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Chemical changes in leachate composition after wood ash application in forest road construction

Master Thesis

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Dedicated to my parents

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Abbreviations

AAO extr.	Acid ammonium oxalate extractable
CBD extr.	Citrate dithionite bicarbonate extractable
CEC	Cation exchange capacity
DOC	Dissolved organic carbon
DW	Austrian ordinance for drinking water quality
EC	Electric conductivity
FBA	Fluidised bed ash 85 vol% + burnt lime 15 vol%
GA	Grate ash
GSW	Austrian ordinance for emission for general sewage water
GW	Austrian ordinance for good chemical condition of groundwater
I	Ionic Strength
IC	Ion chromatography
ICP-MS	Inductive coupled plasma mass spectrometry
ICP-OES	Inductive coupled plasma optical emission spectrometry
Ko	Kobernausserwald soil
LOQ	Limit of Quantification
LSW	Austrian ordinance for emissions from Landfill sewage water
Ö NORM	Norm determined by the Austrian Standards Institute
S1	Test soil 1 (haplic Cambisol (dystric) from Siebenlinden)
S2	Test soil 2 (haplic Cambisol (eutric) from Wiesen)
S3	Test soil 3 (calcic Chernozem (siltic) from Lassee)
SE	Standard error
SOM	Soil organic matter
We	Weyregg soil

Abstract

Due to increasing use of wood products for energy production, recycling of wood ash as an alternative to deposition on landfills is of high interest. Using wood ash in forest road construction to improve mechanical stability has been recently suggested as feasible recycling option. To investigate the environmental impact of this implementation, a two-year field experiment, a column experiment and a water extraction experiment were conducted all including application of grate ash (GA) and fluidized bed ash (FBA). Analysing the leaching waters, surface runoff water and sub-road soil samples of the field experiment on an acidic and an alkaline forest soil, respectively, revealed that wood ash application is generally environmentally acceptable.

However, changes in leachate composition were seen in all experiments. The highest impact of wood ash was found in the acidic forest on the GA treated site. Here Al, As, Fe, Mn, Ni, Co, Cu, Mo, pH und NO_2^- showed initial 'flush events'. In addition a column experiment simulating the forest road set-up was conducted in the laboratory treating pure soil with an ash-soil mixture on top with artificial rainwater. Three test soils of different pH were used. Due to the additional soil layer the direct ash-derived input of contaminants was diminished. Here mainly secondary mobilisation and ion exchange reactions caused increase of some characteristics, including Al, Cd, Co, Pb and Zn on the acidic soil, As, Fe, Mo, PO_4^{3-}, SO_4^{2-}, pH, EC und DOC on the neutral soil and Ni, Cu und SO_4^{2-} on the alkaline soil. In conclusion more alkaline soils of higher clay and silt content were able to cope better with the impact of wood ash. The wide range of soils differing in buffer capacity should be considered in the establishment of thresholds for wood ash application in forest roads.

Zusammenfassung

Mit zunehmender Nutzung von Holz zur Energiegewinnung fallen große Mengen an Holzasche an. Eine ökologisch und ökonomisch sinnvolle Verwendung der Holzasche als Alternative zur Deponierung ist von großem Interesse. Durch ihre puzzolanische Eigenschaften wird Holzasche als geeigneter Baustoff für Stabilisierung von Forststraßen in Betracht gezogen. Die vorliegende Arbeit behandelt die Umweltverträglichkeit von Holzascheeinsatz im Forststraßenbau mit Hinblick auf die mögliche Auswaschung von Schadstoffen. Hierzu wurden ein zweijähriger Feldversuch, ein Säulenversuch und ein Wasserextraktversuch mit Readsorptionstest durchgeführt, jeweils unter Verwendung von Rostasche (GA) und Wirbelschichtasche (FBA). Die Analyse der Sickerwässer, der Oberlächenabflusswässer und Bodenproben zeigten dass Holzascheeinsatz im Forststraßenbau grundsätzlich umweltverträglich ist.

In allen Experimenten wurde jedoch eine Veränderung der Sickerwasserbeschaffenheit festgestellt. Die Auswirkung der Asche war am größten auf dem sauren Waldboden versetzt mit GA. Hier wurden erhöhte Auswaschungen von Al, As, Fe, Mn, Ni, Co, Cu, Mo, pH und NO_2^- in der ersten Probeperiode beobachtet. Im Säulenversuch mit drei Testböden von unterschiedlichem Boden-pH wurden die Bedingungen der Forststraße simuliert und die Böden mit künstlichem Regenwasser versetzt. Hier passierte das Eluent nach der Boden-Asche-Schicht zusätzlich eine Schicht aus reinem Boden. Es wurde deutlich, dass dadurch der direkte Eintrag von Schadstoffen aus der Aschen vermindert wurde und es zu sekundären Mobilisierungen und Ionen- Austauschreaktionen kam. Signifikante Auswaschung von Al, Cd, Co, Pb und Zn wurde auf dem sauren Boden, von As, Fe, Mo, PO_4^{3-}, SO_4^{2-}, pH, EC und DOC auf dem neutralen Boden und von Ni, Cu und SO_4^{2-} auf dem alkalischen Boden beobachtet. Im Allgemeinen vertrugen alkalische Böden mit höheren Ton- und Schluffgehalten die Aufbringung von Holzasche am besten. Die Bandbreite an Böden mit unterschiedlicher Pufferkapazität sollte bei der Festlegung von Grenzwerten für den Einsatz von Holzasche im Forststraßenbau bedacht werden.

1 Introduction

1.1 Wood combustion in Austria

Austria's share in renewable energies of the gross final energy consumption has been rapidly growing over the last decade; with energy supply from renewable resources increasing from 23.7 % in 2005 to 30.9 % in 2011. This is far above the average of 13% among the EU-28 member states (European Environment Agency 2013 a). However, to help the EU comply with its 2020-target of providing 20% of its energy by renewable sources, Austria agreed to further increase the share. Thus, Austria aims at producing 34% renewable energy by 2020 (European Environment Agency 2013 b).

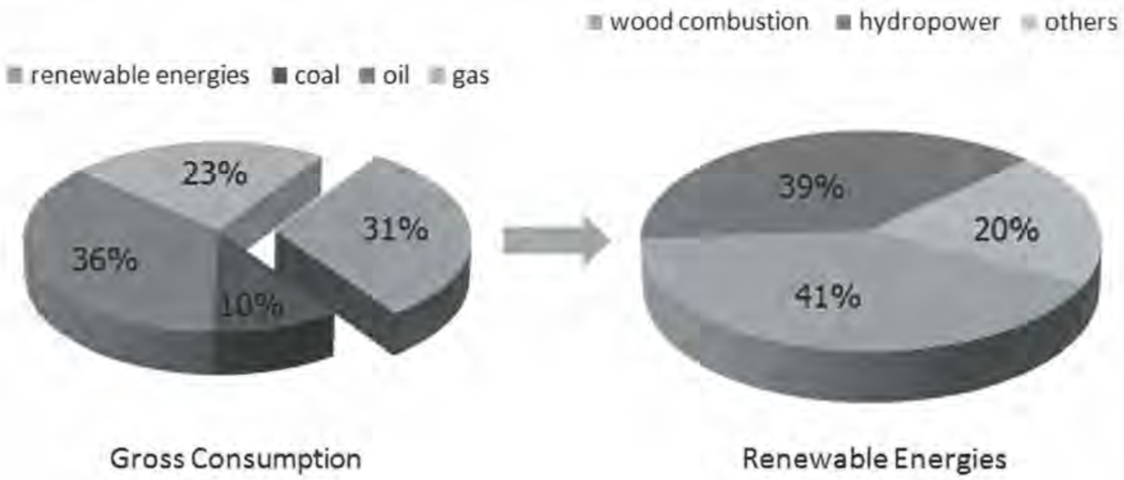

Figure 1 Share of renewable energies on total consumption and portion of wood combustion within the renewable energies 2011 in Austria (Biermayr 2013)

In 2011 wood combustion including district heating from wood fuel produced 41 000 GWh and accounted for 41.4% of Austria's renewable energy resources (Figure 1). Hence, the total contribution of wood combustion to Austria's energy supply amounts to 12.7%.

Wood mainly delivers energy for heat but also electrical power by burning of firewood, wood chips, -pellets and -briquettes, charcoal, waste wood and other biogenic waste. The Austrian Agency of Environment points out that 7.6 Mio tonnes of CO_2 equivalents were saved only from combustion of wood materials in 2011 (Biermayr 2013). In addition wood combustion is of high importance for Austria's economy. About 48% of Austria is covered by forest (Figure 2) (Pfemeter 2013). Wood combustion technologies and expertise have a long tradition in Austria and are further developed and exported abroad resulting in high financial investments and sale volumes. The investments within the wood combustion sector served employment for about 19 000 full-time equivalents in 2011 (Biermayr 2013).

Moreover, wood combustion provides secure energy supply, as it is domestic and distributed promoting independency form rising international oil and gas prices and supporting local energy production (Röser 2008). Hence, due to the ecological advantages, the economic importance and the increasing demand for renewable energies, the amount of wood burnt for energy production is likely to increase further. The Austrian Association for Biomass assumes that the use of biofuels can be further enlarged by 25% in 2020 compared to 2011. (Pfemeter 2013)

Figure 2 Map of Austria indicating areas covered with forest in green (Pfemeter 2013)

1.2 The remaining ash - its features and problems

Despite the advantages of rising energy supply by wood combustion there is one important drawback. Along with increasing amounts of wood firing comes an increase in remaining wood ash as by-product. In 2010 Austria had to deal with 128 000 tonnes of wood ash produced by biomass (mainly wood) combustion of which 49 000 tonnes were disposed of in Austrian landfills (Umweltbundesamt 2012).

Treating the ash as a waste product imposes costs on the incinerator and increases occupation of landfills. If the ash could be used as a valuable product in an ecologically acceptable way instead, both the bioenergy industry and society would benefit.

However, chemical properties of wood ash have to be considered before finding a potential use. During the combustion process the majority of organic material is oxidised to CO_2 and NO_X and released into the air, while most of the inorganic material is transformed into solid oxides forming the remaining ash. Inorganic compounds mainly derive from the constituents of the plant, including all the essential elements like Ca, K and Mg. These are nutrients and returning them to the forest ecosystem would not cause adverse effects. However, what matters are contaminants deposited on the plant surface or taken up by the plant through air and soil such as metals like Cd. This contamination derives from anthropogenic pollution, mostly caused by fossil energy use. During the wood burning process these harmful substances can accumulate to considerable amounts. Similarly elements that serve as micro nutrients such as Cu, Mo or Zn in smaller portions can be up-concentrated in the ash to amounts that cause harmful effects. Besides the plant matter the processing of the wood material can add inorganic compounds to the combustion fuel, for instance through chopping or transportation. (Narodoslawsky and Obernberger 1996, Koppejan 2008) Contents of organic pollutants are mostly negligible and thus not prone to leaching. (Pitman 2006)

A second main feature of the ash is its high alkalinity. Due to the high content in alkali carbonates the ash behaves similarly to a liming agent. The liming effect can benefit the soil, as it might counteract acidification and thus prevent possible subsequent leaching of nutrients or mobilisation of contaminants. On the other hand drastic changes in soil pH can have unpredictable effects on the soil solution equilibria and might lead to undesirable changes in soil chemistry (Sharifi, Cheema et al. 2013).

The final quantity and composition of the wood ash depends on the wood product and the incineration process. A high portion of bark in the burning material leads to higher Ca and Si contents, while stemwood contains more Mn and Al. Burning of hardwood results in ash with higher K and P contents in contrast to softwood ash which contains more Ca and Si (Pitman 2006).

The temperature in the combustion process also plays a crucial role for the ash composition. The effect of the combustion temperature depends on the tree species, but in general the amount of ash decreases with rising temperature, K and S start to volatilise at around 800 and 1000 °C respectively. Different studies showed a decrease in S, B and Cu when raising the combustion temperature, whereas the contents of Mg, Mn, P and Si tend to remain constant in relation to the Ca content. Carbonates of K and Ca are rather formed at low temperatures. To promote high macro-nutrient content in the ash, a temperature between 500 and 800 °C and separation of fly and bottom ash is most appropriate. (Obernberger, Biedermann et al. 1997, Pitman 2006) In addition the single fractions of ash differ within the same combustion. The lightest fraction is the fly ash. Due to vaporisation of metals and subsequent condensation on the boiler walls, it shows higher contents of heavy metals and dioxins than the bottom ash.

Two main combustor systems used for wood incineration are fluidised bed combustion and grate combustion. In the grate system the fuel material is dried, gasified and the charcoal combusted on a fixed or moving grate with primary air entering the process from below. At a higher point above the grate inside the oven secondary air is introduced to promote the burning of combustible gases. In the fluidised bed system the fuel particles are suspended in a self-mixing suspension of gas and solid bed material particles, consisting of e.g. sand, ash or limestone. Combustion air is entering the process from below. The investment and operation costs for the fluidised bed system are higher, more fly ash is formed and it is less flexible as for the grain size of the fuel compared to the grate system. However, the fluidized bed combustion is more efficient in reduction of NO_X, is able to handle a bigger range of water contents and type of fuel, the burning is more homogenous and it provides better heat transfer due to turbulence than the grate combustion (Obernberger 1997, Koppejan 2008).

1.3 Potential use of wood ash

The EU waste framework (Directive 2008/98/EC) sets up a hierarchy of waste treatment, preferring prevention, reuse and recycling over disposal. Following this reasonable principle there have been several attempts to use wood ash, conduct research on practical implementation and to introduce the topic into policy to set a legal base for wood ash usage (Gori, Bergfeldt et al. 2011)

On account of their high amount of bioenergy produced from wood material, the Scandinavian countries are pioneers in investigating ways to make wood ash an economically valuable product. Usage of wood ash as a soil ameliorant dates back to 1935 in Finland. In Sweden research on returning wood ash to the forest has been conducted since the 1970s (Pitman 2006). The liming effect of wood ash was seen as a particularly valuable property in southern Sweden to combat problems caused by atmospheric acid deposition. Nowadays wood ash as fertilizer in agriculture or forestry is of common use in most European countries. There is an attempt to return the minerals to the forest soil. However, due to the ash features mentioned above mostly application is legally limited to high-quality ash application of few tonnes per ha. In Denmark, for instance, wood ash application is regulated under the environmental protection law, allowing not more than 7.5 tonnes ash per stand of single rotation with limited Cd, Pb, Ni and Cr contents (Pitman 2006, Röser 2008). In some countries, including Austria, wood ash also applies as liming agents or additives for compost production. Additionally, the construction industry could potentially use a large portion of the produced wood ash for building roads and landfill surfaces or as an amendment in concrete. Its low density and high bearing capacity would make ash suitable for various uses. However, for a wide range of wood ash recycling options there are still several impediments to be overcome. Besides the mostly unexplored environmental impact, there is also a lack in awareness of producers and potential end-users and missing legal regulations (Ribbing 2007, van Eijk 2012). Also the variety in combustion procedures and burning material leads to big differences in the composition of the ashes and thus incoherent material properties. This is why the regulations for use of ashes have to be detailed and precise. The incineration operators aim for the most efficient energy production disregarding the quality of the remaining ash. However, should ash eventually become a market product, the incinerators would be encouraged to adapt their incineration conditions to enhance ash quality, which might cause a trend towards "designed ashes" (Lagerkvist and Lind 2009). Hence, a larger willingness, knowledge and interest in using wood ash as a product might also facilitate the implementation and design of regulations.

1.4 Using wood ash in forest roads

Using wood ash in a forest road is an approach combining several ideas. On one hand it takes the construction material properties of the wood ash into account. The ash provides stabilisation due to its cementing properties and performs well under freezing and thawing conditions (Lagerkvist and Lind 2009). The approach also aims at a use for larger amounts and easier implementation compared to spreading thin layers of ash on the forest ground to lime or fertilise it. On the other hand by returning the leftovers of burnt wood to the forest, it is an attempt to close the element cycles.

According to the Austrian corporation for federal forests (ÖBf) 50 km of new forest roads are built and 200 km of existing ones are maintained annually (Buchner 2013). Considering a consumption of roughly 250 tonnes ash per km forest road (as implemented in the field experiment of this thesis) a realisation of the procedure could lead to a considerable demand in suitable wood ash. However, so far legal deposition of larger wood ash amounts in forests is not feasible due to Austrian law, which handles wood ash as waste. For liming, only 2 tonnes per ha forest are permitted within 20 years, with special focus on the Cd content (Stangl 2011). The realisation of implementing wood ash in forest road construction needs changes in Austrian legislation and thus approval in Austrian policy.

However, the forest is a sensitive ecosystem and the extreme characteristics of the ash might have a harmful effect on the forest ecology or pose a threat to groundwater quality. The impact of ash used as fertiliser has been previously studied. *Ring et al.* conducted a nine-year long-term study of wood ash fertiliser on soil solution chemistry and investigated wood ash applications of up to 9 tonnes per ha. They found significant increase in K, Ca, Al and total organic carbon, but no significant changes in V, Cr, Mn, Ni, Cu, Zn, As and Pb concentrations (Ring, Jacobson et al. 2006). Similar results were obtained by *Norstrom et al.*, who investigated the impact of 3 tonnes per ha ash in a boreal catchment in Sweden 2 years after application. Increased concentrations for K, Ca and SO_4^{2-} in the soil solution were found, however no increase in As, Cd, Co, Cu, Hg, Ni, Pb and Zn concentrations were found in bilberries (Norstrom, Bylund et al. 2012). A study of *Nunez-Delgado et al.* on the effect of 10 tonnes per ha ash application on runoff water from forest areas did not find any pollution problems (Nunez-Delgado, Quiroga-Lago et al. 2011). However, leaching experiments with pure ash resulted in considerable release of heavy metals, mainly Pb, Zn and Cu (Gori, Bergfeldt et al. 2011).

Currently, little is known about the impact on the chemical composition of leachate from wood ash incorporated into a forest road. To evaluate the possibility of wood ash application in forest road construction a comprehensive study on the environmental effect of this activity is of high interest and importance.

2 Aim of the thesis

This thesis is part of a project, which aims at investigating the feasibility of using wood ash as an amendment in forest road construction. The purpose of my work in particular was to examine the chemical influence of applied wood ash on leaching water quality. It covers the implementation and interpretation of a two-year field experiment, a column experiment and additionally analysis of soil-ash mixtures.

To evaluate the potential environmental risk of using wood ash in forest road construction and to identify the most critical parameters that have to be considered, the results of the field experiment were compared to existing thresholds in Austrian legislation. Even though there is no Austrian regulation for the use of ash in forest roads yet, this will give an indication of the potential impact on water resources.

Aside from analysing the leaching waters, we aimed to find out how different soils react upon wood ash application and whether and to what extent they are able to filter and buffer possible input of harmful substances to the ground water. This is meant to support the development of a legal framework and guidelines for wood ash application in forest road construction.

The overarching goal of the thesis was to contribute to the question under which conditions the use of wood ash in forest road construction is environmentally acceptable.

3 Material and Methods

3.1 The experiments – an overview

We conducted two main experiments. In a long-term field trial, wood ash was incorporated into a forest road and the composition of leaching water and surface runoff was monitored for about 2 years. In the second main experiment we simulated the forest road condition by means of a column experiment in the laboratory. The results of the experiments can not be compared directly though. Besides the differences in scale, natural variability and time frame, in particular the setup differed. Firstly different soils were used and secondly the water leaching through the road was collected right beneath the ash-soil mixture, while the eluate in the columns was passing a layer of pure soil in addition. Due to the differences in water application the redox behaviour most likely differed. In addition the samples of the field experiment were only paper filtered, while the samples of the column experiment were syringe filtered. Therefore colloids might be present in the field experiment samples, which might change the leachate composition in comparison to the column experiment samples. Table 1 provides an overview on the main differences.

Table 1 Overview on similarities and differences between the field and the column experiment. * soil classification according to WRB (2006); the terms dystic, eutric and calconic refer to acidic, near neutral and alkaline soil reaction.

	Field experiment	**Column experiment**
Ashes (Table 3)	Grate Ash (GA), Fluidised Bed Ash augmented with burnt lime (FBA)	Grate Ash (GA), Fluidised Bed Ash augmented with burnt lime (FBA)
Soils (Table 5)	Forest soils Kobernausserwald (Ko), Weyregg (We)	Haplic Cambisol (dystric) (S1), haplic Cambisol (eutric) (S2), calcic chernozem (siltic) (S3)*
Collection point of samples	After leachate passing the ash-soil layer (Figure 4)	After leachate passing the ash-soil layer and a pure soil layer positioned underneath (Figure 6)
Scale	50 cm ash-soil mixture	5 cm ash soil mixture + 2 kg soil corresponds to a scale 1:10 relative to the field experiment
Sampling intervals	Once a month April – October 2012 and April – October 2013	10 times within a week, each after pouring 200 mL artificial rainwater on top
Eluent solution	Natural rainwater (Ko: 11.8 cm yr^{-1}; We: 16.7 cm yr^{-1})	Artificial rainwater (17.7 cm)

To get an impression of the impact the applied ash poses to the soil beneath the ash layer, both in the field and the column experiment soil samples were taken. In the field experiment the roads were opened to collect samples in July 2013, hence roughly 15 months after installation of the ash. In the column experiment samples were collected from the ash and the soil layers right after the eluate experiment was finished.

Finally, to investigate the direct impact of the wood ashes on the water solubility of potential contaminants when brought in contact with different soils, we mixed the ashes with the soils and conducted water extracts. In a second step pure soils were added to the extract solutions to determine as to whether they are able to re-adsorb and thus buffer the substances.

In all extract and leachate samples a total number of 30 environmentally relevant chemical parameters were analysed. Table 2 gives an overview on the investigated parameters including the analytical instrumentation used for analysis.

