobilized by reduction in high quantities and leached out of the soil (see Fig. 42 and Fig. 43). Along with Fe and Mn, many other trace elements previously adsorbed to Fe and Mn oxides were released from the soil (cp. figures below).

Boron, Molybdenum, Arsenic:

The B concentration in the soil leachate (Fig. 45) decreased from 1.3 mg*L^{-1} in the first sampling step to 1.1 mg*L^{-1} in the second sampling step and then continuously increased up to 2.4 mg*L^{-1} in the last sampling step. In the beginning of the experiment, about 50 % of the input B concentration was found in the output leachate; in the end almost 100 % leached through the soil column without being retained by the soil.

Molybdenum concentrations (Fig. 46) decreased during the first four sampling steps from 0.05 mg*L^{-1} to 0.01 mg*L^{-1} and then continuously rose up to 0.06 mg*L^{-1} at the end of the experiment. The ratio of output concentration to input concentration initially was about 0.75, then fell to 0.10 during the first four steps and increased up to 0.90 during the remaining sampling steps, meaning that in the end only 10 % of the input Mo was still getting adsorbed to the soil.

Boron and Mo were probably mainly present in anionic form. The anion adsorption capacity of soils is generally limited. Unspecific anion adsorption depends on the pH, decreases with increasing pH and is already very low at a pH > 5.5. Specific anion adsorption mainly occurs in form of ligand exchanges of Fe and Al oxides and is decreasing with the reduction and destabilization of the Fe oxides. The decreasing adsorption rate of both metal anions illustrates the decrease of anion adsorption capacity. It was approaching zero towards the end of the experiment, as the factor c/c_0 had risen to almost 1 for both elements, meaning they did no longer get adsorbed to the soil.

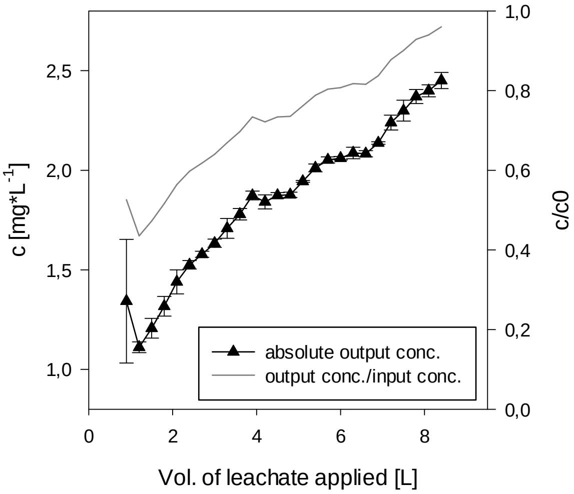

Fig. 45: Boron concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

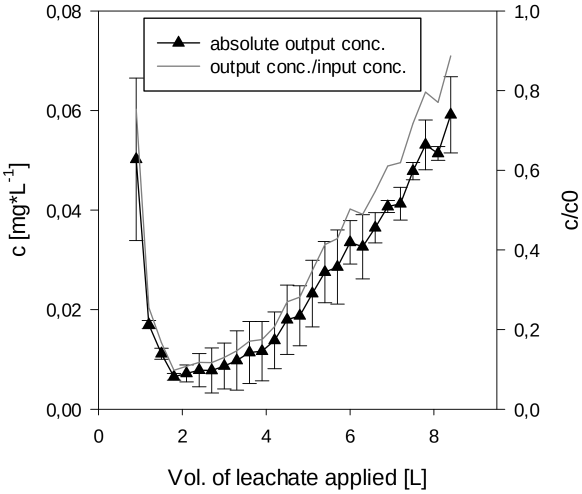

Fig. 46: Molybdenum concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Fig. 47 shows the As concentration in the soil leachate. After an initial decrease from 0.013 mg*L^{-1} to 0.003 mg*L^{-1} during the application of the first 4 L of wood ash leachate, As concentrations in the soil leachate rose again to about 0.022 mg*L^{-1} during the remaining sampling steps. The ratio c/c$_0$ could not be indicated, as the As input concentration was below the LOQ of 0.002 mg*L^{-1}, but output concentrations in the last sampling steps therefore were at least a factor of 10 higher than the input concentrations.