Table 2 Overview on parameters measured and instruments used

Parameter	Method	Instrument
pH	pH Electrode	Ross Ultra pH/ATC Triode, Orion 3 Star
Electric Conductivity (EC)	EC Electrode	Standard Conductivity Cell (LF413T-ID), Scott Instruments
Dissolved organic carbon (DOC)	UV absorption	EnSpire Multimode Plate Reader, Perkin Elmer
Ca, K, Mg, Na	ICP-MS / ICP-OES	Elan 9000 DRCe, Perkin Elmer / Optima 8300pv, Perkin Elmer
Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Se, V, Zn	ICP -MS	Elan 9000 DRCe, Perkin Elmer
F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Ion Exchange Chromatography	881 Compact IC pro, Metrohm

3.1.1 Experimental ashes and ash analysis

All experiments were conducted with two different types of wood ash. Both ashes were used in loose, dry form.

The grate ash (GA) was produced by incineration of wood chips and bark. The method of combustion was grate-firing at a temperature of 850 – 875 °C.

The fluidised bed ash (FBA) originates from incineration of wood chips in bark by fluidised bed combustion at 850 – 875 °C. The FBA had been amended with 15 % burnt lime to improve the mechanical stabilization effect of the ash as a previous experiment revealed unsatisfactory road stabilization by FBA due to its lower CaO content. If not stated otherwise "FBA" will always refer to a combination of 85% vol ash and 15% vol burnt lime.

The total element concentrations in the wood ashes were determined by the BIOS Bioenergiesysteme GmbH in cooperation with the Institute of Process and Particle Engineering at the Technical University of Graz. According to the guideline for use of biomass ash in agriculture and forestry established by the Austrian Federal Ministry for Forestry, both ashes comply with quality class A requirements (Stangl 2011).

Table 3 Total concentrations and other characteristics of the ashes used in the field and the column experiment. FBA was always used as a mixture of 85% FBA and 15% burnt lime. * Theoretical concentrations were calculated assuming the burnt lime consists of CaO only and the density of ash and burnt lime is the same.

	GA	FBA without burnt lime	85% FBA + 15% burnt lime
	Total measured concentrations [mg kg^{-1} DW]		**Theoretical concentrations***
Al	47700	18900	16065
As	11	9.4	8.0
B	86	82	70
Ba	641	713	606
Ca	176000	64700	n.a
Cd	1.1	1.3	1.1
Co	15	3.2	2.8
Cr	76	17	14
Cu	70	46	39
Fe	27400	3940	3350
K	24700	48800	41500
Mg	21000	7760	6600
Mn	3090	1350	1150
Mo	1.4	0.49	0.41
Na	5420	3070	2610
Ni	56	12	10
P	2910	2960	2520
Pb	10	14	12
Se	0.70	0.50	0.43
V	67	9.8	8.3
Zn	161	301	256
		Other characteristics	
pH	12.7	11.7	12.6
EC [µS cm^{-1}]	9460	1460	10000
DOC [mg kg^{-1} DW]	19	11	8.6
Density [g cm^{-3}]	0.94	n.a	1.5

Table 4 water-extractable concentrations [mg kg^{-1} DW] of the ashes in the field and the column experiment. * below LOQ (SI-Table1)

	GA	FBA without burnt lime	85% fluidised bed ash + 15% burnt lime
Al	3.6	1.7	0.1
As	0.004	0.007	0.004
B	0.65	8.0	2.3
Ba	12	4.3	7.4
Ca	6660	581	9751
Cd	0.001	0.001	0.001
Co	0.015	0.001	0.024
Cr	0.34	0.19	0.26
Cu	0.025	0.019	0.041
Fe	31	2.5	41
K	2700	1488	900
Mg	8.4	2.3	0.8
Mn	0.008	0.002	0.003
Mo	0.08	0.053	0.045
Na	394	87	88
Ni	0.29	0.022	0.54
P	0.1	*	0.12
Pb	0.022	*	0.005
Se	0.26	0.065	0.22
V	0.004	0.06	0.003
Zn	1.8	0.37	1.8
Cl^-	62	13	105
F^-	0.86	*	*
NO_2^-	3.3	3.0	3.0
NO_3^-	3.7	3.0	3.0
PO_4^{3-}	*	*	8.7
SO_4^{2-}	29	1735	1379

3.1.2 Experimental soils and soil analysis

A thorough assessment of the environmental impact of wood ashes used in forest road construction is only possible if tested on different soil types, as soils differ widely in their filter and buffer capacity. Therefore, the field experiment was conducted in two forests, namely Kobernausserwald (Ko) and Weyregg (We). We has a considerably higher pH, EC and Cation exchange capacity (CEC) and is more silty compared to Ko, while Ko shows higher DOC. The three soils used in the column experiment were a haplic Cambisol (dystic) (S1) from Siebenlinden, Lower Austria, a haplic Cambisol (eutric) (S2) from Wiesen, Burgenland and an calcic Chernozem (siltic) from Marchfeld, Lower Austria (S3). They rise in their pH, and silt and clay content from S1 to S3. S2 shows the highest EC and DOC values but lowest CEC, while S1 contains most SOM and is the sandiest but contains the least Citrate dithionite bicarbonate (CDB) and acid ammonium oxalate (AAO) extractable Fe and Al (Table 5).

Table 5 Soil chemical characteristics of the field and column experiment soils. Values represent means ± SE (n=2). * below LOQ [SI-Table 1]

	Ko		We		S1		S2		S3	
	mean	SE	mean	SE	mean	SE	Mean	SE	mean	SE
Soil characteristics										
pH	5.5	0.0	7.7	0.0	5.6	0.2	7.8	0.1	8.1	0.0
EC [µS cm^{-1}]	19	0.3	58	1.0	55	0.3	160	1.0	135	1.1
DOC [mg kg^{-1} DW]	204	0.2	160	0.3	219	0.2	725	2.5	206	0.0
SOM [g kg^{-1} DW]	87	0.2	63	0.1	61	1.1	30	0.2	41	2.1
CEC [mmolc kg^{-1} DW]	181	68	314	4	109	20	75	13	275	29
CDB extr. Fe [g kg^{-1}]	21	1.1	20	3.5	13	0.6	12	0.3	5.9	0.0
CDB extr. Al [g kg^{-1}]	9.0	0.7	4.5	1.6	6.9	1.6	3.0	0.4	1.1	0.2
AAO extr. Fe [g kg^{-1}]	7.3	0.1	4.4	0.2	6.2	0.5	3.3	0.3	1.1	0.2
AAO extr. Al [g kg^{-1}]	7.5	0.1	2.2	0.0	5.6	0.2	2.6	0.0	1.7	0.0
Sand [g kg^{-1}]	390	0.6	170	0.1	710	1.5	490	0.1	240	1.0
Silt [g kg^{-1}]	430	2.6	630	0.1	230	1.5	420	1.5	500	0.5
Clay [g kg^{-1}]	180	2.0	200	0.0	53	0.0	88	1.5	270	1.2
Texture	loam		silt loam		sandy loam		loam		silt loam	
Total concentrations (aqua regia digestion) [mg kg^{-1} DW]										
Al	32100	233	34100	122	29200	283	14500	167	16300	110
As	6.3	0.1	7.1	0.2	1.9	0.2	6.6	0.1	10	0.2
B	19	15	62	4.9	17	2.2	25	8.3	51	23
Ba	38	0.0	80	1.8	225	4.0	79	0.2	125	0.2
Ca	1260	32	8420	60	2950	127	7110	228	72100	n.a
Cd	0.10	0.00	0.36	0.01	0.16	0.00	0.16	0.00	0.30	0.01
Co	6.9	0.1	12	0.2	10	0.1	8.2	0.0	9.8	0.0
Cr	46	0.9	49	1.0	31	0.4	17	0.0	59	0.5
Cu	16	0.1	22	0.0	12	0.2	12	0.0	22	0.1
Fe	29900	315	30600	3.1	45200	400	16800	280	22500	358
K	1680	4.2	6050	137	12100	224	4140	64	6210	n.a
Mg	3810	6.5	6320	92	9650	213	4290	82	10300	55
Mn	424	1.2	825	3.0	691	15	782	15	568	12
Mo	0.10	0.01	0.60	0.03	0.22	0.02	0.57	0.01	0.37	0.02
Na	228	0.3	252	7.3	354	12	225	7.5	n.a	n.a
Ni	19	0.6	22	0.1	*	*	11	0.3	52	3.0
P	288	0.3	307	1.8	1280	44	1440	0.8	886	10
Pb	27	0.1	23	0.4	15	0.3	15	0.2	16	0.6
Se	0.32	0.01	0.50	0.01	0.35	0.09	0.21	0.14	0.32	0.04
V	21	1.4	63	0.0	45	1.9	22	0.0	42	0.7
Zn	59	0.1	78	0.3	111	1.4	63	0.3	91	27

EC, pH and DOC were measured in water extracts of 1:10 (w/v) soil-to-solution ratio (as described below). Electrodes (Table 2) were used for the detection of pH and EC, while DOC was measured by absorption of UV light. The concentration of dissolved organic carbon correlates with the absorption of UV light at 254 nm (Brandstetter, Sletten et al. 1996). Therefore the UV absorption of 200 µL of the samples was measured (Table 2) and the DOC concentration was calculated according to Equ 1.

$$c\left(DOC\left[\frac{mg}{L}\right]\right) = 1 + 0.449 * A(254\text{nm})\ \text{m}^{-1} \qquad \text{Equ 1}$$

The soil organic matter (SOM) was determined using the weight-loss-on-ignition method (ÖNORM L 1080). The soil samples were dried at 105 °C to remove the moisture. Afterwards the samples were weighed, heated up to 360 °C for 2 hours and weighed again. The difference in weights before and after ignition was used to calculate the content of soil organic matter.

Cation exchange capacity (CEC) of each soil was determined by $BaCl_2$ extraction according to ÖNORM L 1086. We added 100 mL of 0.1 M $BaCl_2$ solution (Merck, Darmstadt) to 5 g of the soil (< 2mm), shook the samples for 1 hour at 20 rpm and paper-filtered them (150 mm Munktell 14/N). The resulting solutions were measured for their Ca, K, Na, Mg and Al concentration by ICP-MS (Table 2) and CEC was expressed as cumulative charge equivalent (mmolc kg^{-1}).

Citrate dithionite bicarbonate (CBD) and acid ammonium oxalate (AAO) extractable Fe and Al were analysed according to the methods of Loeppert and Inskeep (1996).

We determined the texture of the soils by their grain size distribution according to ÖNORM L 1061. Soil samples (< 2mm) were air dried and 10 g were added to 25 mL of 0.1 M pyrophosphate (Merck, Darmstadt). After 6 hours of dispersing, 200 mL of water was added and the dispersions were shaken overnight at 22 rpm in an overhead shaker. The next day the mixes were transferred into an Atterberg-cylinder and filled up with water to 1000 mL. The 0.02-mm and the 0.002-mm fractions were taken by means of a Köhn-pipette 4 min 15 sec and 7 hours 5 min, respectively, after shaking up the cylinder by hand at 24° C. The 0.63-mm, 0.2-mm and 0.063-mm fractions were collected by wet sieving. The samples of all fractions were dried at 105° C to constant weight.

The total concentration of the soils was measured by digestion with aqua regia adding 4.5 mL 37% HCl (WVR Chemicals, Fontenay-sous-Bois) and 1.5 mL 65% HNO_3 (Merck, Darmstadt) to 0.5 g of the finely ground soil in line with ÖNORM L 1085. The samples were left to react overnight and heated to 150 °C for 3 hours the next day. After diluting them with high quality water, the samples were filtered (150 mm Munktell 14/N) and stored at room temperature. The concentrations of Ca, K, Mg and Na were determined by ICP-OES, while the concentrations of Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Se, V and Zn were measured by ICP-MS (Table 2).

Table 6 Water extractable concentrations [mg kg^{-1} DW] of the experimental soils. Values represent means ± SE (n=2). * below LOQ (SI-Table 1)

	Ko		We		S1		S2		S3	
	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE
Al	6.6	0.2	4.7	0.8	7.1	0.0	10	0.0	1.8	0.2
As	0.005	0.000	0.009	0.001	0.006	0.000	0.060	0.000	0.028	0.000
B	0.19	0.01	*	*	0.20	0.00	0.69	0.02	0.19	0.03
Ba	0.37	0.01	0.13	0.03	1.0	0.0	0.24	0.02	0.07	0.03
Ca	4.7	2.0	87	1.5	36	4.4	108	4.0	191	10
Cd	0.001	0.000	0.001	0.000	0.002	0.000	0.001	0.000	0.001	0.000
Co	0.007	0.000	0.002	0.000	0.018	0.000	0.012	0.000	0.003	0.000
Cr	0.023	0.000	0.009	0.002	0.005	0.000	0.016	0.001	0.006	0.001
Cu	0.018	0.002	0.080	0.036	0.018	0.001	0.095	0.000	0.074	0.001
Fe	0.67	0.04	9.3	1.1	2.9	0.0	7.5	0.1	1.9	0.1
K	4.5	0.9	8.6	0.4	38	0.2	277	10	65	0.1
Mg	2.5	0.0	4.2	0.1	7.1	0.1	36	0.8	26	0.6
Mn	0.40	0.03	0.056	0.009	4.6	0.1	0.51	0.01	0.068	0.013
Mo	*	*	0.007	0.002	*	*	0.034	0.000	0.020	0.001
Na	3.1	1.0	1.8	0.2	1.5	0.1	3.8	0.1	1.0	0.3
Ni	0.017	0.000	0.025	0.002	0.018	0.003	0.040	0.002	0.032	0.001
P	0.097	0.011	0.94	0.09	2.0	0.0	56	0.5	1.4	0.0
Pb	0.006	0.000	0.005	0.001	0.016	0.011	0.005	0.000	0.002	0.000
Se	0.003	0.001	0.004	0.003	0.005	0.003	0.006	0.002	0.012	0.002
V	0.001	0.000	0.015	0.002	0.010	0.000	0.062	0.000	0.065	0.000
Zn	0.51	0.04	0.48	0.01	0.59	0.01	0.26	0.01	0.28	0.00
Cl^-	2.6	0.8	3.6	0.1	1.6	0.6	2.7	0.4	6.6	0.3
F^-	*	*	1.0	0.0	1.3	0.1	1.4	0.0	9.4	0.0
NO_2^-	*	*	0.93	0.03	*	*	2.2	0.2	2.1	0.0
NO_3^-	3.3	1.2	2.4	0.1	143	3.0	37	0.9	53	1.7
PO_4^{3-}	*	*	0.32	0.04	0.43	0.05	150	10	1.3	0.0
SO_4^{2-}	12	0.1	3.2	0.0	12	0.1	20	0.0	17	0.1

We conducted the water extracts based on ÖNORM L 1092-93. Water was added to the soils in a 1:10 (w/v) soil-to solution ratio, shaken up by hand, and left for equilibration overnight. The next day, samples were shaken for 1 hour at 20 rpm in an overhead shaker, filtered first by paper (150 mm Munktell 14/N) and then by syringe (0.45 µm, nylon, Whatman™ GD/X). Afterwards they were split. Two subsamples for IC and DOC analysis were stored at -20 °C, whereas the third subsample used for ICP-MS/OES analysis was acidified with 65% HNO_3 (Merck, Darmstadt) and stored at 4 °C. Water extractions were carried out in duplicates. Parameters were determined as described in Table 2.

3.1.3 The field experiment

We conducted a field experiment to investigate the influence of wood ash incorporated for forest road stabilisation on the leachate and surface runoff water under real-world conditions. The two ashes, GA and FBA (Table 3) were each used in forest road construction in two different forests in Upper Austria. The forests Kobernausserwald und Weyregg (Figure 3) differ in soil characteristics and soil pH (Table 5). The soil in Kobernausserwald is rather acidic while Weyregg has a neutral to alkaline pH. Selected sections of both roads were treated with the ashes. About 8 cm of ash was spread onto the section, the ash layer was mixed into the soil material to a depth of 50 cm and the resulting ash-soil mixture (15% vol ash) was compacted to create a solid road (Stampfer 2014). Control sections, which were prepared by mixing and compacting 50 cm soil without ash, were included into the setup and each treatment was done in duplicates, resulting in 6 sampling sections per road.

Figure 3 Location of the Kobernausserwald (Ko) and the Weyregg (We) forest close to Attersee in Upper Austria.

3.1.3.1 Leachates and surface runoff

Two lysimeters were installed in each wood ash or control section right underneath the ash-soil layer at a depth of 50 cm. A concrete ring with drainage layer and a PE-foil at the bottom were ensuring the collection of lateral seepage water only (no horizontal flow). To collect the surface runoff, a foil was fixed next to the road leading into a halved drainage tube and subsequently a second sampling barrel (Figure 4).

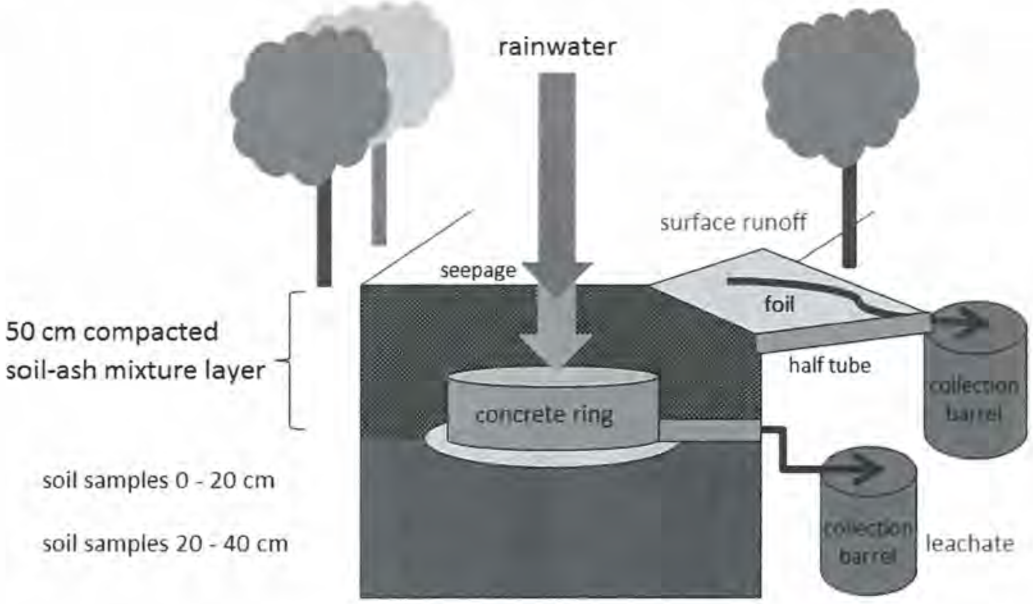

Figure 4 setup of the field experiment

We collected leachate and surface runoff samples once a month from April to October in the years 2012 and 2013. Sample collection and analysis in 2012 was carried out by Alexander Pasch, the sampling and data analysis from 2013 was carried out within the experimental work of this master thesis. For completeness, data from both years will be presented and discussed.

Due to the inherent variability in soil and road compaction, some barrels happened to be empty at some sampling times. This resulted in a variable amount of samples taken at each sampling point. Therefore the data of 14 months were merged into 4 sampling periods and averaged (Table 7).

Table 7 Number of field experiment samples taken per period with individual sample numbers per lysimeter in brackets.

Sampling period	Mar-Jun 12	Jul-Oct 12	Mar-Jun 13	Jul-Oct 13		Mar-Jun 12	Jul-Oct 12	Mar-Jun 13	Jul-Oct 13
Ko GA	5 (3:2)	7 (4:3)	6 (3:3)	5 (3:2)	**We GA**	3 (3:-)	4 (4:-)	3 (3:-)	4 (4:-)
Ko FBA	3 (3:-)	4 (4:-)	3 (3:-)	4 (4:-)	**We FBA**	4 (1:3)	8 (4:4)	6 (3:3)	6 (2:4)
Ko Control	1 (1:-)	3 (2:1)	2 (2:-)	4 (4:-)	**We Control**	5 (3:2)	5 (4:1)	6 (3:3)	6 (3:3)

At each sampling time point a 100 mL subsample was collected from each barrel which was thereafter completely emptied by a water-pump. Samples were taken to the laboratory, filtered by paper filtering (150 mm Munktell 14/N) and split. Two subsamples for IC and DOC analysis were stored at -20 °C, whereas the third subsample used for ICP-MS/OES analysis was acidified with 65% HNO_3 (Merck, Darmstadt) and stored at 4 °C. All parameters were measured as described in Table 2.

3.1.3.2 The field experiment sub-road soil samples

To investigate potential changes in total aqua regia and water soluble concentrations of the soils underneath the road, sub-road soil samples were taken in July 2013. Soil samples of one representative site for FBA, GA and control treatment in each forest were taken from a depth of 0 to 20 and 20 to 40 cm beneath the 50 cm ash-soil mixture layer, respectively. The samples were air dried, sieved (<2 mm) and analysed by water extractions and aqua regia digestion as described above.