Arsenic in soils is also mainly present in anionic form, but to a major part it is immobilized by Fe oxides (Giménez, et al., 2007). Therefore, As showed a stronger correlation with the change of Fe concentrations (cp. Fig. 42) than B and Mo. With the destabilization of Fe oxides due to the reducing conditions in the soil columns during the experiment, As got co-dissolved with Fe and washed out of the soil.

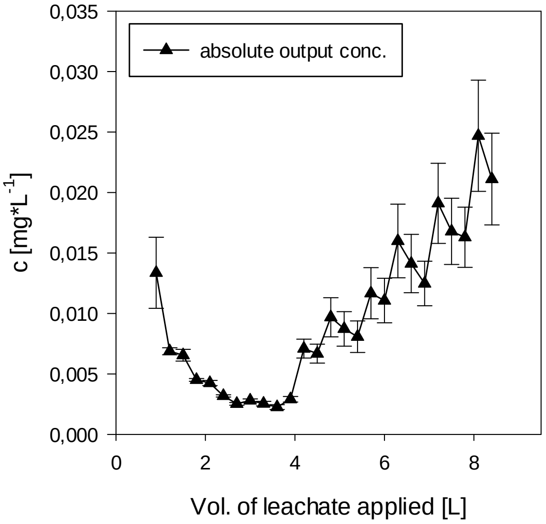

Fig. 47: Arsenic concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Vanadium:

The V concentration in the soil leachate (Fig. 48) decreased from initial 0.008 mg*L^{-1} to 0.001 mg*L^{-1} after the application of 3 L of wood ash leachate. It then started to increase again and was around 0.004 mg*L^{-1} at the end of the experiment. In the beginning of the experiment, 5 times the V input concentration was found in the output leachate. This factor decreased to 1 when the V output concentrations had reached their minimum and increased again up to 3 at the end of the experiment, which means that V was mobilized from the soil. Połedniok and Buhl (2003) have observed a simultaneous reduction of V^{5+} to V^{4+} along with the reduction of Fe^{3+} to Fe^{2+}, resulting in a co-extraction of V together with Fe.

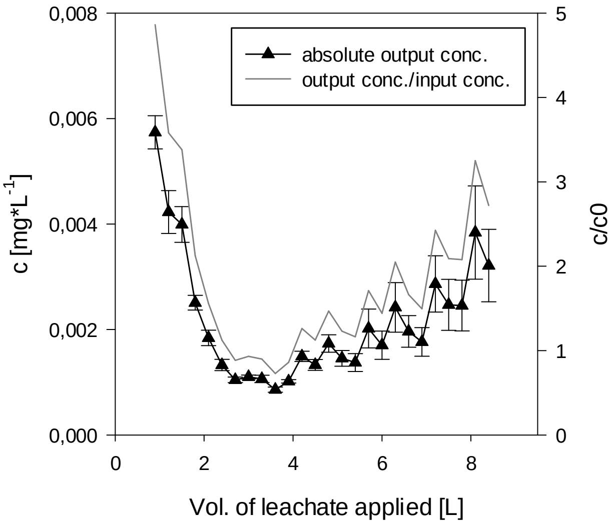

Fig. 48: Vanadium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Cobalt:

Cobalt concentrations in the soil leachate (Fig. 49) increased during the application of the first 4 L from 0.003 mg*L^{-1} to about 0.013 mg*L^{-1} and remained in this range during the rest of the experiment, with variations of about 0.002 mg*L^{-1}. Initially, the output concentration was about 5 times higher than the input concentration, towards the end of the experiment this factor reached almost 40, meaning that Co had been mobilized in from the soil, where it was contained at a concentration of 8.5 mg*kg^{-1}.

The qualitative development of Co concentrations in the soil column leachate is very similar to the one of Mn concentrations (cp. Fig. 43). The major part of Co in soils, on average 79 %, is associated to Mn (Alloway (Ed.), 1999). The Co solubilization in soil was found to be directly dependent on the reduction and solubilization of Mn^{4+}-oxides (Ehrlich, et al., 1973).