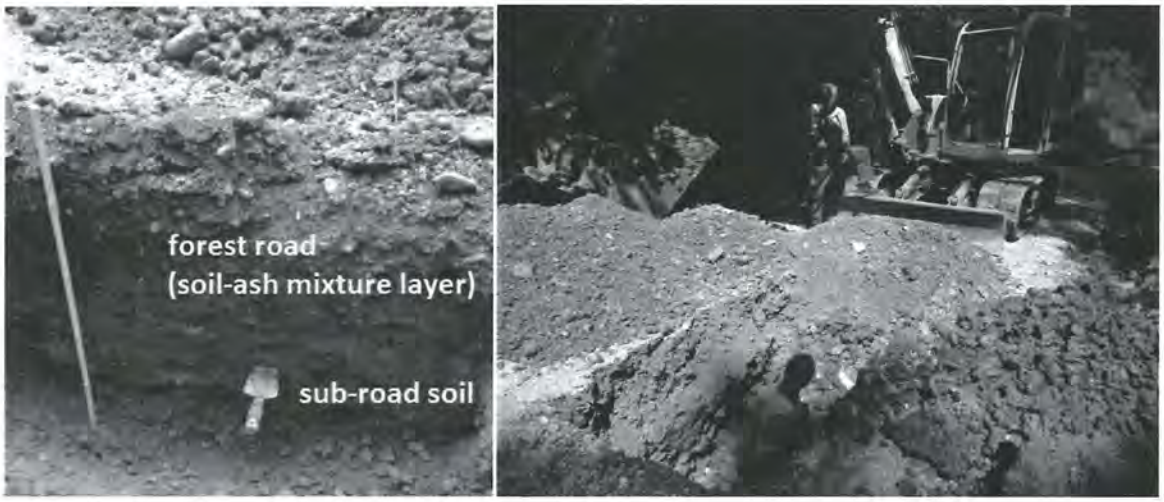

Figure 5 Pictures of the sub-road soil sampling in July 2013

3.1.4 The column experiment

To test the impact of ash on a broader range of soils and examine the buffering capacity of a soil layer beneath the ash-soil mixture layer we conducted a column experiment attempting to simulate a forest road with incorporated ash. We examined the three different soils S1, S2 and S3 (Table 5). We filled the columns by putting a 5 cm layer of ash-soil mixture (15% vol ash) of GA and FBA (Table 3), respectively, on top of 2 kg sieved (<4 mm) and dried, pure soil (≈ 20 cm) inside a 12 cm diameter column. A 2-cm layer of glass wool and a nylon mesh (mesh size 30 µm, SEFAR 03-30/18) at the bottom of the columns prevented the soil material to be washed out. On top of the ash-soil mixture polyethylene granulates (d = 0.35 cm) ensured the applied liquid to be spread equally and diminished evaporation (Figure 6). Two replicates per soil-ash combination were tested, resulting in a total number of 12 soil columns. At the start of the experiment, columns containing the dry soils were re-saturated with artificial rainwater from the bottom. The artificial rainwater solution was composed of 0.01 M NaCl (Sigma-Aldrich, Steinheim), 0.01 M KCl (Sigma-Aldrich, Steinheim), 0.001 M NH_4Cl (Sigma-Aldrich, Seelze), 0.001 M $MgCl_2$ (Merck, Darmstadt), 0.001 M $CaCl_2$ (Merck, Darmstadt), 0.001 M $NaNO_3$ (Sigma-Aldrich, Steinheim), 0.001 M Na_2SO_4 (Sigma-Aldrich, Seelze) and pH was adjusted to ~ 4.3 by adding 0.1 M HCl (WVR Chemicals, Fontenay-sous-Bois) (*Anderson et al 2000*).

Additionally, leaching column experiments using the experimental soils without the soil/ash mix layer on top were tested as control. Control column experiments containing soil only have already been carried out by Alexander Pasch in 2012. For completeness, this data will also be presented here and used for interpretation and discussion of obtained results.

3.1.4.1 The column experiment eluates

After the columns were saturated from the bottom to field capacity, 200 mL of artificial rainwater was applied 10 times to the top of each column, simulating a precipitation volume of 177 mm rainwater (Figure 6). Leachate water was collected at the bottom of the columns after every rainwater application, samples were filtered using syringe filters (0.45 µm, nylon, Whatman™ GD/X) and split and analysed as described above (Table 2).

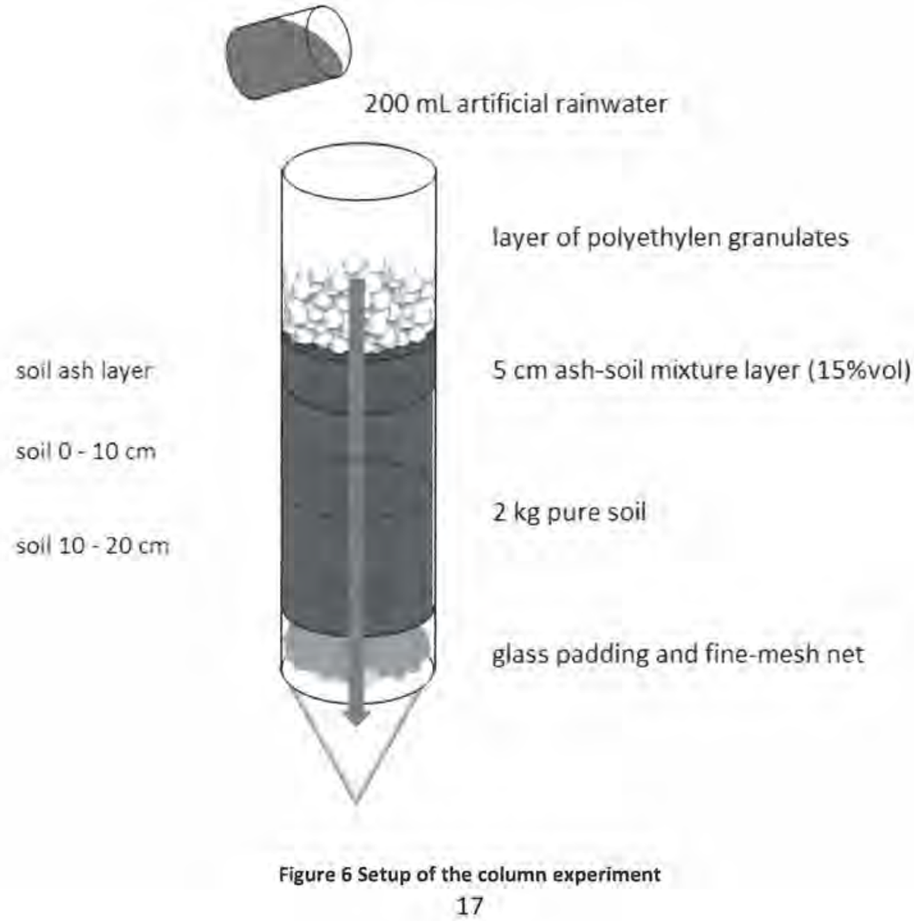

Figure 6 Setup of the column experiment

3.1.4.2 The column experiment soil extractions

At the end of the leaching experiment, we took soil samples from the ash-soil mixture layer, as well as the upper (0 to 10 cm) and lower (10 to 20 cm) layer of soil (Figure 6). Water extractions were carried out as described above to investigate potential changes in element water-solubility (chapter 3.1.2).

3.1.5 The 2-step extraction experiment of soil-ash mixtures

To investigate the influence of mixing ashes with different soils on the water solubility of elements and other characteristics we created ash-soil mixtures of dry soils (Ko, We, S1, S2, S3; all <2 mm) and dry ashes (GA, FBA), imitating the combinations and mixing ratio in the field and column experiment respectively. Pure soils and pure ashes were used as controls and all combinations and controls were done in two replicates. Water extractions of the mixtures and controls were conducted as described above.

All ash-soil mixture extracts were produced in double amount. One half of the resulting extract solution was used for analysis and the other half was used for the second step of the experiment (readsorption test).

To investigate whether the pure soils are able to re-adsorb contaminants released by the soil ash mixture, 50 mL of the extraction solution from the soil/ash mixture were added to 5 g of pure soil and treated the same way as the water extracts (Figure 7). This step is further on called "readsorption test".

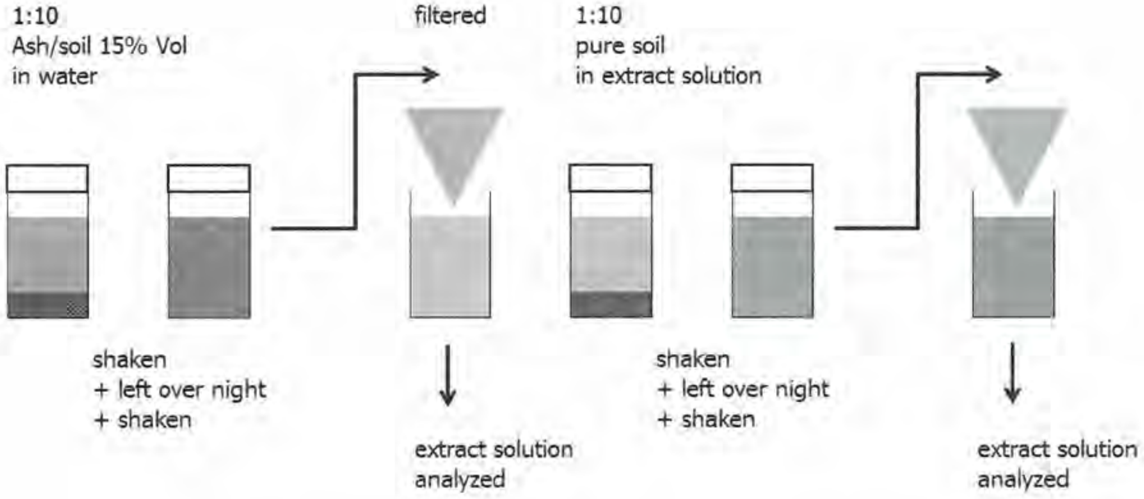

Figure 7 Schematic representation of the water extracts and subsequent readsorption experiment

3.2 Statistical and data analysis

All statistical analysis was carried out using the SPSS 15.0 (SPSS Inc., Chicago, IL). All data from the different experiments were analysed by one-way ANOVA including a *Student-Newman-Keuls* Post Hoc test.

For each field site, concentrations in the leachate and surface runoff from the field experiment were grouped into four sampling periods as described in Table 7 and compared separately within each sampling period. Differences in water soluble and total concentrations between ash and control treatments from the sub-road soil sampling of the field sites were tested within each site and soil depth layer.

For the column leaching experiment, the final cumulative elemental loads after 10 leaching steps were tested for significant differences. Column soil samples (water extractions) from the forest road simulation experiment were compared with the control within each soil.

Results from the 2-step water extractions of soil/ash mixtures were compared with results from pure soils respectively within each soil.

Ionic strength (I) was calculated from EC according to Equ 2 (Simón and García 1999)

$$I\ (\mathrm{mol\ dm^{-3}}) = 0.017\ EC\ (\mathrm{dS\ m^{-1}}) \qquad \text{Equ 2}$$

3.3 Comparison to legal thresholds

As the results gathered in the course of this thesis are supposed to be a basis for a legal framework of wood ash application in forest roads, a comparison to existing legal thresholds can serve as the preliminary evaluation of use of wood ash in forest road construction. It has to be pointed out, that a threshold exceedance is not equal to acute environmental threat, especially in case of the drinking and groundwater thresholds. They rather serve as indications of characteristics to focus the discussion on. Sample-period-averaged concentrations (Table 7) in the seepage water collected in the field experiment were compared to relevant thresholds given in Austrian legislation (Table 8).

- Ordinance for emissions from landfill sewage water (LSW), version of May 2013
- Ordinance for emissions from general sewage water (GSW), version of May 2013

  Both regulations contain thresholds for (I) direct discharge into running waters and (II) discharge into public sewerages.

- Ordinance for good chemical condition of the groundwater (GW), version of May 2013; this regulation contains concentration thresholds (th) and values for an indication of change in tendency (tc)[1]

- Ordinance for drinking water quality (DW); this regulation contains concentration thresholds (th) and indication values (ind)

Table 8 Concentration thresholds in Austrian legislations (empty fields indicating no existing threshold). LSW: thresholds for emissions from landfill sewage water into running waters (I) and public sewerages (II); GSW: thresholds for emissions from general sewage water into running waters (I) and public sewerages (II); DW: thresholds for drinking water including concentration thresholds (th) and indicator values (ind); GW: thresholds for groundwater including concentration thresholds (th) and indication values for change in tendency (tc).

		LSW		GSW		DW		GW	
		I	II	I	II	th	ind	th	tc
Al	µg L^{-1}			2000			200		
As	µg L^{-1}	100	100	100	100	10		9	7.5
B	µg L^{-1}					1000		900	750
Ba	µg L^{-1}			5000	5000				
Cd	µg L^{-1}	100	100	100	100	5		4.5	3.75
Co	µg L^{-1}			1000	1000				
Cr	µg L^{-1}	500	500	500	500	50		45	37.5
Cu	µg L^{-1}	500	500	500	500	2000		1800	1500
Fe	µg L^{-1}			2000			200		
Mn	µg L^{-1}						50		
Na	mg L^{-1}						200		
Ni	µg L^{-1}	500	500			20		18	15
P	µg L^{-1}				2000				
Pb	µg L^{-1}	500	500	500	500	10		9	7.5
Se	µg L^{-1}					10			
Zn	µg L^{-1}	500	500	2000	2000				
pH		6.5 - 8.5	6.5 - 9.5	6.5 - 8.5	6.5 - 9.5		6.5 - 9.5		
EC	µS cm^{-1}						2500	2250	1875
DOC	mg L^{-1}	20		25					
Cl^-	mg L^{-1}						200	180	150
F^-	mg L^{-1}			10	20	1.5			
NO_2^-	mg L^{-1}	2.00	10.00	1.00	10.00	0.10		0.09	0.075
NO_3^-	mg L^{-1}					50		45	37.5
PO_4^{3-}	mg L^{-1}							0.30	0.225
SO_4^{2-}	mg L^{-1}				200		250	225	187.5

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[1] If more than 30% of measurement sites exceed these values and a significant rise in concentration is detected, special measures have to be undertaken to secure the ground water quality.

The extractable amounts and total concentrations of relevant parameters found in the sub-road soil samples were compared to Austrian legal thresholds for excavated soils (Deponieverordnung 2008, version Sept 2013, Table 9).

Table 9 Austrian legal thresholds for extractable amounts and total concentrations of excavated soils (Deponieverordnung 2008, version Sept 2013)

	Water extractable concentrations [mg kg^{-1}]	Total concentrations [mg kg^{-1}]	
		Background values	high geogenic concentrations
As	0.5	50	200
Ba	10		
Cd	0.1	2	4
Co	1.0	50	
Cr	1.0	300	500
Cu	2.0	100	500
Ni	1.0	100	500
Pb	1.0	150	500
Zn	20	500	1000
NO_2^-	2.0		
NO_3^-	100		
PO_4^{3-}	5.0		
EC [µS cm^{-1}]	150		
pH	11		

4 Results

4.1 Results of the field experiment leachates and surface runoff

Only the leachate results will be presented in detail, as changes in leachate composition are expected to be more severe and a higher threat to the environment than changes in surface runoff water quality. The results of the surface runoff analysis were only compared to legal thresholds as further elaboration was not within the scope of this thesis.

The leachate results are presented as concentration averages of the leachate samples within the 4 sampling periods. For data interpretation, the variable number of samples per period and the high natural variability need to be considered (Table 7).

In general the highest concentrations and most threshold exceedances were found for the combination of GA on Ko soil (Table 11). However, due to lower natural variability of the We soil results, most significant differences were found for the application of GA on We soil (Table 10).

Table 10 Occurrence of significant differences in leachate concentrations of the GA and FBA treatment on Ko and We soil, respectively (combinations indicated as "soil-ash") compared to the control in at least one of the sampling periods. "+" = sign. higher, "-" = sign. lower, "nd" = no sign. difference; ($p < 0.05$).

	Ko - GA	Ko - FBA	We - GA	We - FBA
pH	nd	nd	nd	nd
EC	nd	nd	nd	nd
DOC	nd	nd	nd	nd
Ca	nd	nd	nd	nd
K	nd	nd	+	nd
Mg	nd	nd	nd	nd
Na	nd	nd	nd	nd
Al	nd	nd	+	nd
As	nd	nd	+	nd
B	nd	nd	+	nd
Ba	nd	nd	nd	nd
Cd	-	-	nd	nd
Co	nd	nd	+	nd
Cr	nd	nd	+	nd
Cu	-	-	+	nd
Fe	+	nd	-	-
Mn	nd	nd	nd	nd
Mo	nd	nd	+	+
Ni	+	nd	+	nd
P	-	-	nd	nd
Pb	nd	nd	nd	nd
Se	nd	nd	+	nd
V	+	nd	+	nd
Zn	+	+	nd	nd
Cl^-	nd	nd	nd	nd
F^-	nd	nd	+	nd
NO_2^-	nd	nd	nd	nd
NO_3^-	nd	nd	+	nd
PO_4^{3-}	nd	nd	nd	nd
SO_4^{2-}	nd	nd	+	+

Despite the indication of an initial increase in pH in case of the GA treatment in Kobernausserwald, the ashes had little influence on the pH of the leaching water, as no significant differences and no tendencies between treatments were observed (Figure 8, SI-Fig. 1).

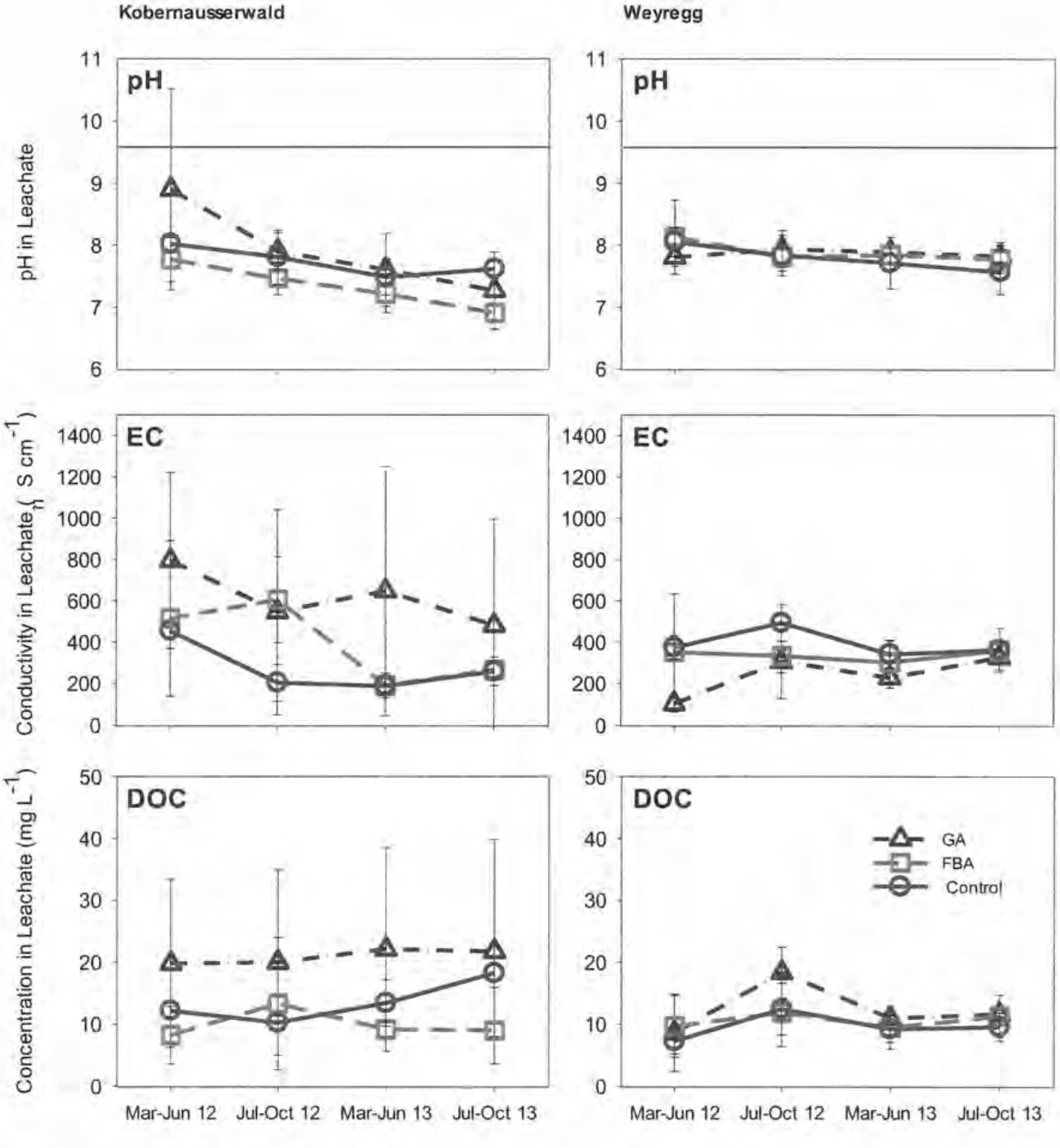


Figure 8 Leachate values of pH, EC and DOC from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period (p < 0.05). The red line indicates the threshold in Austrian ordinance fort Drinking Water.

The EC in Kobernausserwald was subjected to high natural variability. Though not statistically significant ($p < 0.05$), the GA treatment resulted in higher EC values throughout the sampling periods compared to the control. In the FBA treatment samples the EC was similar to the control. In Weyregg the EC of the ash treatment leachates was rather similar or even lower than the control (Figure 8, SI-Fig. 1).

Similar to EC, a higher variation in DOC concentrations within and between the treatments was observed in Kobernausserwald compared to Weyregg, but no statistically significant differences were found at both experimental sites (Figure 8, SI-Fig. 1).

The concentrations of the alkali (K, Na) and alkaline earth metals (Ca, Mg) revealed large variability. The ash treatments showed few significant differences to the control due to the high variability within the same treatment (Table 10). In Kobernausserwald, concentrations of the metals in the ash leachates of the ash treatments (particularly GA) tended to be lower than in the control, but this was not statistically significant. In Weyregg the same tendency was found for K only, with the GA treatment showing significantly higher concentrations in the last three periods (Figure 9, SI-Fig. 2).

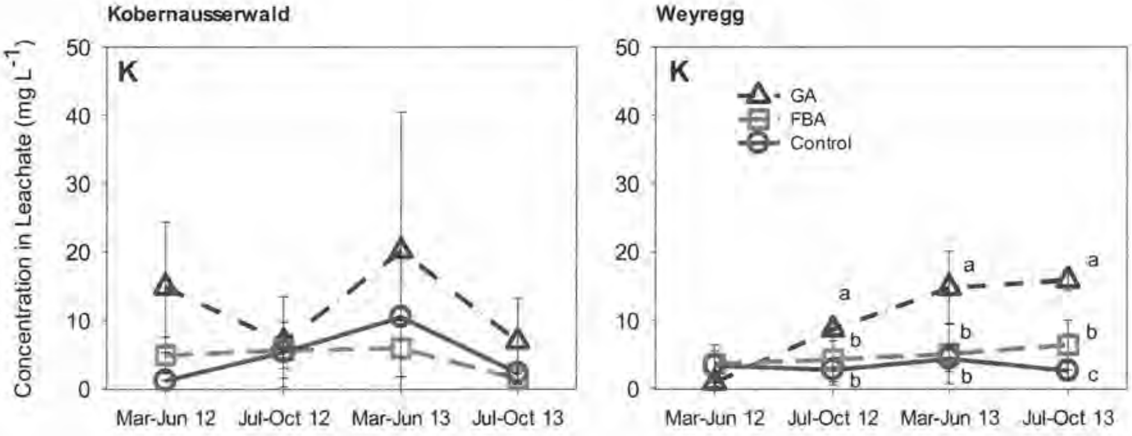


Figure 9 Leachate concentration of K from the forest road field sites in Kobernausserwald and Weyregg over time. Data represents means of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$).

Calcium, Mg and Na in contrast showed similar to lower concentrations in both ash treatments compared to the control in the Weyregg forest. The values for EC reflect the findings for the macronutrients (SI-Fig. 1 and 2).

Aluminium, Fe and Mn (Figure 10, SI-Fig 3) showed a statistically insignificant increase in concentrations during the first period of the GA treatment in Kobernaussernwald. However, in the fourth period the concentration of Fe rose close to the initial flush resulting in a significant difference to the FBA and control treatment. In Weyregg the concentrations of Al, Fe and Mn of GA and FBA treatment stayed low and close to the control treatment throughout all periods. In the fourth period even significantly lower Fe leachate concentrations were observed in both ash treatments.

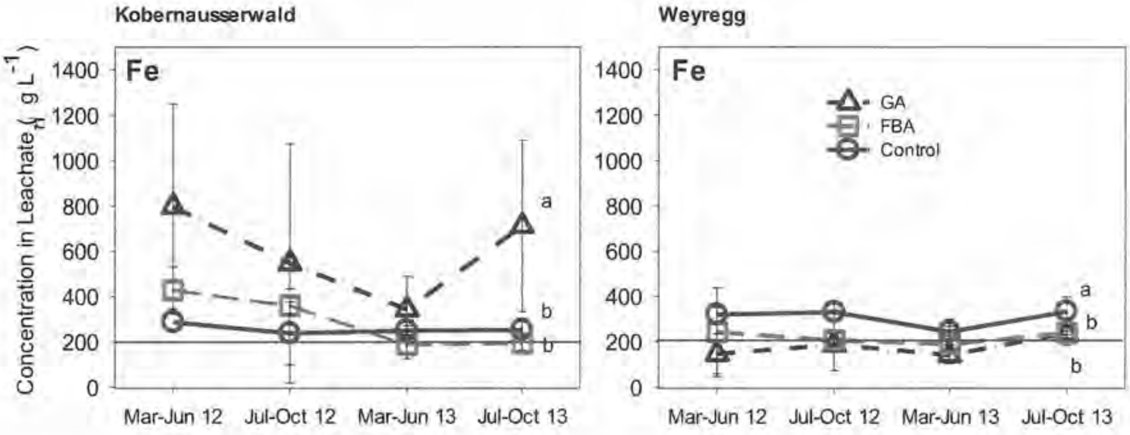


Figure 10 Leachate concentration of Fe from the forest road field sites in Kobernausserwald and Weyregg over time. Data represents means of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). The red line indicates the threshold in Austrian ordinance fort Drinking Water.

A particular temporal pattern in element concentration in the collected seepage water was observed for As, Co, Cu, Mo, Ni and V. In each of those cases the GA treatment showed a clear, however due to high variability insignificant initial flush occurring in Kobernausserwald (Figure 11, SI-Fig. 4,5,6,7). To a lesser extent the same pattern was observed in the FBA treatment. The curves of element concentrations in the GA and FBA treatments levelled off in the second period, while the concentrations in the control remained low.

Leachate concentrations of the same elements in Weyregg showed a different pattern. Here we found a delayed flush event for the GA treatment. While no significant difference was found in the first period, the concentrations increased in the second period followed by a slow decrease in the third or fourth. In these three periods the concentrations were significantly higher in the GA compared to the FBA and the control treatment for all six elements (Table 10). In the FBA treatment the concentrations were similar to the control. The concentrations observed during the delayed flush in Weyregg were much lower than the initial flush event in Kobernausserwald.

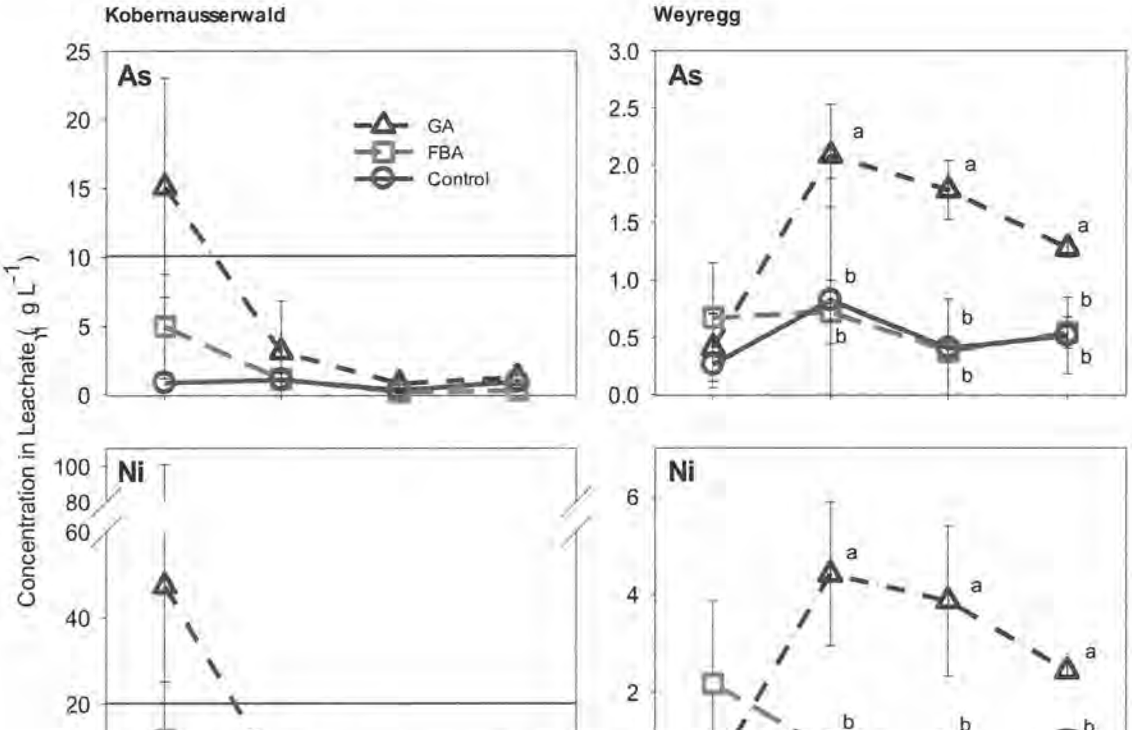


Figure 11 Leachate concentration of As and Ni from the forest road field sites in Kobernausserwald and Weyregg over time. Data represents means of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period (p < 0.05). The red lines indicate the threshold in Austrian ordinance fort Drinking Water. Note the different scales.

Despite their different temporal pattern, B, Cd, Pb and Se are similar in showing mostly higher values (though not significant) in the GA treatment than the FBA and Control treatment (Figure 12, SI-Fig. 4, 6). Initial flushes were observed for B and Cd in Kobernausserwald, however therafter the ash treatment concentrations of Cd decreased to concentrations significantly lower than the control in the 2nd period. In Weyregg significantly higher concentrations in the GA treatment were found for B with a tendency to increase further and for Se with a tendency to decline.

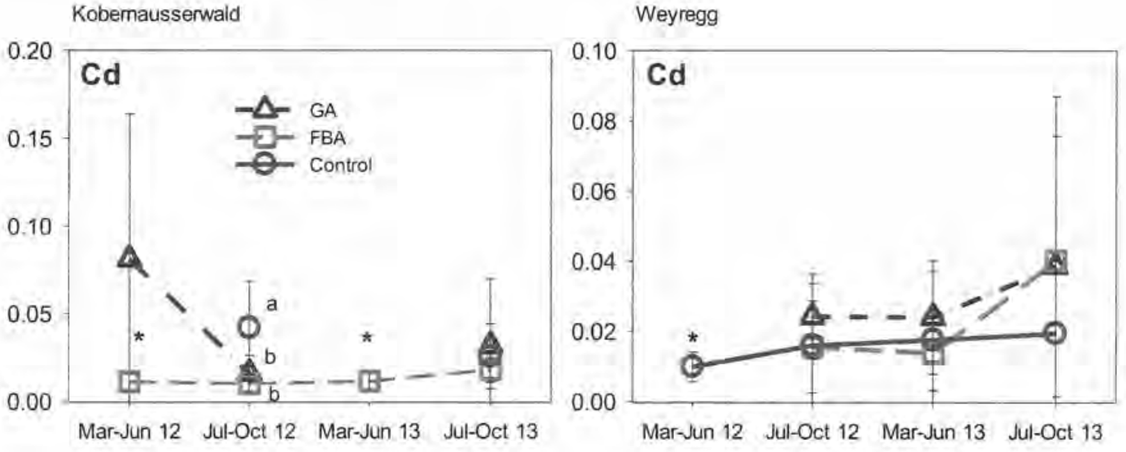


Figure 12 Leachate concentration of Cd from the forest road field sites in Kobernausserwald and Weyregg over time. Data represents means of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales. *values below LOQ (SI-Table 1).

No significant differences in leachate concentrations in the different treatments and experimental sites could be observed for Ba. The Cr concentrations behaved similarly, except for increasing concentrations of the GA-treated sites in Kobernausserwald leading to a significant higher concentration compared to FBA and control in the last period. Zinc concentrations in the FBA treatment in Kobernausserwald increased in the last period significantly exceeding those in the other treatments, while no differences were observed in Weyregg (SI-Fig. 4, 5, 7).

Investigated anions (Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) did not resemble each other in their temporal leaching pattern (Figure 13 SI-Fig. 7, 8). In Kobernausserwald, the concentrations in the GA treatment pictured a statistically insignificant initial flush for Cl^-, F^- and NO_2^-. The NO_3^- and SO_4^{2-} concentrations start at similar level in all treatments. In the third and fourth period, the GA treatment resulted in considerably higher concentrations compared to FBA and Control. However, the difference was not statistically significant. Apart from a smaller flush in case of Cl^-, the concentrations of the FBA treatment stayed close to the control concentrations (Figure 13, SI-Fig. 7, 8). In Weyregg the concentrations of all treatments were in a lower range than in Kobernausserwald for Cl^-, NO_2^-, NO_3^- and SO_4^{2-}. In Weyregg the FBA treatment concentrations of Cl^-, F^- and NO_3^- stayed close to the control, while the GA treatment showed significant higher values for F^- in the third and NO_3^- in the fourth period. Both ash treatments had higher SO_4^{2-} concentrations than the control in most periods, with a significant difference in the 4th period. In accordance with P concentrations, the PO_4^{3-} concentrations of the ash treatments stayed lower or close to the control treatment in Kobernausserwald. However in Weyregg the FBA treatment PO_4^{3-} and total P concentrations increased over time compared to GA and Control. Due to high variances though, the differences were not significant.

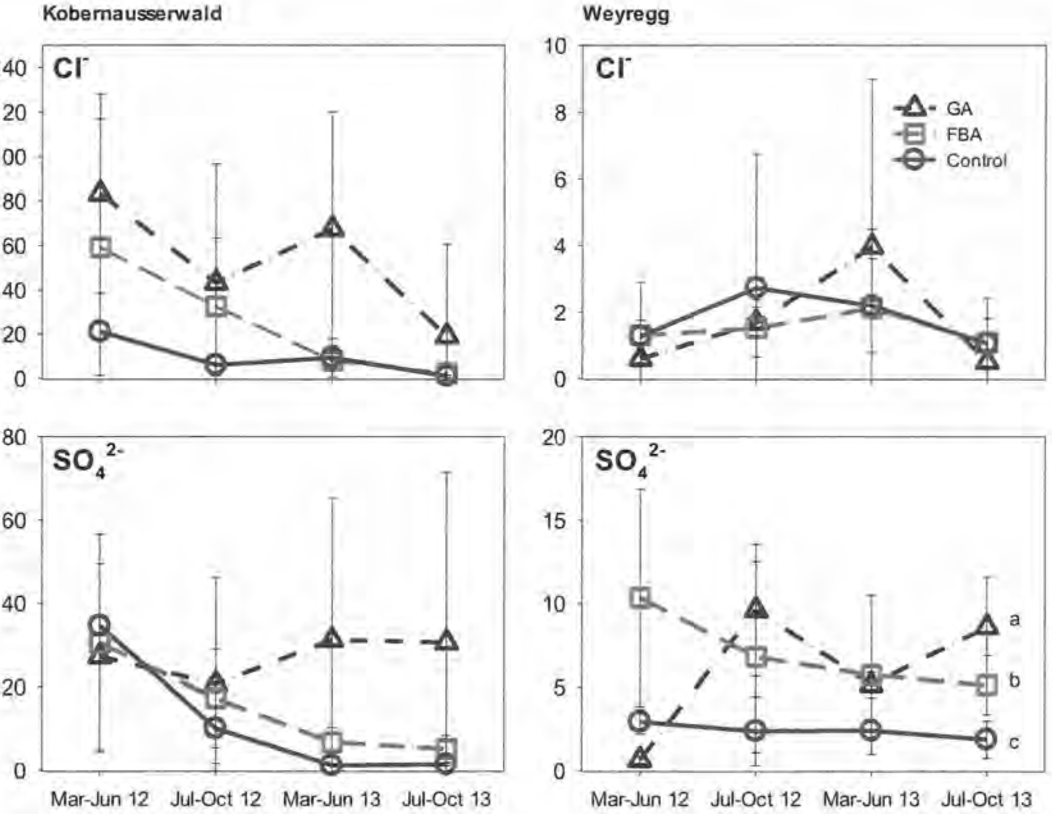


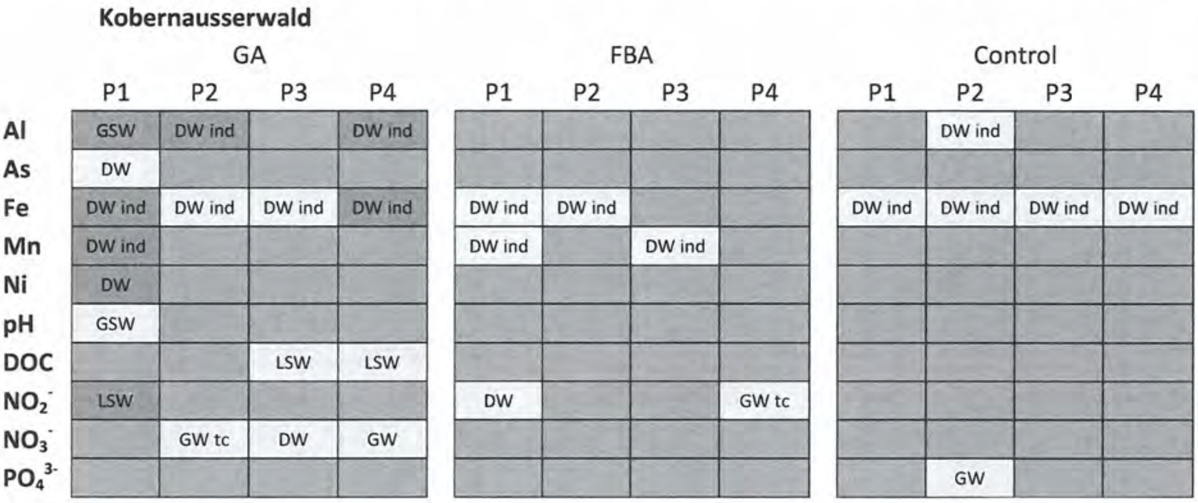
Figure 13 Leachate concentrations of Cl^- and SO_4^{2-} from the forest road field sites in Kobernausserwald and Weyregg over time. Data represents means of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales.

All eight periodic averages of leachate concentrations obtained for each parameter were compared to the corresponding thresholds in Austrian legislation (Table 8). Results are shown in Table 11. Most exceedances were found for GA treatment in the acidic Kobernausserwald forest. Here the majority of exceedances occurred in the first sampling period during the initial flushes (Al, As, Fe, Mn, Ni, pH, NO_2^-). In the remaining three periods thresholds were exceeded less often for fewer elements (Al, Fe, DOC, NO_3^-). In the same forest, treatment with FBA only led to threshold exceedances for Fe, Mn and NO_2^-. However, even the control treatment samples exceeded thresholds (Fe, Al, PO_4^{3-}). In the leachates from Weyregg considerably less concentrations exceeded thresholds. Only Al, Fe and NO_2^- thresholds under

GA treatment and Fe and PO_4^{3-} thresholds under FBA treatment were exceeded in this forest. Here the control samples exceeded thresholds for their Fe, NO_2^- and PO_4^{3-} concentrations.

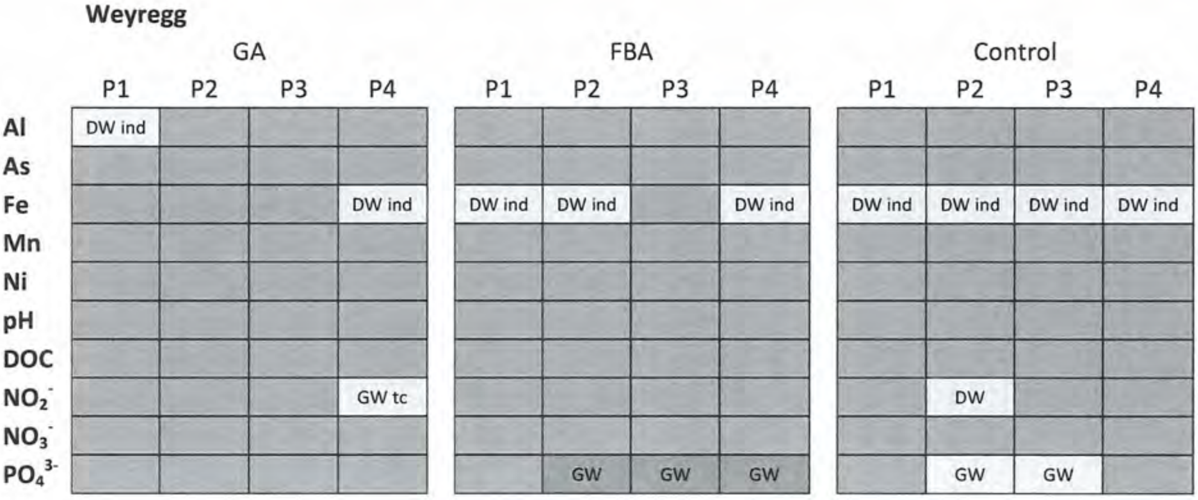
No threshold exceedances were observed for B, Ba, Cd, Co, Cr, Cu, Na, P, Pb, Se, Zn, EC, Cl^-, F^-, PO_4^{3-} and SO_4^{2-}. Where the concentrations in the ash treatments were exceeding a threshold, there was no significant difference to the controls found at the same time. Only in the case of the Fe values in the Kobernausserwald GA treatment the threshold was exceeded and the concentration was significantly higher than the control. However in this case the control treatment exceeded the threshold as well (Figure 10, Table 11). Except for initial flushes of pH, Al and NO_2^- (and close-to-threshold values of DOC) on the GA-treated site in Kobernausserwald, no thresholds of the LSW and GSW ordinance were exceeded. The comparison of concentrations to DW and GW ordinance aims at finding critical parameters to be looked at in more detail.

Table 11 Comparison of periodic averages of leachate water concentrations of the field experiment with legal thresholds. Green: no threshold exceeded; yellow: concentration exeedes threshold, but lower than 3-fold the lowest threshold; red: concentration exeeds threshold and is higher than 3-fold the lowest threshold. Thresholds and abreviations see Table 8.



Kobernausserwald

	GA				FBA				Control			
	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4
Al	GSW	DW ind		DW ind						DW ind		
As	DW											
Fe	DW ind	DW ind	DW ind	DW ind	DW ind	DW ind			DW ind	DW ind	DW ind	DW ind
Mn	DW ind				DW ind		DW ind					
Ni	DW											
pH	GSW											
DOC			LSW	LSW								
NO_2^-	LSW				DW			GW tc				
NO_3^-		GW tc	DW	GW								
PO_4^{3-}										GW		

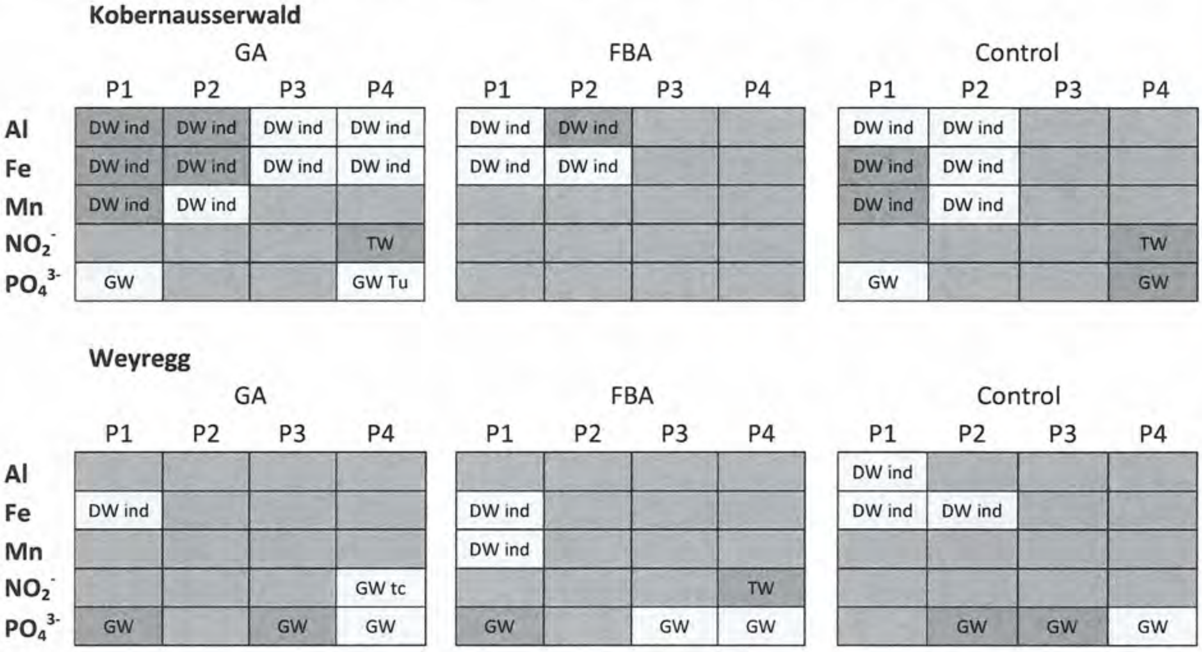


Weyregg

	GA				FBA				Control			
	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4
Al	DW ind											
As												
Fe				DW ind	DW ind	DW ind		DW ind	DW ind	DW ind	DW ind	DW ind
Mn												
Ni												
pH												
DOC												
NO_2^-				GW tc						DW		
NO_3^-												
PO_4^{3-}						GW	GW	GW		GW	GW	

The surface runoff samples exceeded thresholds for Al, Fe, Mn, NO_2^- and PO_4^{3-} (Table 12). However, this is mainly attributed to high natural values, as seen in the exceedances of the control samples. Thus, it is confirmed that the ashes have little impact on the surface runoff concentrations.