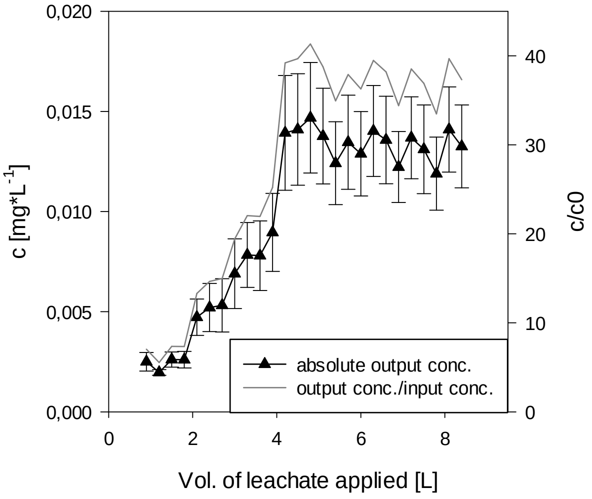

Fig. 49: Cobalt concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Cadmium, Lead:

The Cd concentration in the soil leachate (Fig. 50) was 2.5*10^{-4} mg*L^{-1} in the first sampling step and then fell below the LOQ of 1.6*10^{-4} mg*L^{-1}. After the application of 6 L, it rose again above the LOQ and increased up to 3*10^{-4} mg*L^{-1} at the end of the experiment. In the last five sampling steps, Cd was mobilized from the soil, as around 130 % of the input concentration was detected in the output leachate.

Lead concentrations (Fig. 51) ranged around the LOQ of 1.8*10^{-4} mg*L^{-1} during the application of the first 4 L and then increased up to 0.01 mg*L^{-1} in the last sampling steps. Lead concentrations strongly varied between the consecutive sampling steps during the second half of the experiment, but no direct correlation with the time intervals between the steps was found. Lead concentrations in the soil leachate were up to 50 times higher than the input concentration of 1.9*10^{-4} mg*L^{-1}. The Pb contained in the experimental soil at a concentration of 17.2 mg*kg^{-1} was partly mobilized under the reducing conditions along with the Fe and Mn oxides (Alloway (Ed.), 1999).

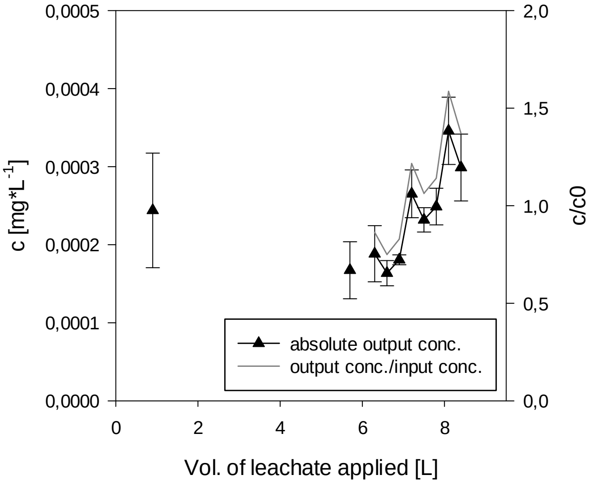

Fig. 50: Cadmium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

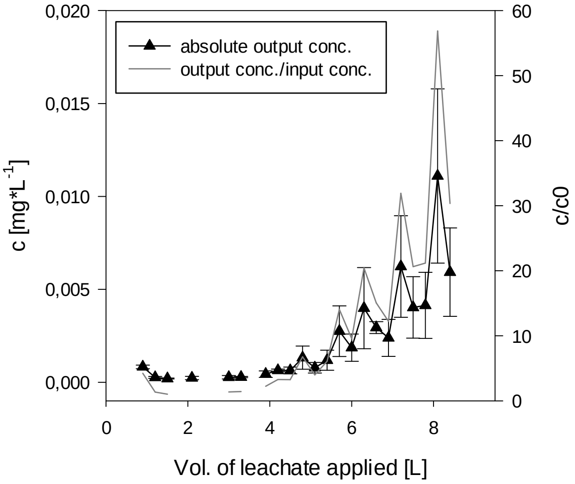

Fig. 51: Lead concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Nickel, Zinc:

Nickel (Fig. 52) and Zn (Fig. 53) concentrations showed a very similar development during the experiment, both, qualitatively and quantitatively. During the application of the first 3-4 L of wood ash leachate, the output concentrations lay around 0.01 mg*L^{-1}. Then they rose to an average of 0.02 mg*L^{-1} for Ni and 0.03 mg*L^{-1} for Zn and were strongly varying (in the range of 0.02 mg*L^{-1}) between the consecutive sampling steps, but again no direct correlation with the time intervals between the sampling steps was found.

The factor c/c_0 was around 1 during the application of the first 3-4 L and then rose to almost 5 in some of the consecutive sampling steps, also strongly varying between the sampling steps. This mobilization of Ni and Zn goes along with the finding that Ni and Zn in soil, apart from the residual fraction, are mostly associated to Fe and Mn oxides (Ma and Rao, 1997).

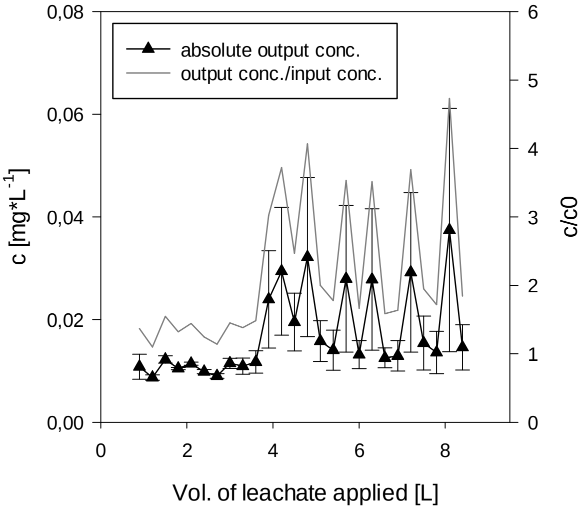

Fig. 52: Nickel concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

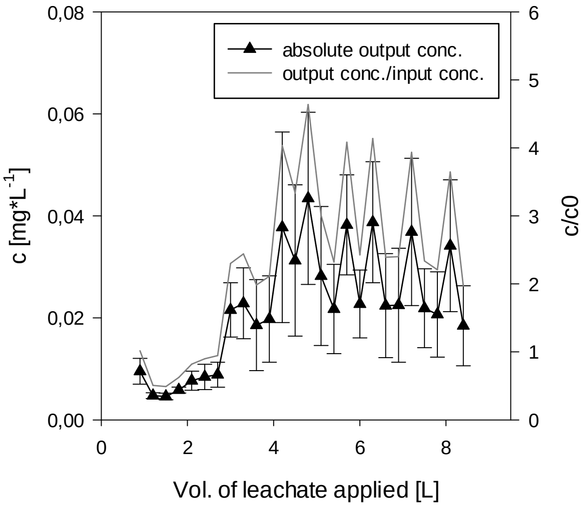

Fig. 53: Zinc concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Copper:

The initial Cu concentration in the soil leachate (Fig. 54) was 0.09 mg*L^{-1}; it then decreased to 0.01 mg*L^{-1} during the first four sampling steps. After the application of half of the amount of wood ash leachate (4.2 L), the Cu output concentrations started to slightly rise again and were around 0.03 mg*L^{-1} at the end of the experiment. The ratio of output to input concentration was always at least 5; in the end of the experiment it was around 10, indicating that Cu got mobilized from the soil.

Copper solubilization was found to be only partly dependent on the reduction and solubilization of Mn^{4+}-oxides (Ehrlich, et al., 1973), as in soil it is mainly present in the residual fraction or attached to soil organic matter, and only in the third place associated to Fe and Mn oxides (Ma and Rao, 1997).