Table 12 Comparison of the field experiment surface runoff period mean values to thresholds in legal legislation. Green: no threshold exeeded; yellow: concentration exeedes threshold, but lower than 3 fold the lowest threshold; red: concentration exeeds threshold and is higher than 3 fold the lowest threshold. Thresholds and abreviations see Table 8.



Kobernausserwald

	GA				FBA				Control			
	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4
Al	DW ind	DW ind	DW ind	DW ind	DW ind	DW ind			DW ind	DW ind		
Fe	DW ind	DW ind	DW ind	DW ind	DW ind	DW ind			DW ind	DW ind		
Mn	DW ind	DW ind							DW ind	DW ind		
NO_2^-				TW								TW
PO_4^{3-}	GW			GW Tu					GW			GW

Weyregg

	GA				FBA				Control			
	P1	P2	P3	P4	P1	P2	P3	P4	P1	P2	P3	P4
Al									DW ind			
Fe	DW ind				DW ind				DW ind	DW ind		
Mn					DW ind							
NO_2^-				GW tc				TW				
PO_4^{3-}	GW		GW	GW	GW		GW	GW		GW	GW	GW

4.2 Results of the field experiment sub-road soil samples

The sub-road soil samples were analysed by water extraction (water soluble fraction) and acid digestion (total concentrations) to investigate a potential lateral accumulation or a change in element solubility in the undisturbed soil profile underneath the soil/ash mix layer. Overall results are strongly influenced by natural variations and it has to be pointed out, that the replicates within one treatment were taken at the same sampling site, hence the results only depict the soil features of a single sampling site for each treatment.

4.2.1 Total concentrations (Aqua regia)

A summary overview is given in Table 13 revealing that significant changes in total concentrations were observed on both experimental sites, however obviously eluviations of elements happened to a higher extend in the Weyregg forest. It has to be pointed out though, that a significant elevation not always means a considerable elevation at the same time (e.g. see Ko 20-40, Figure 14).

Table 13 Occurrence of significant differences in total concentrations of the sub-road soil samples in 0-20 and 20-40 soil layers comparing the GA and FBA treatment to the control. "+" = sign. higher, "-" = sign. lower, "nd" = no sign. difference.

	Ko - GA		Ko - FBA		We - GA		We - FBA	
	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40
Ca	nd	nd	nd	nd	nd	nd	nd	+
K	nd	+	nd	+	nd	+	+	+
Mg	nd	nd	-	nd	nd	+	nd	+
Na	nd	nd	nd	nd	nd	+	nd	nd
Al	nd	nd	nd	nd	+	+	nd	nd
Fe	nd	nd	nd	nd	nd	nd	nd	nd
Mn	nd	nd	+	+	nd	nd	nd	+
As	nd	nd	nd	+	nd	nd	nd	+
B	+	nd	+	nd	nd	nd	nd	+
Ba	-	nd	-	+	+	+	nd	+
Cd	nd	nd	nd	nd	nd	+	+	+
Co	-	nd	nd	+	-	nd	-	nd
Cr	nd	+	nd	+	nd	+	nd	nd
Cu	nd	nd	-	nd	nd	+	+	+
Mo	nd	nd	nd	+	+	nd	nd	-
Ni	nd	nd	nd	nd	nd	+	nd	+
P	nd	nd	+	+	+	+	+	+
Pb	nd	nd	+	nd	+	+	nd	-
Se	nd	nd	nd	nd	nd	nd	nd	nd
V	nd	nd	nd	nd	+	+	nd	+
Zn	nd	nd	nd	nd	+	+	+	+

The soils underneath the roads did not differ much between treatments with respect to their alkali (Na, K) and earth alkali metal (Ca, Mg) total concentrations (Figure 14, SI-Fig. 9). Only in Weyregg the soil underneath the FBA-treated road section contained considerable amounts of Ca with a significant difference to control in the lower layer (20-40). Also the total concentrations of K, Mg and Na were mostly significantly higher in this layer, however this can be attributed to the low concentration values in the control, which might be a result of natural variation. For K a significant increase was also found in the 0 - 20 cm layer of the FBA-treated site in Weyregg and in the 20 - 40 cm layer of both ash treatments in Kobernausserwald. Here the total difference, however, is negligible.

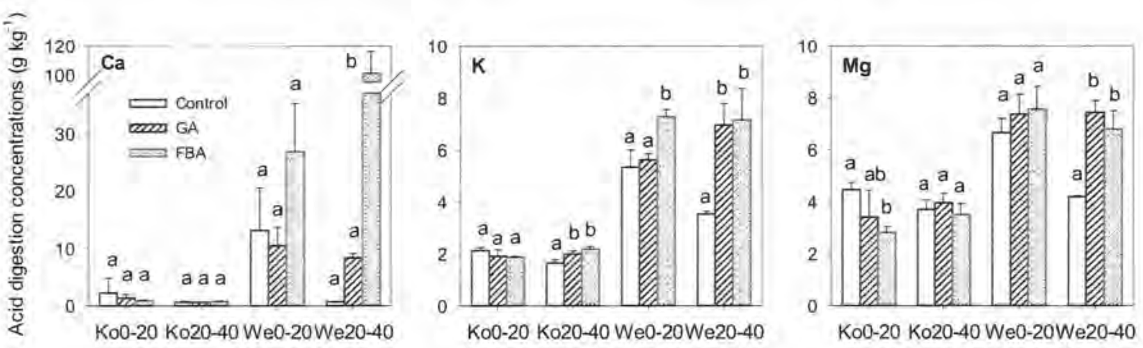


Figure 14 Total Ca, K and Mg concentrations of the field experiment sub-road samples in the upper (0-20 cm) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest. Note the values in g kg^{-1}.

Al and Fe total concentrations were elevated on the GA-treated road section in Weyregg, but only significantly for Al. The same pattern was found for the Ba concentrations (Figure 15, SI Fig. 9,10). Also the Cr, Mo, Pb and V total concentrations showed a similar pattern to Al and Fe in Kobernausserwald. The difference was significant for Pb and V in both layers, for Cr in the lower (20-40cm) and Mo in the upper (0-20cm) layer only (SI-Fig. 10).

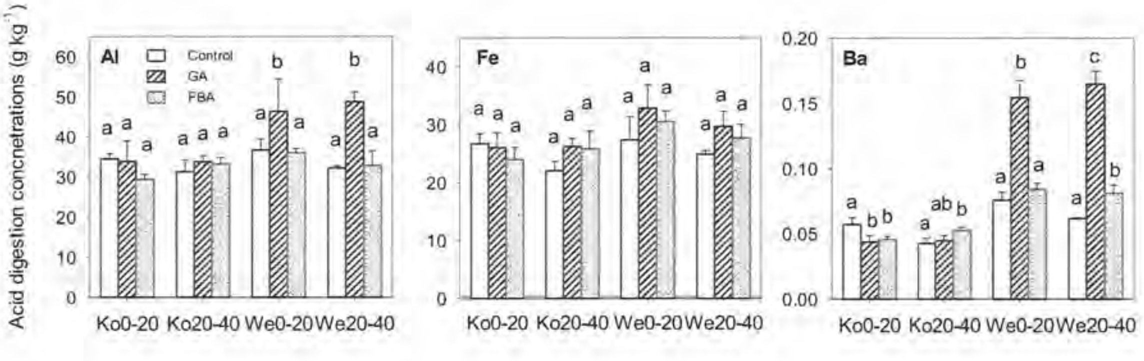


Figure 15 Total Al, Fe and Ba concentrations of the field experiment sub-road samples in the upper (0-20 cm) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest. Note the values in g kg^{-1}.

In contrast, the Mn total concentrations were significantly higher in the FBA-treated sites in both Kobernausserwald layers and in the 20 - 40 cm layer in Weyregg. As total concentrations showed a similar pattern. Particularly higher total concentrations on the FBA-treated sites were found for P (Si-Fig. 10). Boron, Cd, Cu and Ni total concentrations in Weyregg were also often significantly elevated on the FBA treatments in both layers (Figure 16, SI-Fig. 10).

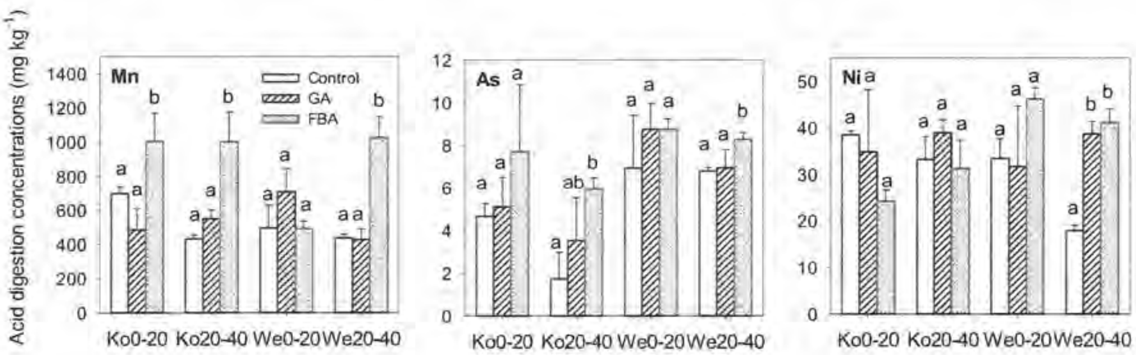


Figure 16 Total Mn, As and Ni concentrations of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest.

The total concentrations were compared to Austrian legal thresholds for excavated soils (Deponieverordnung 2008, version Sept 2013; Table 9). No threshold exceedances were found.

4.2.2 Water soluble concentrations

The water extractions were conducted to see whether water solubility and therefore environmental availability is significantly altered underneath the road due to the use of wood ash in forest road construction and whether a change in total element concentration is also reflected by a significant increase in solubility. Significant differences for the forest-ash combinations in 0-20 and 20-40 cm layers underneath the road are shown in Table 14. In accordance with the total concentrations more significant differences were found in the Weyregg forest. Generally we found more significantly higher water soluble concentrations of elements in the 20-40 cm than in the 0-20 cm layer. Table 14 also indicates for which elements a significant increase in total concentrations led to a significant increase in extractability at the same time (*). This was observed mainly in the 20-40 cm layer in Kobernausserwald treated with GA and in Weyregg for both ashes. However, considerably lower concentrations for various elements were found in the Weyregg 20-40 cm control layer (SI-Fig. 11, 12, 13). Hence, here the differences to the control might be caused by natural variation of soil properties.

Table 14 Occurrence of significant differences in water extractable concentrations of the sub-road soil samples in the 0-20 and 20-40 cm soil layers comparing the GA and FBA treatment to the control. "+" = sign. higher, "-" = sign. lower, "nd" = no sign. difference. * total contents were significantly elevated as well (Table 13)

	Ko - GA		Ko - FBA		We - GA		We - FBA	
	0-20	20-40	0-20	20-40	0-20	20-40	0-20	20-40
pH	-	nd	nd	+	nd	+	nd	+
EC	+	+	nd	+	nd	+	nd	+
DOC	-	nd	nd	+	nd	+	nd	+
Ca	nd	+	nd	nd	nd	+	nd	+*
K	nd	nd	nd	+*	nd	+*	nd	+*
Mg	nd	+	nd	nd	nd	+*	nd	+*
Na	nd	+	nd	nd	nd	nd	nd	nd
Al	-	-	nd	+	nd	+*	nd	+
Fe	nd	nd	+	+	nd	+	nd	+
Mn	nd	nd	nd	nd	+	+	-	nd
As	-	nd	nd	+*	nd	+	-	nd
B	-	+	nd	+	nd	nd	nd	nd
Ba	-	+	nd	+*	nd	+*	nd	+*
Cd	+	nd	nd	nd	nd	+*	nd	+*
Co	nd	nd	nd	nd	nd	+	nd	nd
Cr	-	-	-	+*	nd	+*	nd	+
Cu	-	nd	-	+	nd	+*	nd	+*
Mo	nd	nd	+	+*	nd	+	nd	+
Ni	nd	nd	nd	nd	nd	+*	nd	+*
P	-	nd	+*	+*	+*	+*	+*	+*
Pb	-	nd	nd	+	nd	+*	nd	+
Se	-	-	nd	+	+	+	+	nd
V	-	-	nd	+	nd	+*	nd	nd
Zn	-	nd	nd	+	nd	+*	nd	+*
Cl^-	nd	nd	nd	nd	nd	nd	nd	nd
F^-	nd	nd	-	-	nd	+	nd	+
NO_2^-	nd	nd	nd	nd	-	nd	+	nd
NO_3^-	nd	+	nd	nd	nd	nd	nd	nd
PO_4^{-3}	nd	nd	+	+	+	+	+	nd
SO_4^{-2}	nd	nd	nd	nd	nd	-	nd	-

In the water extracts pH, DOC and EC of the soils were also measured. The pH was significantly increased in the 20 - 40 cm layer of both ash treatments compared to the control in Weyregg, while no difference was found in the upper soil layer (0-20 cm). In Kobernausserwald, the 0 - 20 cm layer right underneath the GA treatment even showed a significantly lowered pH compared to the control and the FBA treatment (Figure 17, SI-Fig. 11).

A high variability in DOC concentrations was observed. The FBA treatments showed no significant difference in the upper (0-20cm) soil layer, while a significant increase compared to the control was observed for the 20-40 cm layer at both experimental sites. The application of GA significantly decreased DOC concentrations in the upper soil layer (0-20cm) in Kobernausserwald, however a significant increase could be observed in the lower soil layer (20-40 cm) in Weyregg. The EC was found to be significantly higher in the 20 - 40 cm layers of both ash treatments in both forests, in the 0 - 20 cm layer only for the GA treatment in Kobernausserwald (Figure 17, SI-Fig. 11).

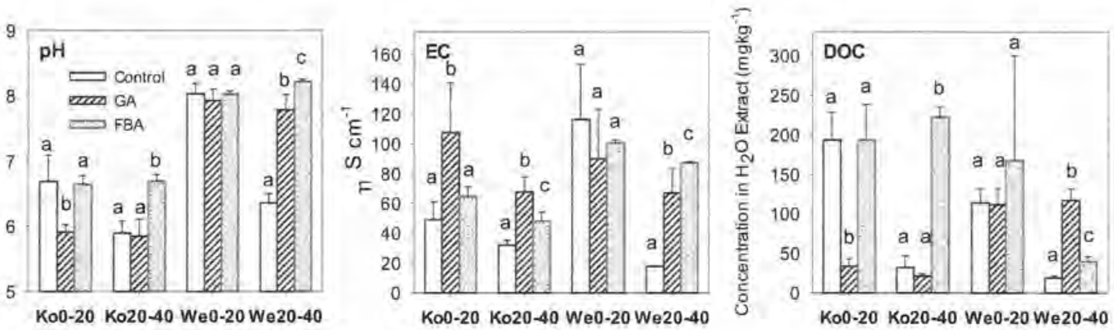


Figure 17 pH, EC and DOC values of the field experiment sub-road sample water extracts in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest.

The Ca- and Mg- extractable concentrations are closely related to the findings for EC (Figure 18, SI-Fig. 12). Higher concentrations were found in the GA-treated sites in Kobernausserwald (significant for the lower soil layer). Also in the lower soil layer in Weyregg both treatments resulted in significant increase of extractable Ca, Mg and EC compared to the control. For extractable Na and K significant differences were only found in Kobernausserwald in the 20 - 40 cm layer, with soluble Na concentrations being higher in the GA treatment (Figure 18), while higher K solubility was observed in the FBA treatment (SI-Fig 12).

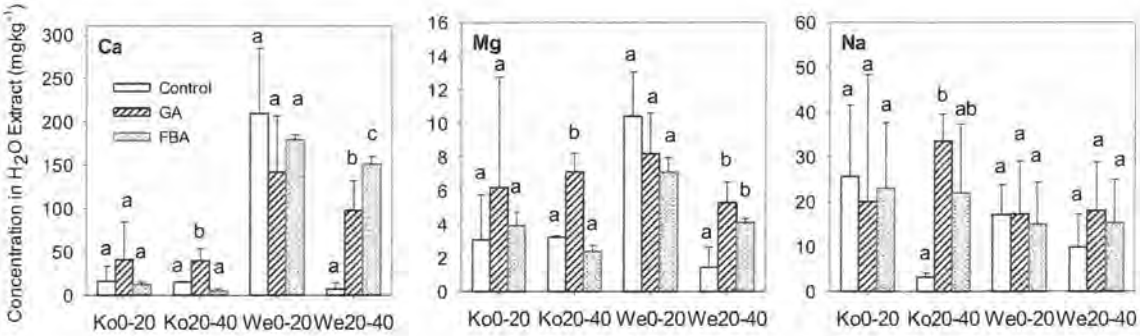


Figure 18 Calcium, Mg and Na concentration in the water extracts of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest.

Aluminium and Fe showed a similar pattern of extractable concentrations (Figure 19, SI-Fig. 12). Similar to DOC (Figure 17), particularly high concentrations were found on the FBA-treated site in Kobernausserwald. The difference was significant compared to the GA treatment and the control in the 20 - 40 cm layer, but not to the control in the upper layer (0-20 cm). In Weyregg the Al- and Fe-extractable concentrations showed little difference between the treatments. Increased concentrations were found in the lower soli layer (20-40 cm) of the ash treatments compared to the control, but the differences were only significant for Fe. Interestingly similar patterns were found for As, Cr, Pb, V and Zn. Some of the analysed elements like B, Ba, Cu and Ni followed their trend especially in Kobernausserwald (Figure 19, SI-Fig. 13).

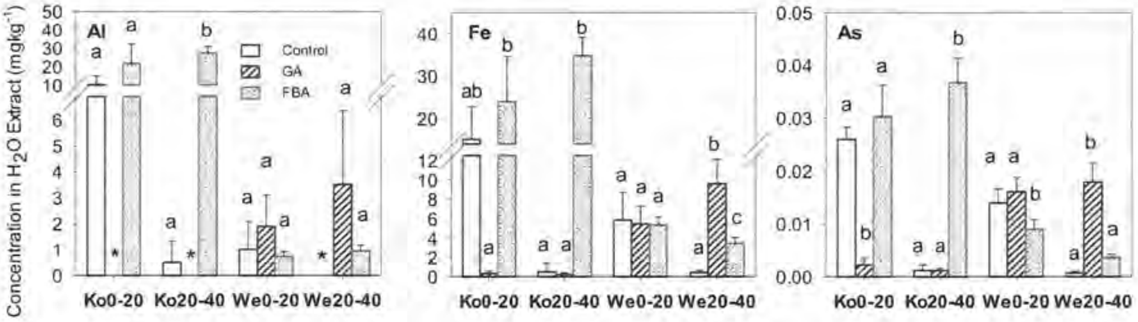


Figure 19 Aluminium, Fe and As concentration in the water extracts of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest. * below LOQ.

In contrast no differences between treatments were found for Mn concentrations in Kobernausserwald, where the natural extractable concentrations were comparatively high. However, in Weyregg the GA-treated site contained significantly higher extractable concnetrations than the control in both soil layers (SI-Fig. 12).

The IC analysis of the water extractable anions resulted in inconsistent findings and high variability. No significant differences were found for Cl^-. Nitrate only showed significant increase on the GA-treated site in the Kobernausserwald 20-40 cm layer compared to the other treatments. Most samples contained no quantifiable concentrations of PO_4^{3-} and NO_2^-, however in the upper layer (0-20 cm) in Weyregg significant higher concentration of extractable NO_2^- was found in the FBA-treated site compared to the control. Sulfate showed a particularly high natural variation with concentration averages of the GA treatment being up to 70-fold higher compared to the control in Kobernausserwald. However, the difference was not significant (SI-Fig. 14).

The water soluble concentrations were compared to Austrian legal thresholds for excavated soils (Deponieverordnung 2008, version Sept 2013; Table 9). No threshold exceedance was found.

4.3 Results of the column experiment eluates

As a main result, the two ash types hardly differ in their influence on the eluate, while the three soil types strongly affected the leaching pattern of elements in the eluates. This is mainly attributed to the layer of pure soil beneath the ash-soil mixture layer, which might buffer the direct input by the ashes to a large extent. On the other hand it is influenced by indirect impact such as changes in redox-potential and pH or Ion-exchange reactions, which are highly dependent on the individual soil properties. This is confirmed by the fact, that no flush events at the beginning of the application time were observed. Highest differences between columns applied with ash and control columns were found for the S2 soil. Here soil chemistry is obviously more prone to change by indirect impact of the ashes.

Incorporation of a wood ash layer resulted in a significant increase in pH in the neutral soil (+ 1 units) while in the alkaline soil we observed a decrease in pH (-0.5 units), this applies for both ash types. The pH hardly changed over time on these soils. On the acidic soil only the GA treatment caused significant increase in pH, but the curve pattern was similar (Figure 20, SI-Fig.15).