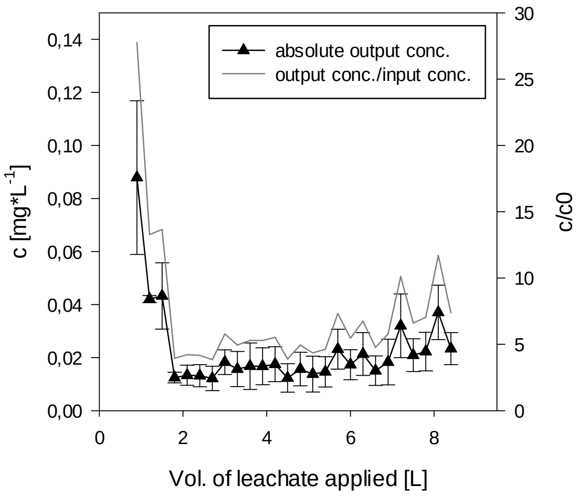

Fig. 54: Copper concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

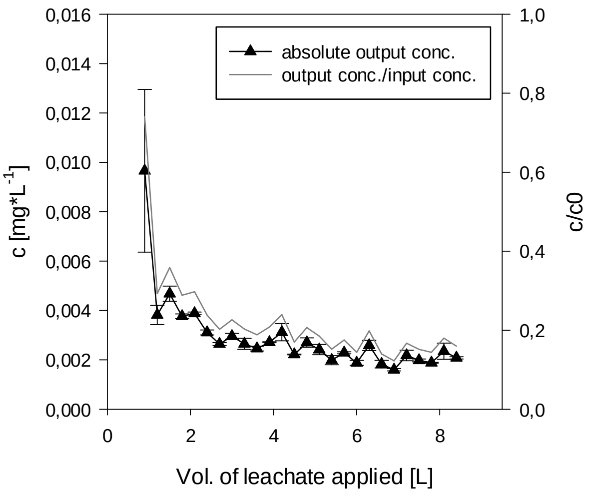

Fig. 55: Chromium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Chromium:

Chromium concentrations in the soil column leachate (Fig. 55) decreased from initial 0.01 mg*L^{-1} to 0.002 mg*L^{-1} at the end of the experiment. At the beginning of the experiment, around 75 % of the input concentration was found in the soil output leachate. During the experiment, this factor dropped to 15 %, meaning that Cr was efficiently retained by the soil. Under reducing conditions, as established during the experiment, an immobilization of Cr takes place as Cr(VI) is reduced to the less mobile form Cr(III) (Alloway and Ayres, 1997). The mobilization of Fe and Mn oxides showed no effect on Cr concentrations, as Cr is preferentially retained by the soil organic matter (Lin et al., 2008).

Barium:

Barium concentrations in the soil leachate (Fig. 56) ranged between 0.06 mg*L^{-1} and 0.08 mg*L^{-1} in most sampling steps and did not show an increasing or decreasing trend during the experiment.

Barium has a higher binding affinity than the macroelements Na, Mg and Ca and is therefore rather bound to negatively charged exchange surfaces. Throughout the whole experiment, only around 25 % of the Ba input concentration was found in the output soil leachate.

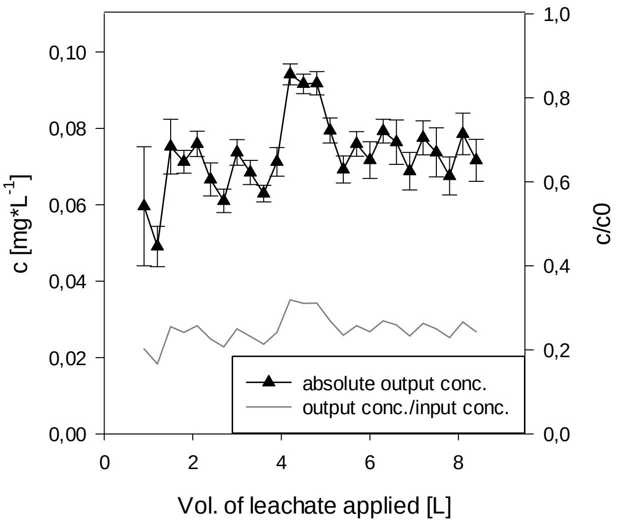

Fig. 56: Barium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

Lithium:

The Li concentration in the soil leachate (Fig. 57) fell from initial 0.007 mg*L^{-1} below the LOQ of 6*10^{-4} mg*L^{-1} after the first seven sampling steps. Almost the whole amount of input Li was retained by the soil.