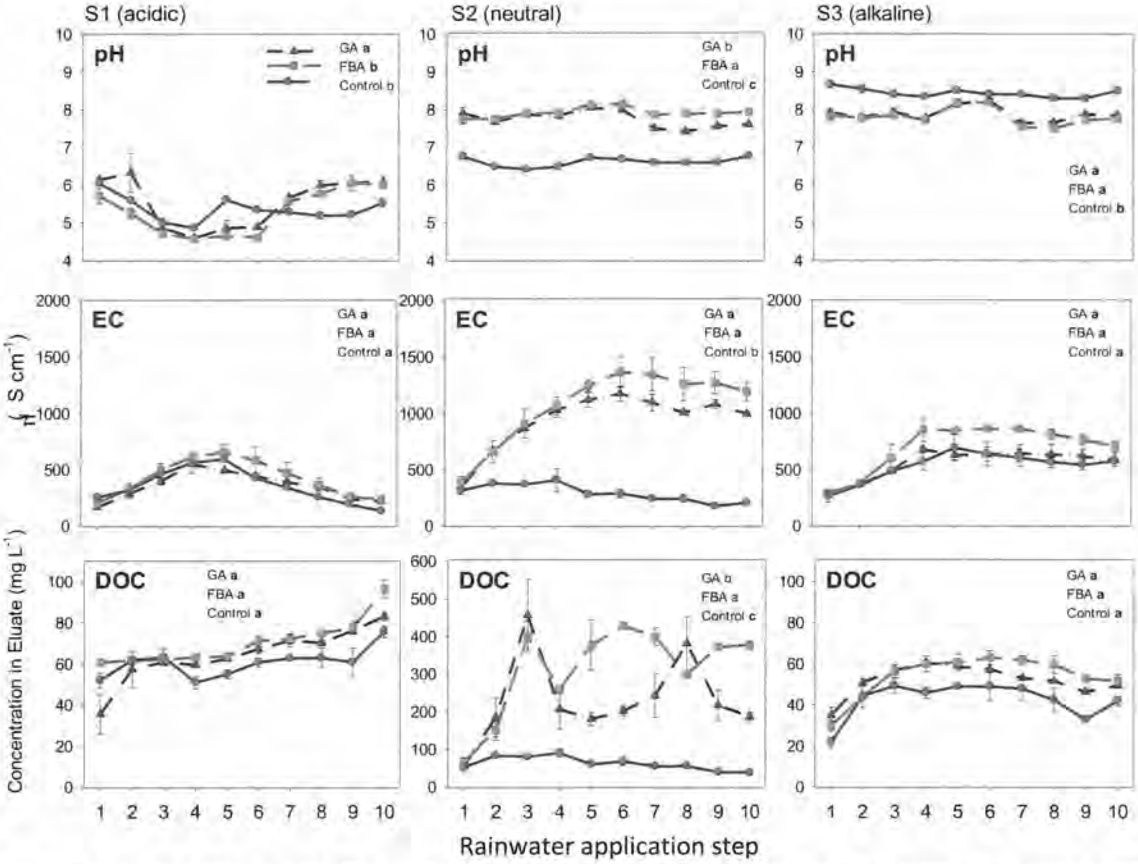


Figure 20 Leaching pattern of pH, EC and DOC concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the DOC graphs.

The EC only differed significantly on the neutral soil between ash treatments and control. Starting at a similar value after the first application, the ash treatments increased in EC and levelled off after the 6th application, while the control rather constantly stayed at low level. The loads of the ash treatments were statistically higher than the control. The curves resembled a first order reaction curve. On the other soils (S1, S3) the EC of ash treatments and control resulted in similar curves, peaking at the 5th application (S1) or levelling off after the 4th (S3). The two ashes showed same curve pattern on all soils and did not differ in loads significantly (Figure 20, SI-Fig.15).

Similar pattern can be seen for the DOC curves in respect to little and insignificant differences between the ash treatments and the control on the acidic and the alkaline soil. On the neutral soil however, the ash treatment curves differ significantly from the control with DOC in the ash treatments being constantly higher and showing strong, dissimilar fluctuations over time. The DOC load of the FBA treatment was significantly higher than the load of the GA treatment (Figure 20, SI-Fig.15).

A similar pattern of leaching was observed for K and the earth alkali metals (Ca, Mg) in accordance with EC (Figure 21, SI-Fig.16). In the acidic soil the ash treatments showed no obvious and significant difference to the control. Similar to EC the concentrations increased until about the 5th application time and afterwards decreased to about the initial concentration. The concentration maxima on this soil were low compared to the other soils. Also on the neutral and alkaline soil K, Ca, and Mg concentrations followed the pattern observed for EC, with significantly higher loads in the ash treatments in the neutral soil, while no difference was found in the alkaline soil. On all three soils the FBA ash treatment resulted in higher loads than the GA treatment, however only in case of Mg and K on the neutral soil the difference was significant (SI-Fig 16).

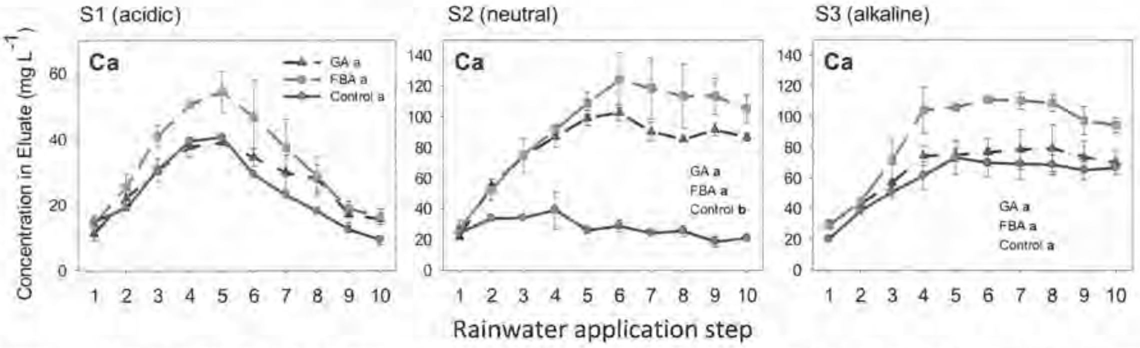


Figure 21 Leaching pattern of Ca concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the graphs.

The curves for Na concentrations, however, did not resemble the pattern observed for the other macro-cations. On all three soils the ash treatment loads were significantly lower than the control loads. While the Na concentrations in the ash treatments on all soils remained constantly at a low level, the concentrations of the control column samples started at high values and declined with time. However, in the alkaline soil Na loads increased until the 5th rainwater application and decreased thereafter to about the initial concentration. No differences between the ashes were found (Figure 22, SI-Fig.16).

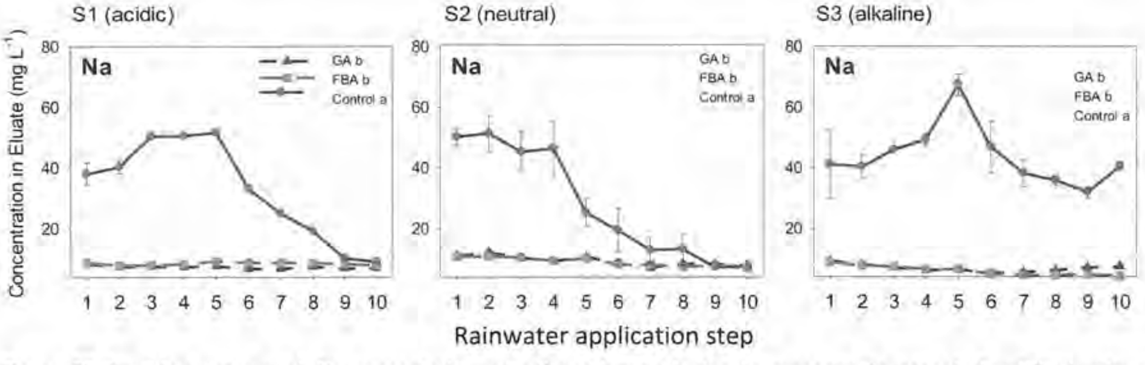


Figure 22 Leaching pattern of Na concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step.

Al, Fe and Mn showed differential curve developments. Highest amounts of Al were leached on the acidic soil. The ash treatments resulted in significantly higher loads being washed out on the acidic and the alkaline soil, while no differences were found on the neutral soil (Figure 23, SI-Fig.17). Fe in contrast, showed the highest significant difference between ash treatments and control on the neutral soil. To lower extend, but also significant higher values were found on the acidic (GA and FBA) and alkaline (only FBA) soil compared to the control (Figure 24, SI-Fig.17). In contrast ash application resulted in significant lower concentrations of Mn being washed out from the ash treated columns compared to the control on the neutral soil. The highest values were found on the acidic soil, without significant difference between treatments though. Comparably little Mn was leaching in the alkaline soil columns. The ash treatments, however, led to significant higher concentrations with a tendency to rise (Figure 25, SI-Fig.17).

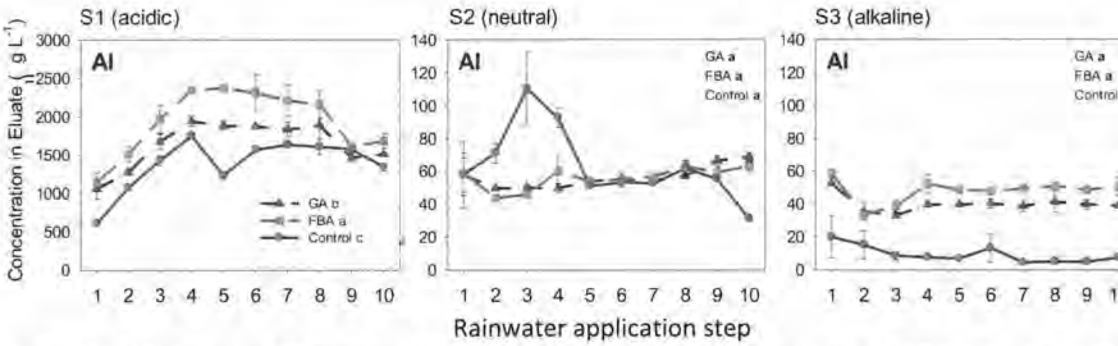


Figure 23 Leaching pattern of Al concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the graphs.

The curves of Al, Ba and Cd showed similar patterns (Figure 23, SI-Fig. 17,18). For all of them the highest concentrations and peaking curves were found on the acidic soil. The ash treatments resulted in significant higher loads of Al and Cd (GA and FBA) and of Ba (only FBA) compared to the control. The concentrations were lower on the neutral soil. The ash treatments and the control remained within the same concentration range, but they showed various curve patterns and the loads of the ash treatments were significantly higher than the control in case of Ba and Cd. The concentrations of ash treatments and control on the alkaline soil remained constantly at a low level comparable to the neutral soil. The loads of the ash treatments were significantly higher for Al and Cd. For all three elements the FBA treatment resulted in significantly higher loads than GA on the acidic soil.

With slight variations in curve pattern, Zn and F^- leached similarly, showing highest concentration on the acidic soil with peaks and significant higher loads in the ash treatments (SI-Fig. 21). The concentrations were lower on the other soils. On the neutral soil the ash treatments had significant lower loads of F^- and higher loads of Zn and on the alkaline soil the ash treatments had significant lower loads of Zn and higher loads of F^-. NO_2^- and NO_3^- concentrations peaked in all soils, with highest concentration in the acidic soil and on a lower level partly below quantification limit on the other soils (SI-Fig. 22). There was no significant difference in loads compared to the control though.

Cl^-, Cr, Cu, Fe and Ni could be combined to a group of characteristics for which the concentrations stay roughly in the same concentration range on all three soils (Figure 24, SI-Fig. 19, 20, 21). However, in all cases the ash treatment curves proceeded slightly above the control curves. The loads of the ash treatments were significantly higher than the control in most cases excluding the Cr load of the FBA treatment and the Fe load of the GA treatment on the alkaline soil, as well as the Ni loads of both ash treatments and Cl^- loads of the FBA treatment on the neutral soil. The pattern of the curves was rather constant and did not vary much between treatments. However, on the neutral soil the Cr curves of the ash treatments pictured a bowed course peaking in the 5th application time in contrast to the control curve which was tendentially falling. The Fe curves of the ash treatments on the neutral soil were rising by time with a peak after the 7th application in contrast to the control curve, which was falling towards the end. On the alkaline soil the Cu and Ni concentrations of the ash treatments were obviously higher than on the other soils. The ash treatments only differed significantly on the acidic soil in the Fe and Ni loads, with higher amounts eluting from the FBA treatment columns (Figure 24).

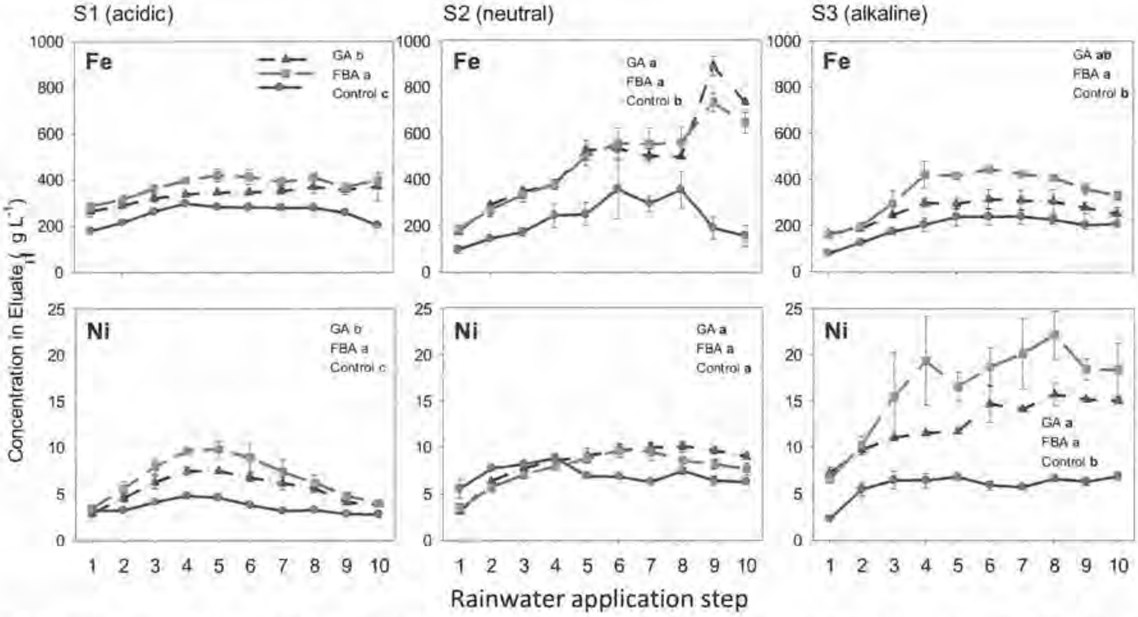


Figure 24 Leaching pattern of Fe and Ni concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step.

Very resembling curves were found for Mn and Co (Figure 25; SI-Fig. 17,19). Both gave a peaking concentration on the acidic soil, similar to Ca, Mg and K (Figure 21). The loads of Co were significantly higher in the ash treatments compared to the control. On the neutral soil the concentration ranges were low and the ash treatment loads were significantly lower than the control one. The curve of the control was slightly concave, while the ash treatment curves are slightly rising. On the alkaline soil the control treatment was constantly at low concentration. The ash treatments started at roughly the same concentration, but constantly increased and had significantly higher loads than the control. On the acidic and the alkaline soil the FBA concentration curves were obviously higher than the GA curves, however the difference in loads was only significant on the alkaline soil for Mn.

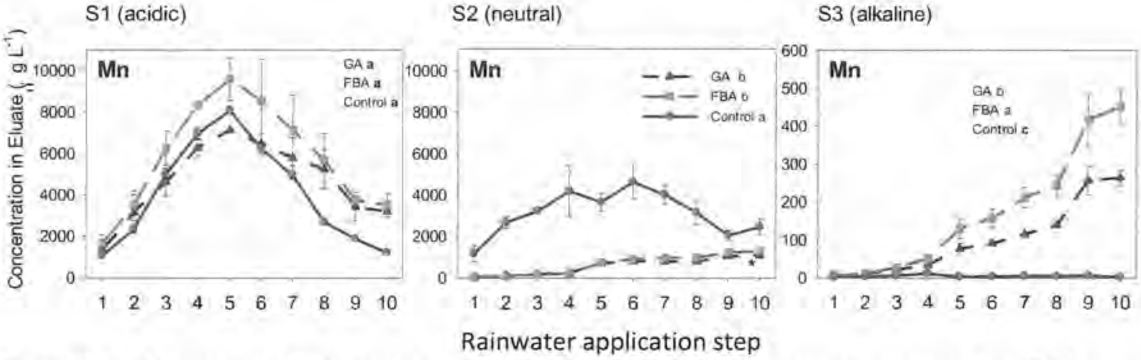


Figure 25 Leaching pattern of Mn concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the graphs.

While the B and Se curves remained in the same concentration range on all soils as well, the loads of the ash treatments were significantly lower compared to the control, except for B on the neutral soil without significant differences and for Se on the alkaline soil, where the control column had a significant lower load than the ash treatments (SI-Fig. 18, 20). The courses of curves did not differ much. However, the control curves of Se on the acidic and neutral soils were decreasing towards the lower concentrations of the ash treatments, in some way resembling the pattern of Na on these soils.

Finally, there is a group of anionic parameters, for which the highest concentrations were seen on the neutral soil, similar to Ca, Mg and K. These are As, Mo, PO_4^{3-} and SO_4^{2-} (Figure 26, SI-Fig. 18, 19, 22). In all cases the concentrations on the acidic soil were quite constant and comparably low. Only As showed a significant difference in loads with higher values for the ash treatments. On the neutral soil the concentrations of the control were low and constant as well. In contrast the ash treatment concentrations were comparably high with a rising curve tendency, except for SO_4^{2-} curves which peak after the 6th rainwater application. The loads of the ash treatments were all significantly higher, except for the SO_4^{2-} load of the GA treatment. On the alkaline soil the graphs gave a different picture. The As curves were all rising, but in a lower concentration range compared to the neutral soil. The ash treatments had significantly higher loads than the control. The Mo concentrations of the ash treatments were rising, while the control remained rather constant. The loads were not significantly different though. Due to values below the detection limit, the PO_4^{3-} curves were not complete, but remained in low range of concentrations and showed no significant differences in loads. The SO_4^{2-} curves were similar to the SO_4^{2-} concentrations on the neutral soil, but the FBA treatment was peaking in the 7th application point with significantly higher loads. The GA treatment curve remained close to the control.

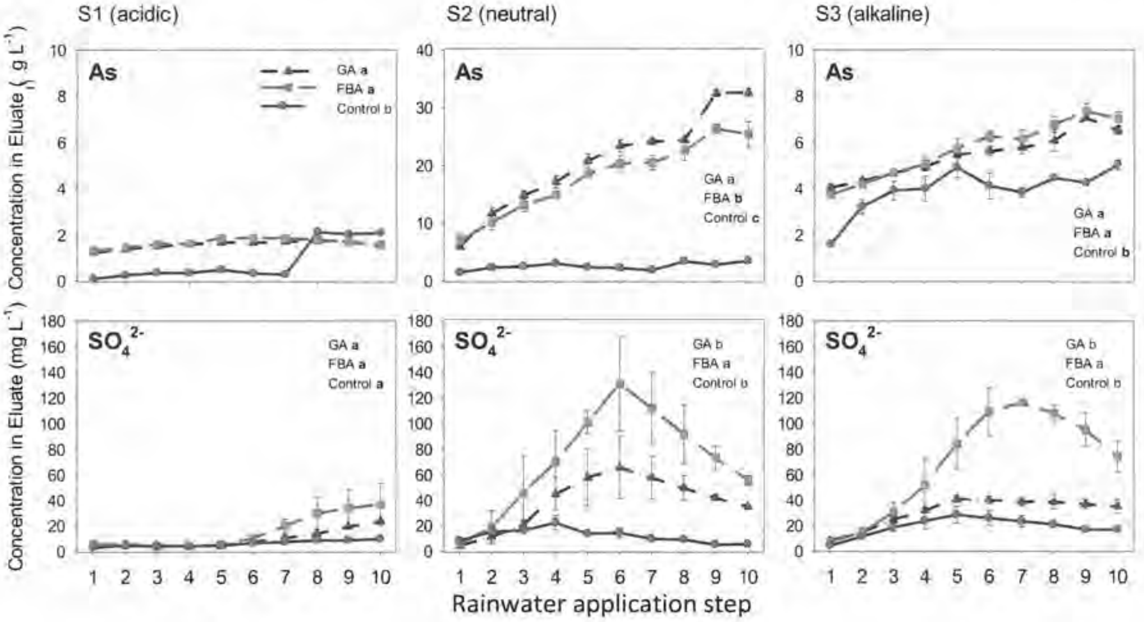


Figure 26 Leaching pattern of As and SO_4^{2-} concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the As graphs.

The P curves resembled the PO_4^{3-} curves (SI-Fig. 20, 22). However, on the acidic soil the P concentrations of all treatments started on higher concentrations and decreased afterwards. On the neutral soil the P concentrations of the ash treatments were lower compared to PO_4^{3-}, but still significantly higher than the control. The P and PO_4^{3-} curves on the alkaline soil were in a comparable range of concentrations.

4.4 Results of the column experiment water extracts

The water extracts of the column material were taken after the elution experiment. They give a picture of how much extractable amount of a parameter in mg per kg soil was left in the different layers afterwards.

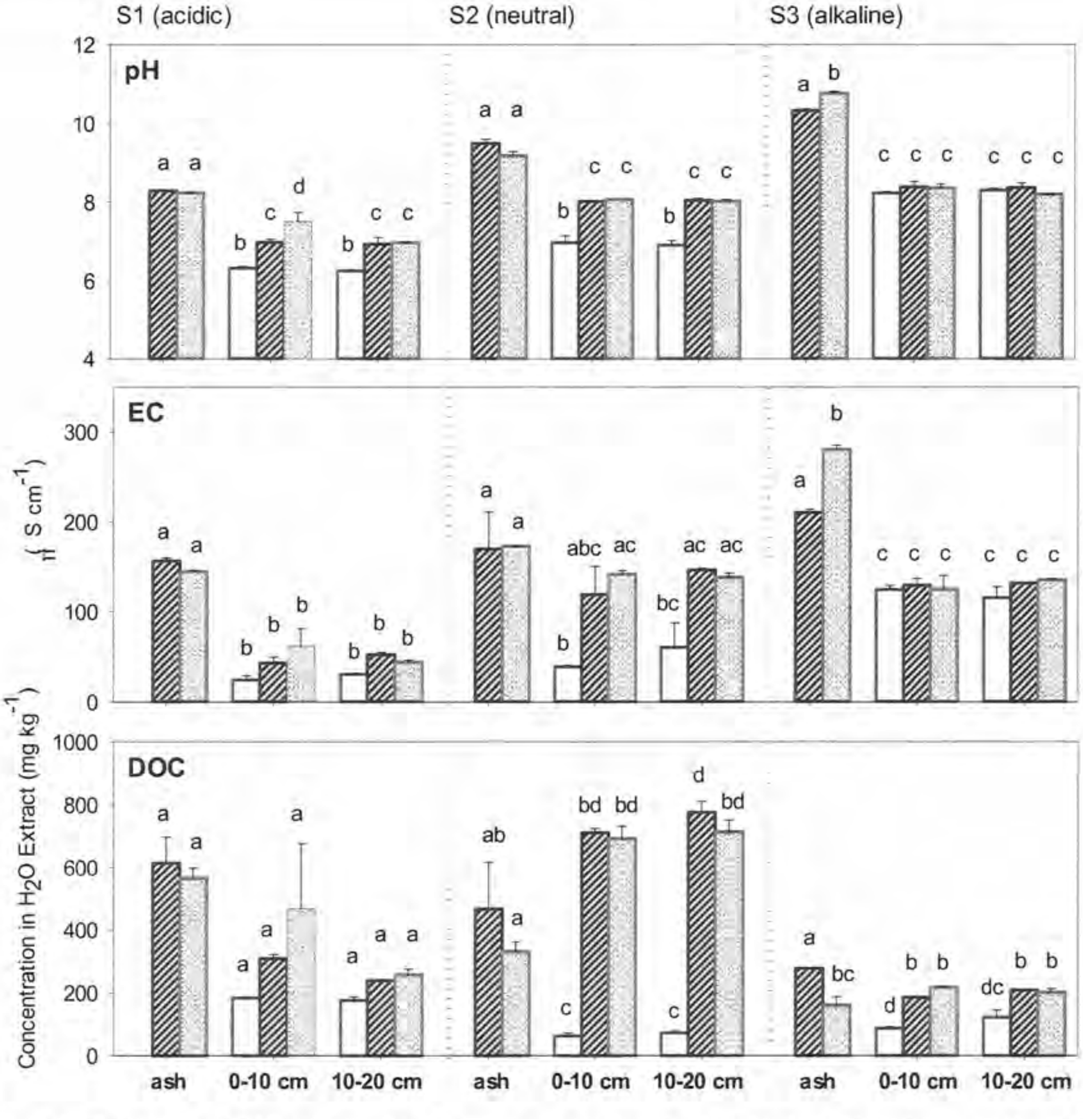


Figure 27 The pH, EC and DOC concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.

The pH of the extract solutions was significantly higher in the ash treatments compared the control in case of the acidic and neutral soil. No differences were found on the alkaline soil. On all soils the pH of the ash layer was significantly higher than the pH of the sub-ash layers (Figure 27, SI-Fig. 23).

The results of the Ca, K, and Mg, as well as EC and DOC concentrations match the column eluate pictures (SI-Fig. 23, 24). Hardly any differences between ash treatments and control are found on the alkaline and acidic soil. But on the neutral soil the extractable amounts were higher in the ash treatments in both layers, with a significant difference for K, Mg and DOC in both layers and Na in the 10 to 20 cm layer. The extractable amounts in the ash layers compared to the other layers were usually higher, significantly for Ca and EC on acidic and alkaline and K on acidic and alkaline (only GA treatment). Significantly lower concentrations were found for Mg on neutral and alkaline soil (Figure 28, SI-Fig. 24). The two ashes rarely differ.

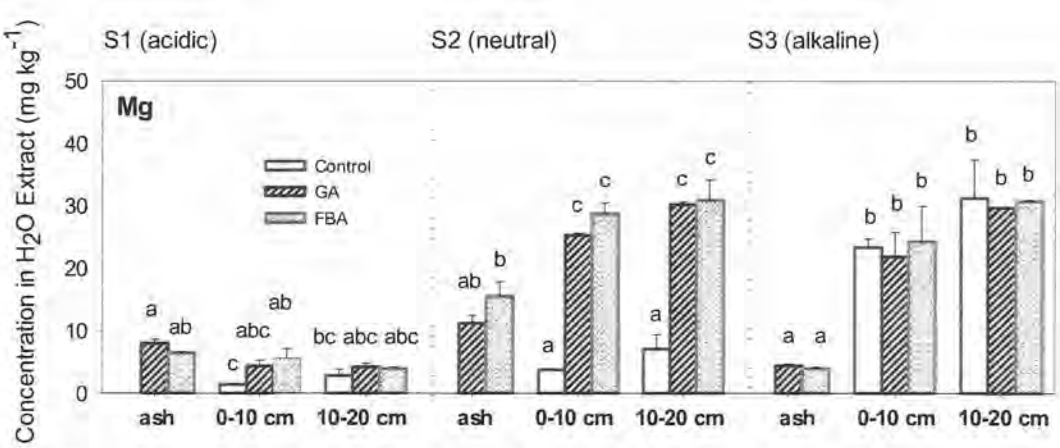


Figure 28 Magnesium concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.

Co and Mn extractable amounts did not match well, but Al and Mn (Figure 29, SI-Fig. 25, 27). For Al and Mn the control showed mostly higher values than the ash treatments with significance, mostly significant for Al but hardly significant in case of Mn. The Co amount of the ash treatments was similar or higher than the control, significantly in the 0 to 10 cm layer of the alkaline soil. There was little difference between the ash and the sub-ash layers for Co and Mn and Al.

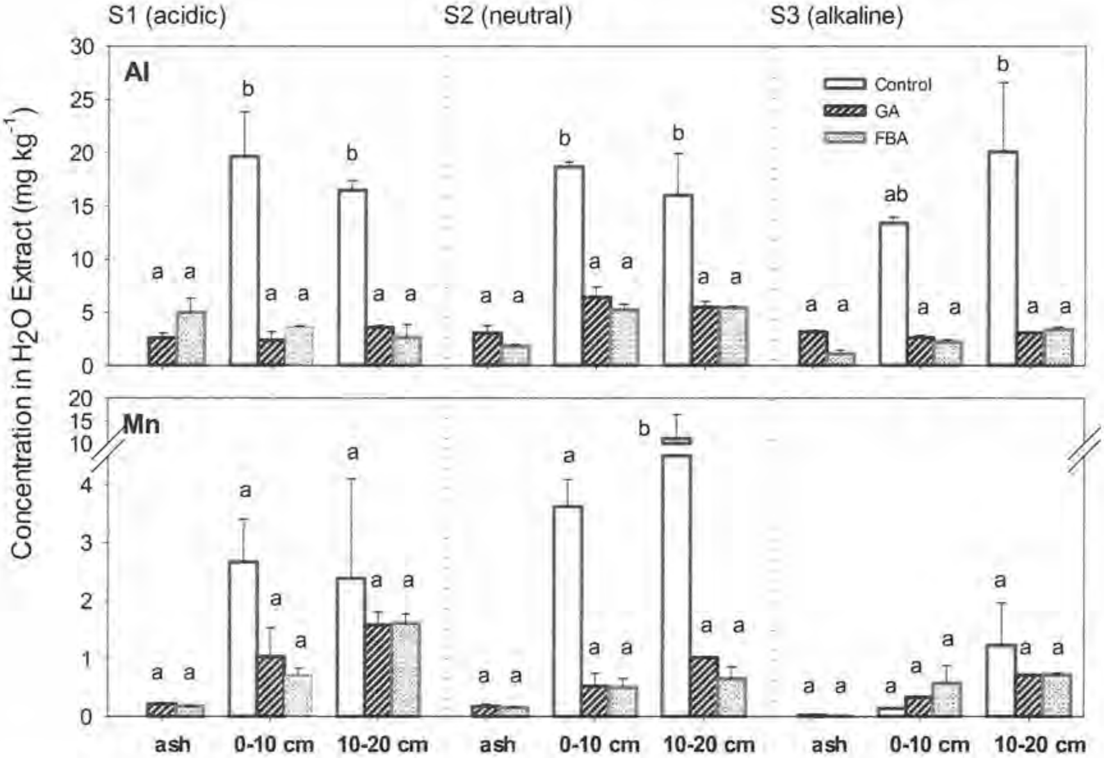


Figure 29 Aluminium and Mn concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.

Ba and Cd extractable amounts did not differ significantly between soils, treatments and layers, however the ash treatments showed tendentially higher amounts of Ba compared to the control (SI-Fig. 26). The extractable amounts of Zn were significantly higher in the ash treatments compared to the control on the neutral soil and of F^- in the 0 to 10 cm layer of the alkaline soil. The ash layer had significant lower extractable amounts than the sub-ash layers of Zn on the neutral soil and significant higher amounts of F on the acidic soil. Low concentrations and no significant differences between layers and treatments were found for NO_2^- and NO_3^- (SI-Fig. 29, 30)

Cr and Fe extractable amounts give a similar picture (Figure 30, SI-Fig. 25, 17). The different extracts do not reveal many significant differences, however on the acidic and alkaline soil the controls have higher values than the ash treatments and lower values on the neutral soil. The Cu and Ni diagrams are similar in a way that they picture higher amounts extractable in the ash treatments compared to the control on the acidic and significantly on the neutral soil (Figure 30, SI-Fig. 27, 28). On the alkaline soil, however the Ni amounts are significantly lower in the ash treatments compared to the control in the 10 to 20 cm layer.

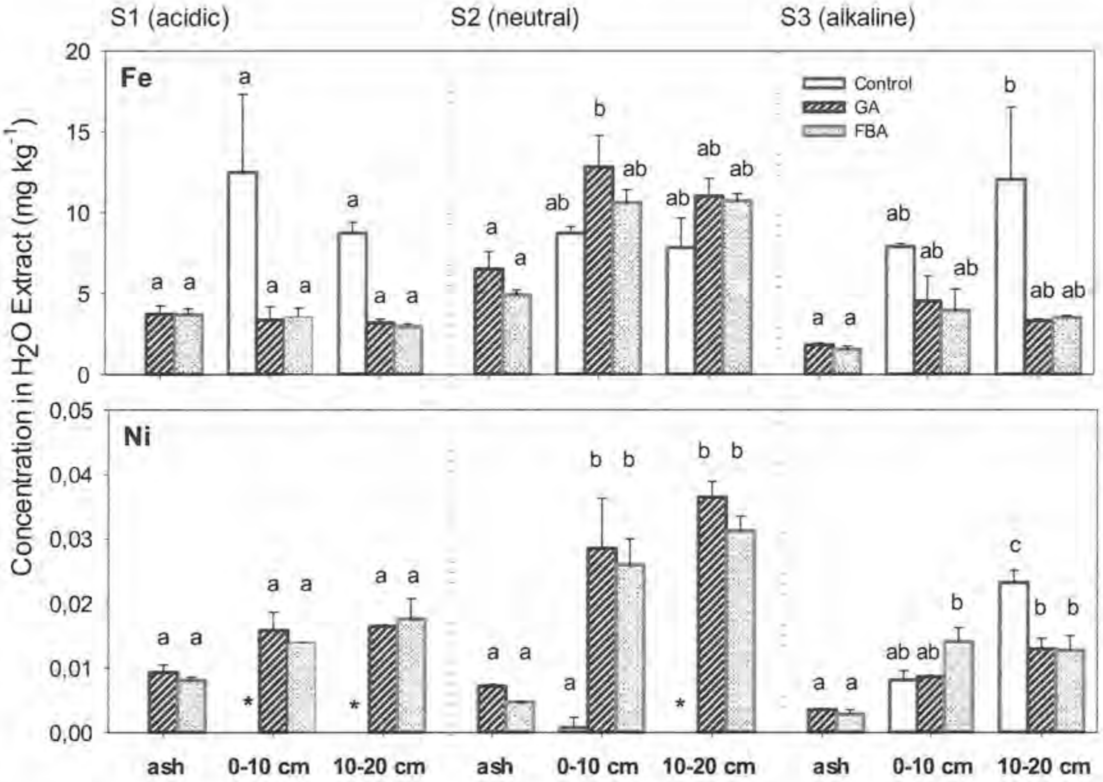


Figure 30 Iron and Ni concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.

The B and Se values are hardly significantly different between layers or treatments and show no tendencies, except for the controls being lower in Se and the Se concentrations being in general higher in the extracts of the alkaline soil (SI-Fig. 26, 28).

As, Mo, PO_4^{3-} and P extractable amounts are all significantly higher in the ash treatments on the neutral soil compared to the control (Figure 31, SI-Fig. 26, 27, 28, 30). Also they are higher in the sub-ash layers compared to the ash layer, with significance in case of Mo, PO_4^{3-} and P. On the other soils the concentrations are generally lower. On the acidic soil there are no considerable differences, except for higher amounts in the ash layer compared to the other layers, significantly in case of As (Figure 31). On the alkaline soil the extractable amounts of PO_4^{3-} and Mo are significantly lower in the ash layer compared to the sub-ash layers. For SO_4^{2-} no significant differences or tendencies between treatments or layers were found (SI-Fig. 30).

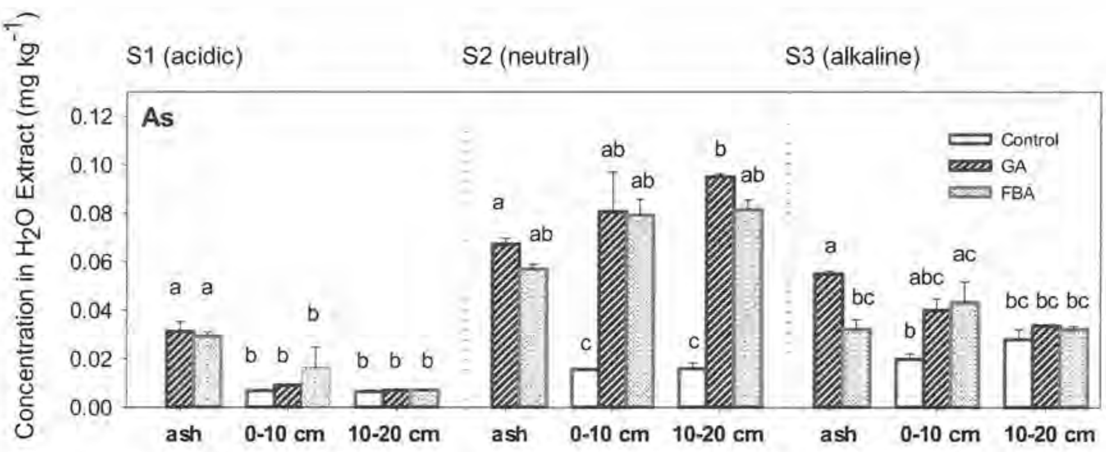


Figure 31 Arsenic concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.

4.5 Results of the 2-step extraction experiment of soil-ash mixtures

The experiment was conducted to find out, whether addition of ash to different soils results in increasing extractable amounts of harmful substances. In a second step pure soil was added to the extract solution to see whether the pure soil can take up the substances and thus reduce the concentration in the solution. This pattern could be seen in many cases, however the measured elements and characteristics reacted quite differently on each of the five different soils used (Ko, We, S1, S2, S3).

For Ca, EC and pH a coherent picture was found on all soils. In each case the ash-soil mixtures had significantly higher extractable concentrations/pH-values than the pure soil. After addition of pure soil to the extract solution, the concentrations/values were significantly lowered, partly resulting in similar concentrations/values to the pure soil. The differences in pH between the soils had the same tendency in the pure soils and the soil-ash mixtures. In contrast the EC and Ca concentrations increased through ash-addition especially on the alkaline soil S3 (Figure 32, SI-Fig. 31, 32).

This buffering feature was also found for DOC on the acidic soils Ko and S1. On S2 the DOC was significantly increased by mixing the soil with ash, however, addition of pure soil to the extract solution did not change the extract concentration. On the neutral soil S2 significantly less DOC could be extracted from the ash mixtures compared to the pure soil. The readsorption test, however, resulted in significantly higher concentrations compared to the control. On the alkaline soil mixing with ashes did not change the extractability of DOC. Also addition of pure soil to the extract only led to a comparably small increase in DOC (Figure 32, SI-Fig. 31).

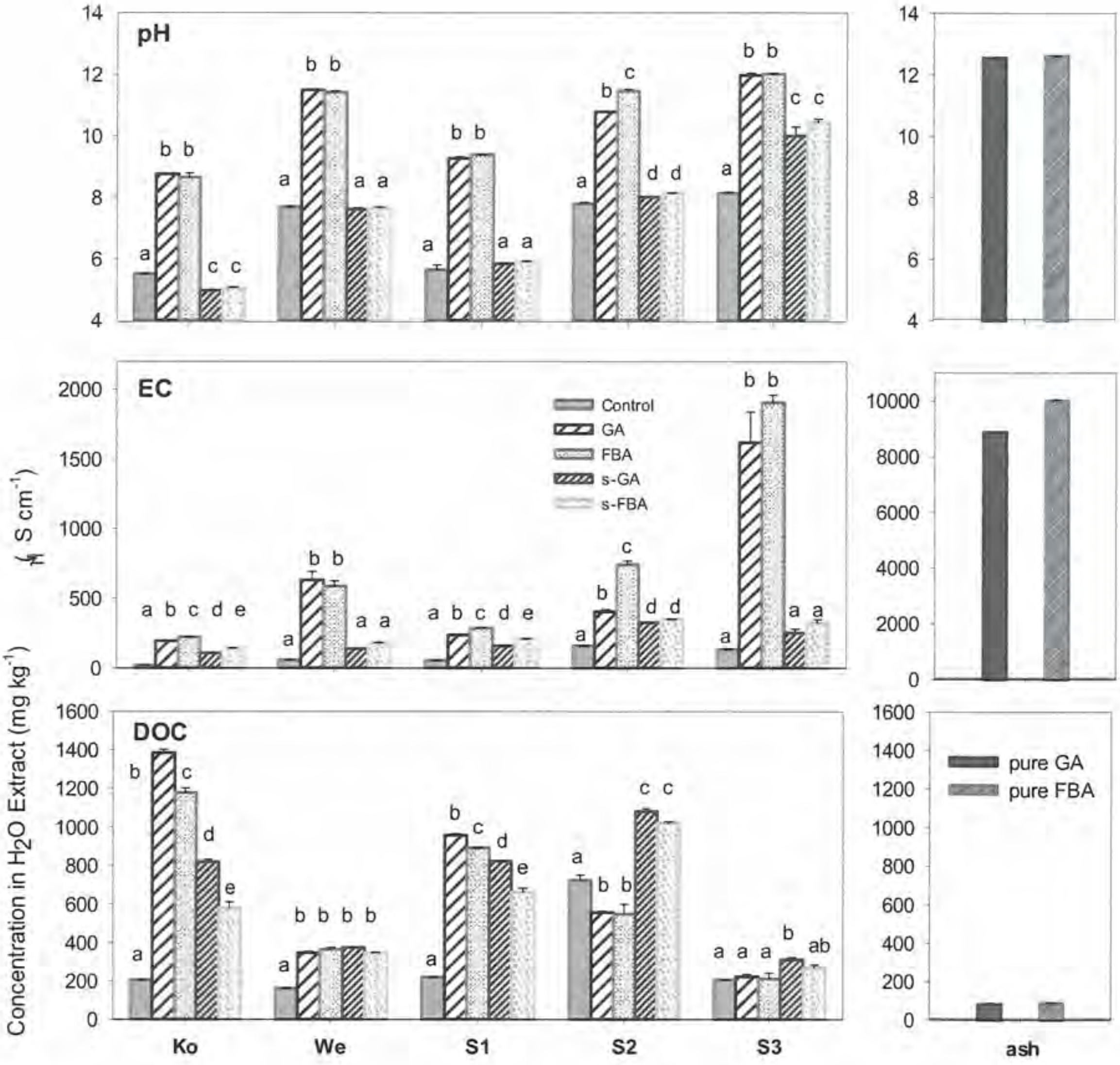


Figure 32 pH, EC and DOC concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales.

Other than Ca, the extractability of Mg was mostly significantly lowered by mixing the soils with the ashes, partly down to unquantifiable concentrations (SI-Fig. 31). Only on the Ko soil the concentration did not change (GA) or increased significantly (FBA), but still comparably little. By effect of the readsorption experiment the concentrations were elevated up to significantly above the original value of the pure soil on all soils except for the alkaline soil S3. Here the concentrations remained low after the readsorption test, but were still significantly higher than the ash-soil mixture concentrations.

On all soils the concentration of K was significantly elevated in the ash-soil mixtures compared to the pure soils (SI-Fig. 31). Adding pure soil to the extract solution only led to comparably small, mostly insignificant decreases. Only on the neutral S2 soil, the readsorption test led to a further significant increase in K concentration.

Sodium is one of few elements, where the difference between the two ashes was the most prominent finding. While mixing the soils with GA lead to a roughly ten-fold increase in extractable Na on all soils, a mixing with FBA only lead to a significant but comparably small increase on S2 and S3. The readsorption test did not show much effect on the GA-treated extracts. Only on S1 the extractable Na was further increased. Adding pure soil to the FBA-treated extracts though resulted in a significant increase on all soils (Figure 33, SI-Fig. 31). Chloride concentrations reacted in a similar way (SI-Fig. 37). GA addition to the soils initially led to a significant increase in extractable Cl^-, while FBA addition resulted in mostly significantly lower concentrations of extractable Cl^-. The readsorption test led to a significant increase for both ash mixtures compared to the initial concentration in the pure soil. For SO_4^{2-} the FBA had a higher influence (SI-Fig. 38). The extractable amount was increased to up to 40 times by mixing the soils with FBA compared to the pure soil. Also GA-treatment led to an increase of lower extent, but still significant for Ko, We and S1. The readsorption test changed the extractability of SO_4^{2-} comparably little, however significantly in the FBA-treated extracts on Ko, S1 and S2.