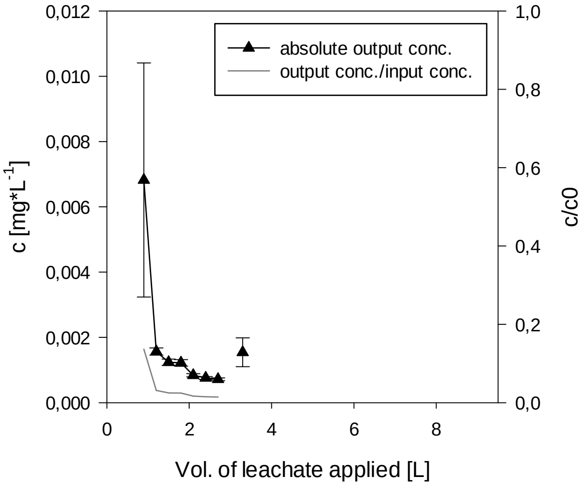

Fig. 57: Lithium concentrations and standard errors of the soil leachate during the soil column experiment (n=3)

3.2.2 Comparison with legal thresholds

The soil column leachate concentrations were also compared to the thresholds given by the Austrian Drinking Water Ordinance[14] and the Austrian Wastewater Directive on landfill leachates[15] using the traffic light scale shown in Fig. 58, in order to illustrate how filtering through soil affected the different parameters in terms of compliance with the legal framework.

'Traffic light' scale:
🟩 < threshold Austrian Drinking Water Ordinance / Austrian Wastewater Directive on landfill leachates
🟨 1-3* threshold Austrian Drinking Water Ordinance
🟧 > 3*threshold Austrian Drinking Water Ordinance
🟥 1-3* threshold Austrian Wastewater Directive on landfill leachates
🟫 > 3*threshold Austrian Wastewater Directive on landfill leachates
⬜ no data / no threshold

	pH:	EC [µS*cm^{-1}]:
🟩	< 9.5	<2500
🟨	9.5-10	2500-5000
🟧	10-11	5000-7500
🟥	11-12	7500-10000
🟫	>12	>10000
⬜	no data / no threshold	

Fig. 58: Extended traffic light logic for the comparison of the soil column leachate concentrations with legal threshold values

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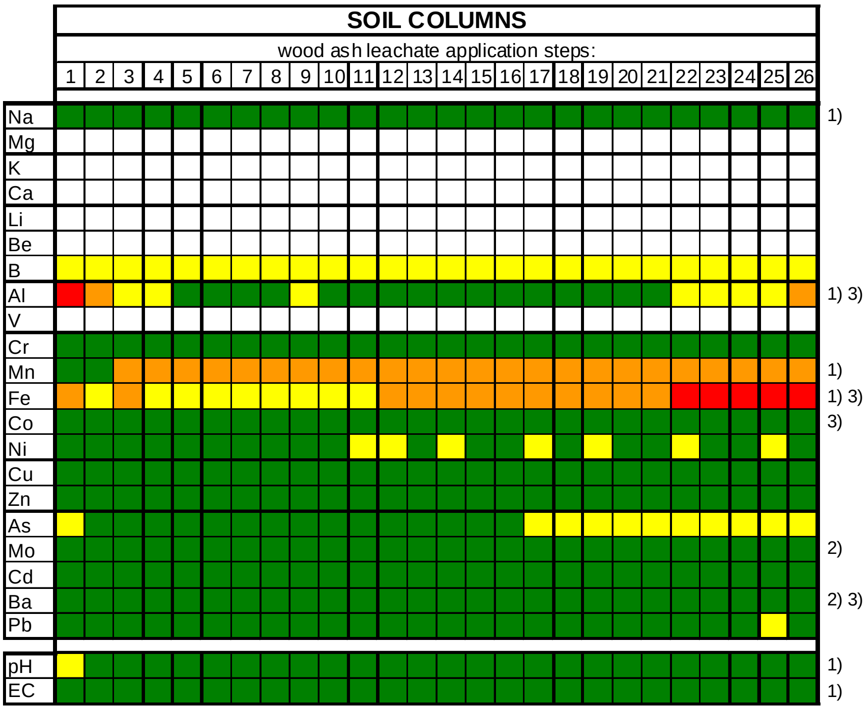
[14] Österreichisches BGBl. II Nr. 304/2001, Verordnung des Bundesministers für soziale Sicherheit und Generationen über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung), 2001.

[15] Österreichisches BGBl. II Nr. 263/2003, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Sickerwasseremissionen aus Abfalldeponien (AEV Deponiesickerwasser), 2003.

Table 3: Comparison of the soil column leachate to legal thresholds using an extended traffic light logic (n=3)



	SOIL COLUMNS																										
	wood ash leachate application steps:																										
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	
Na	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	1)
Mg	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
K	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
Ca	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
Li	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
Be	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
B	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	
Al	🟥	🟧	🟨	🟨	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟨	🟨	🟨	🟧	1) 3)
V	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	
Cr	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
Mn	🟩	🟩	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	1)
Fe	🟧	🟨	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟥	🟥	🟥	🟥	🟥	1) 3)
Co	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	3)
Ni	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟨	🟩	🟨	🟩	🟩	🟨	🟩	🟨	🟩	🟩	🟨	🟩	🟩	🟨	🟩	
Cu	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
Zn	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
As	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	
Mo	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	2)
Cd	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
Ba	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	2) 3)
Pb	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟩	
pH	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	1)
EC	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	1)

1) *Drinking water: trigger value*
2) *Drinking water threshold from WHO Drinking Water Guideline*
3) *Wastewater threshold from Austrian General Wastewater Directive*

As illustrated in Table 3, most parameters in the soil column leachate complied with the drinking water thresholds. The main problematic elements were B, Al, Mn and Fe.

The B concentration in the soil leachate exceeded the drinking water threshold in all sampling steps and was increasing during the experiment, probably due to the low anion adsorption capacity of the soil (cp. chapter 3.2.1).

Aluminum concentrations decreased from high initial values to concentrations below the trigger value for drinking water after the first four sampling steps. Aluminum concentrations started to increase again towards the end of the experiment, probably due to reduction processes, and rose above the drinking water trigger value during the last five sampling steps.

Manganese, from the third sampling step on, was over 3 times higher than the trigger value for drinking water. Iron exceeded the trigger value for drinking water in all steps and rose above the threshold for wastewater during the last five steps. These high element concentrations in the soil leachate mainly resulted from the mobilization of Mn and Fe from the soil under the reducing conditions during the experiment. Iron, however, already exceeded the drinking water trigger values during the first ten steps, when the factor c/c_0 was still below 1, meaning that the drinking water trigger value was already exceeded when Fe was not yet getting mobilized from the soil.

Nickel, As and Pb concentrations also exceeded the drinking water thresholds in some sampling steps during the second half of the experiment, owed to the increasing mobilization along with the Fe and Mn oxides.

In the course of the soil column experiment, the amount of “one year’s precipitation” was applied to the soil within two weeks, leading to predominantly reducing conditions during the experiment. This caused a mobilization of elements from the soil by reduction, which is not expected to occur in this extent in the field. Additionally, the leachate applied to the soil columns derived from pure wood ash, while in the field soil-ash mixtures containing only 15 % or 30 % of wood ash are applied to the forestry roads. Moreover, the wood ash leachate in the experiment filtered trough only 20 cm of soil, whereas in real field situations it would pass a much thicker soil layer before reaching the groundwater table.

Attention however needs to be paid in case of moist or waterlogged soils and soils with high groundwater table. Wood ash should not be used in soils with high groundwater table, and a limitation of its application to soils that do not exceed a certain number of days per year of water saturation might be considered.

4. Conclusions

Wood ash leaching experiment

The wood ash leaching experiment has shown that the leaching potential of wood ash in general decreases over time. For some elements, however, this scheme does not apply; some elements like Ca, Fe and Ba in some ashes apparently first need to react to soluble compounds before leaching out of the ashes.

Total leachate concentrations for some elements, like for example Cr or Al, differed considerably between the four experimental ashes, and some elements did not even show the same qualitative leaching trend in all four ashes. This illustrates the very heterogeneous composition of wood ashes in total element concentrations as well as in the speciation of element compounds, depending on the input materials and combustion parameters. For most elements, the highest concentrations were leaching out from SP ash. As the combustion material was only wood chips, this suggests that the heavy metal fractionation during the combustion process is not well optimized. Some elements, particularly Ca and Fe, showed a different leaching behavior in SIM ash which derived from a fluidized bed furnace, than in the other three ashes that derived from grate furnaces. This suggests that the firing technology has a great influence on the speciation of elements in the accruing wood ash.

The comparison of the water-extractable concentrations of Cr, Co, Cu and Ba according to Austrian Norm of the ashes before and after the wood ash leaching experiment showed a reduction during the experiment for all elements, by factors of 2 to 100.

In comparison to the water-extractable concentrations, the concentrations in the wood ash leachates were higher for some elements in some of the ash leachates (up to factor of 35 for Pb in BH ash), but no general pattern could be found. This illustrates that the water-extractable concentrations according to Austrian Norm do not indicate the actual leachate concentration, which can be much higher.

The most critical parameters concerning the compliance with the legal thresholds for drinking water and landfill leachate were pH, EC, B, Al, Cr, Fe, Ba, Pb and NO_2, although concentrations strongly differed between the four experimental ashes.

Soil column experiment

The soil column experiment showed that even an only 20-cm soil column has a strong buffering effect on most parameters. However, the leaching of some elements like Fe, Mn, Co and As increased during the experiment, owed to the reducing conditions in the soil columns due to almost permanent water saturation. These conditions are though considered to be an artifact of the experimental set-up and would not occur to this extent in the field (though attention should be paid to waterlogged forest soils).

The comparison with legal threshold values showed that most parameters were buffered to a large extent by the soil and complied with the drinking water thresholds after filtering through the soil columns. This, however, did not apply to B, Al, Mn, Fe, Ni and As concentrations. While the elevated Mn, Fe, Ni and As concentrations might be attributed to the reducing conditions in the soil columns, B and Al might pose a problem also in well aerated soils.

Overall, the soil column experiment was not suitable to draw general conclusions about the buffering of wood ash leachate by soil, as it was only performed with one soil and one ash leachate; it rather served to estimate the magnitude of the buffering effect the soil may have on the elements leaching out from wood ash applied in forestry roads.

External validity

These lab experiments represent a “worst case scenario” that is unlikely to occur in the field.

Firstly, in the wood ash leaching experiment, the leaching of elements from pure wood ash was investigated, whereas in the field soil-ash mixtures containing only 15 % or 30 % of wood ash would be applied.

Secondly, in the soil column experiment, the wood ash leachate was applied to only 20 cm of soil, whereas in nature the groundwater table might lie several meters below the forestry road and the leachate would pass through a much thicker soil layer.

Thirdly, the annual average precipitation was applied within 10 weeks in the wood ash leachate experiment and within 2 weeks in the soil column experiment, which created conditions of water saturation and oxygen deprivation that in nature might only occur temporarily after heavy precipitation events. Therefore, elements were mobilized which might not be mobilized under outdoor conditions.

Therefore, the element leachate concentrations exceeding the threshold values might (1) not be emitted in this extent as wood ash is already mixed with soil at its installation, (2) might be buffered to a bigger extent by the soil layers beneath, and (3) might not get mobilized by reducing conditions if annual precipitation is distributed over one year. The soil beneath the forestry roads, however, is stressed in its buffer and filter function and its buffer capacity is lowered.

Assessment of ecological innocuousness

Overall, from the ecological point of view, wood ash seems to be suitable for utilization in forestry road construction, though the composition of ashes can differ strongly in its element concentrations and speciation and might need to be assessed for each particular ash before its application to forestry roads.

The differences in element concentrations and speciation, apart from the input material, appeared to strongly depend on the firing technique and combustion parameters, which still might have a high potential for optimization.

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