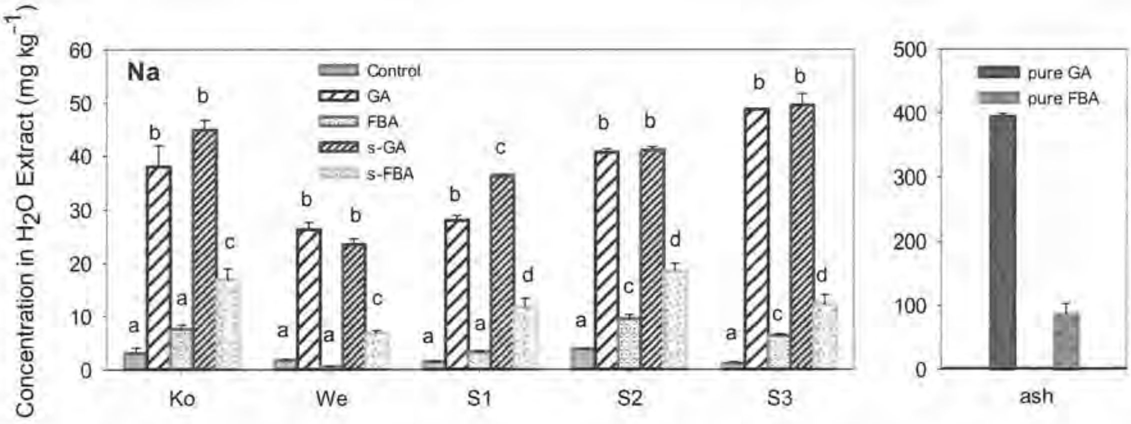


Figure 33 Sodium concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales.

Aluminium concentrations increased by mixing with ash and subsequent reuptake by the pure soil similar to Ca on all soils except for the neutral S2 soil (Figure 34, SI-Fig. 33). Here the concentrations were significantly decreased by the ash-mixing and not further influenced by the readsorption test.

In accordance with Al, As concentrations significantly increased in the first and significantly decreased in the second extraction step on the Ko, We and S1 soils (Figure 34, SI-Fig. 34). On the S2 and S3 soils in contrast, a significant decrease in the ash-mix extractions was followed by a significant increase through the readsorption test. Highest extractable amounts were found on the neutral S2 soil after the readsorption test.

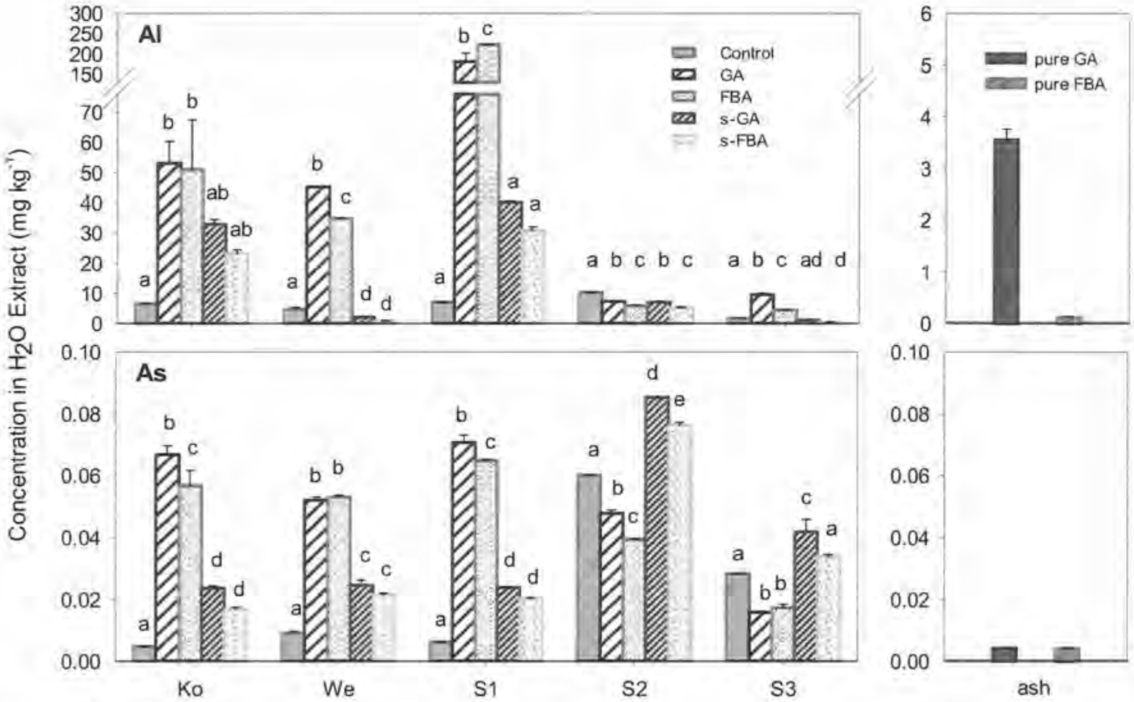


Figure 34 Aluminium and As concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales.

Also P showed the reuptake pattern on the Ko, We and S1 soil (SI-Fig. 36). On the S2 soil P extractability was diminished as well. On the second extraction step, extractable P was significantly increased but still significantly lower than the initial pure soil concentration. On the S3 soil, P extractability was further increased in every extraction step, however the concentrations were still comparably little. The extractable concentrations of PO_4^{3-} were mostly below quantification limit (SI-Fig. 38). Only on the S2 soil, considerable amounts were extracted. In accordance with the P values, PO_4^{3-} was significantly decreased in the ash-mixture extracts and afterwards significantly increased by adding the pure soil to the extract solution. However, the concentrations were still significantly lower than the initial concentration of the pure soil.

Iron concentrations behaved differently on each of the soils (Figure 35, SI-Fig. 33). On the acidic soils Ko and S1, they were significantly increased compared to the pure soil. In the readsorption test they were furthermore significantly rising (GA) or not significantly changed (FBA). Whereas on the We and S2 soil, significantly less Fe was extractable after mixing the soils with the ashes. The concentration was significantly elevated by adding the pure soil to the extract solution, however still significantly lower than the initial concentration of the pure soil. No significant changes between treatments were found on the S3 soil.

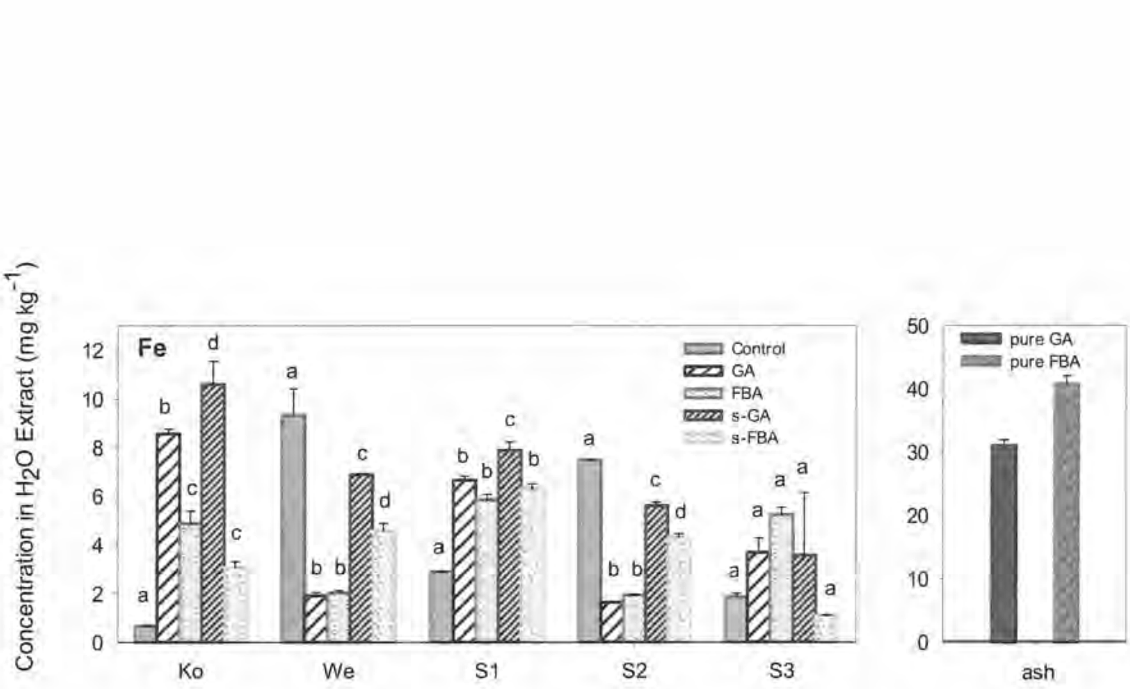


Figure 35 Iron concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales.

Manganese, similar to Mg, was significantly less extractable in the ash-mixes compared to the pure soils (SI-Fig. 33). The readsorption test led to a subsequent increase to concentrations significantly higher than the initial concentrations on the acidic soil K and S1. S1 was the soil where Mn was released the most after the readsorption test. On the other soils the concentrations remained comparatively low, even after adding the pure soil to the extract solution. Ba showed a closely related concentration pattern (SI-Fig. 34). The release of Ba was diminished to below quantification limit by mixing with ash on all soils except for S3. Highest concentrations were found on the S1 soil after the readsorption test. On the S3 soil initial extractable Ba was comparably low and did not change by ash addition or the readsorption test. Also extractability of Zn was inhibited by mixing the soils with the ash (SI-Fig. 37). By addition of pure soil to the extract solution Zn was released to an extent similar to the initial concentration. Only on the S3 soil, Zn remained inextractable after the readsorption test.

Extractable concentrations of Co were little related to Mn in this experiment (SI-Fig. 35). In contrast to Mn, Co concentrations were increased by mixing the soils with the ashes in case of Ko and S3. Little to no change was observed at We and S1 and a significant decrease was found on S2. On all soils the extractable amounts were significantly rising after addition of pure soil to the extract solution. Only on We the concentrations did not change. In accordance with Mn, highest extractable amounts were found on S1 after the readsorption test.

One group of elements showed similarities especially in their concentration pattern on the alkaline S3 soil, namely Ni, Se and V (Figure 36, SI-Fig. 36, 37). After significant increase in the ash-mixture extracts compared to the pure soils, the readsorption test led to a significant and comparably high increase in extractable concentrations on the alkaline S3 soil. On the other soils, however, they behaved differently. Vanadium showed the typical reuptake pattern (as explained for Ca) on the remaining soils. Ni concentrations were increased by ash addition as well, but only significantly on We and S2. The readsorption test led to further decrease on We and no change on S2 respectively. On the acidic soils Ko and S1, extractability of Ni was not changed considerably by mixing with the ashes, however significantly increased in the readsorption test. Selenium was increased in the ash mixture extracts, however only significantly on Ko and We. The readsorption test did not influence the extract concentrations considerably on Ko, We, S1 and S2.

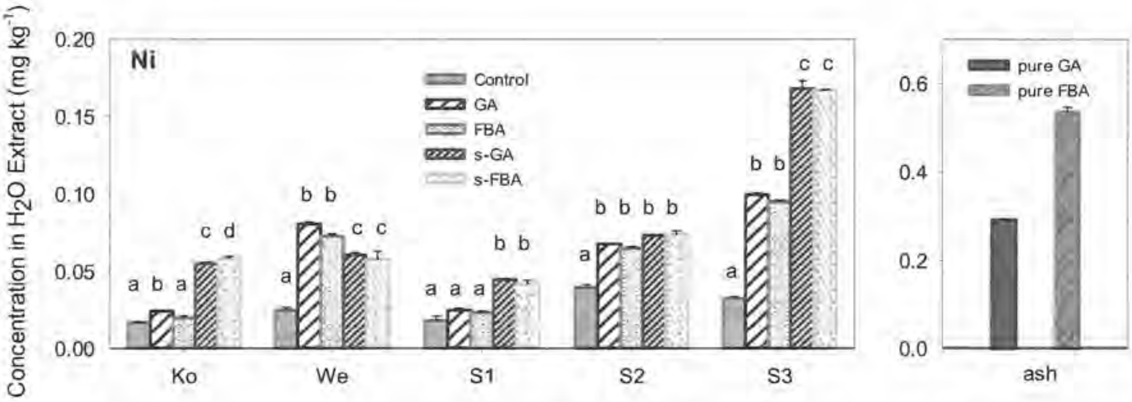


Figure 36 Nickel concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales.

Similarly to Al and As, Cr showed reuptake behaviour on the Ko, We and S1 soils (SI-Fig. 35). However here similar to Na, a considerable significant difference between the ashes was found, where GA lead to a more than double increase in extractable amounts compared to FBA on all soils. While Ko, We and S1 buffered the input significantly in the readsorption test. The pure S2 and S3 soils had little influence on the extract solutions of the soil-ash mixtures.

Reverse concentration pattern was observed for B (SI-Fig. 35). Similarly to SO_4^{2-}, the FBA had a significantly higher influence on the pure soils than GA. In the first extraction step, B extractability was significantly increased by FBA-treatment. In the second extraction step, the extractability was further significantly increased on Ko and S1, however significantly decreased on We, S2 and S3. Mixing the soils with GA led to an increase on all soils except for S2. Here the extractable concentration was significantly decreased. The readsorption test led to significant increase compared to the ash-mixture extracts on Ko, and S2. No significant change was observed on the other soils.

Extractable concentrations of NO_3^- showed a coherent pattern on most soils (SI-Fig. 38). Mixing the soils with the ashes did not change the extractability on any soil, except for S1, where it was significantly decreased. On all soils the readsorption test led to significant increase of about double the extractable concentrations compared to the pure soils.

The extractability of NO_2^- was decreased by mixing with the ashes on We, S2 and S3 (SI-Fig. 38). In the second extraction step the concentrations in the extract solutions were significantly increased on We and especially S2. No effect was observed on S3. On the acidic soils Ko and S1 NO_2^- extractability was below quantification limit on the pure soils at first. By mixing with the ashes the concentrations were increased to be quantifiable, but still comparably low. The readsorption test led to decrease below quantification limit on Ko and comparably low increase on S1.

Fluoride extractability was below quantification limit on Ko (SI-Fig. 37). On We and S1, F^- concentrations were significantly increased by ash addition to the soils. In the readsorption test the extractability decreased significantly on S1, but comparably little on We. No significant differences were found between pure soil and ash-soil mixtures on S2 and S3. The readsorption test had no further influence on S2, however significantly increased extractability of F^- on the alkaline S3 soil.

The extractable concentrations of Cd, Cu, Mo and Pb were partly prone to high variances (SI-Fig. 34, 35, 36). For Cd, significant change could only be observed at an increase after the readsorption test on Ko, and an increase after mixing the ashes with the S1 soil. Comparably little but significant increase in Cu extractability in the ash mixtures compared to the pure soils was found on S1 and S2. In the readsorption test the concentrations were slightly lowered. Molybdenum showed significant reuptake pattern on Ko and S1, however concentrations were partly below quantification limit. On S3 the Mo concentrations were stepwise significantly increased. Extractability of Pb was only significantly increased in the readsorption test on the Ko soil.

5 Discussion

Only few threshold exceedances of the GSW and LSW, which are the most relevant for potential environmental acceptability of wood ash application in forest roads were found in the leachate waters of the field experiment. Considering, that the samples were taken at the most critical point right beneath the soil-ash mixture layer and that hardly any GSW and LSW threshold exceedance was found from the second sampling period on, the results of the field experiment indicate that wood ash application in forest road construction is generally environmentally acceptable under the given conditions.

However, it is important to find out about the mechanisms of ash impact and to look at the buffer capacities of a wider range of soil types. The characteristics exceeding drinking- and groundwater thresholds were considered to be the most relevant to focus on and to discuss in more detail (Table 11; Table 12). They are discussed by comparing the expected impact (hypothesis) to the results of the experiments. Secondly a comparison of the different soils is supposed to give an impression on the suitability of different soils for ash application. Finally the differences between the impact of the two ashes is discussed.

5.1 Conceptual model of the impact of ash application on soil chemistry

Our hypotheses on changes in soil chemistry caused by application of wood ash or ash leachates and relevant interactions are summarized in Figure 37.

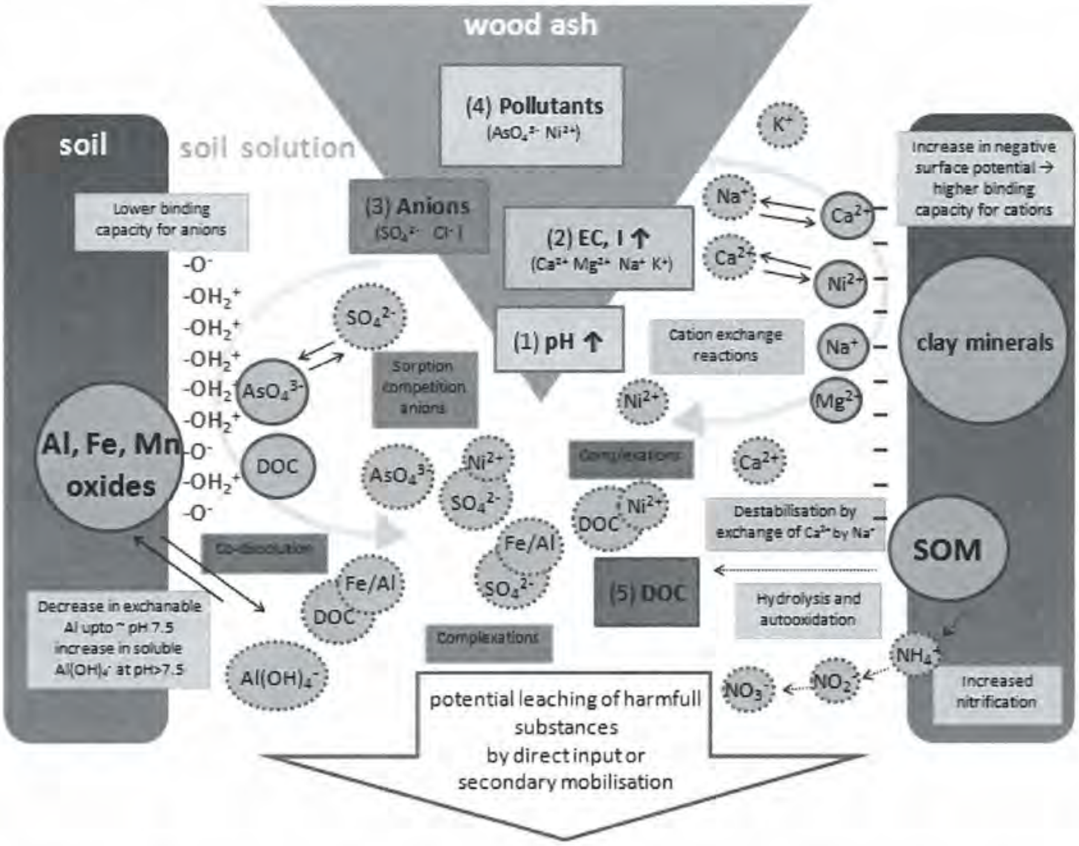


Figure 37 Possible soil-ash interaction mechanisms. The main ash -driven processes affecting soil solution chemistry and therefore the solubility of potential pollutants (e.g. Ni, As) are shown: (1) increase in pH: rendering the average surface potential more negative therefore increasing cation but decreasing anion sorption capacity as well as triggering SOM hydrolysis and autoxidation, changing solubility of Al and Fe and increasing nitrification (2) increase of ionic strength (I) due to the high input of Ca, Mg, Na, K affecting cation exchange (3) input of inorganic anions (Cl^-, SO_4^{2-}) increasing the solubility of potential pollutants (As, Ni) by complexation and/or sorption competition. (4) Input of polluting substances adsorbing to oxides or clay minerals, forming complexes or leaching directly (5) indirect effect: increase in DOC, occupying anion binding sites, complexing cations and co-dissolution of some elements from Fe and Al (oxy)hydroxides.

In general the high alkalinity, high ionic strength caused mainly by Ca, Mg, K and Na, high concentrations of complexing and competing anions (Cl^-, SO_4^{2-}) as well as the input of pollutants contained with the ash are expected to induce changes in soil chemistry and affect the leachability of pollutants.

5.1.1 General expected changes of the soil solution chemistry

A considerable increase in pH can cause various changes in the soil chemistry. It will neutralize H^+ in soil solution and on negatively charged binding sites thus increasing the negative surface potential. Consequently, the effective cation exchange capacity and thus the ability of the soil to adsorb cations will rise. Especially in soils of low pH but high potential CEC, a rise in pH can enhance their ability to buffer cation inputs. At the same time the increased amount of OH^- in solution will occupy binding sites for anions at positively charged Fe and Al (oxy)hydroxides (Scheffer, Blume et al. 2010). Also the concentration of DOC in the soil solution will be highly affected by the pH changes. It will not only rise due to release from binding sites by competing OH^- ions, but also due to hydrolysis and autoxidation of humic substances fostered by the OH^- ions (Stevenson 1994). These various pH buffer reactions will significantly affect the solubility of both anionic and cationic species in the soil solution. Nevertheless, a considerable change in soil pH is likely to only occur initially, particularly if wood ash is applied only once like in our case.

The ionic strength of the soil solution has an important influence on solubility of elements and the cation exchange reactions. The high salt content of the ashes (as reflected in the high Ca and EC values) of the wood ash will increase the ionic strength when mixed with soil. At increasing ionic strength, the activity coefficients of ions generally decrease (Figure 38). This effect is stronger for the higher charged cations (Sparks 2003). Therefore the affinity of monovalent cations (Na,K) to negatively charged binding sites will increase relative to that of the divalent (Ca,Mg) or trivalent cations (Al), rendering the monovalent cations more competitive. Therefore it is expected that the ratio of Na and K (monovalent) to Ca and Mg (divalent) in soil solution will decrease by impact of the ash (Scheffer, Blume et al. 2010). Similar to pH, the increase in ionic strength is expected to be buffered by the soil by time particularly in soils with high CEC. Especially in the field experiment, due to single-time application of the ash, the impact is likely to be reduced as slower buffer reactions come into action gradually and the acute changes will be mitigated as the ash substances are washed down the soil.

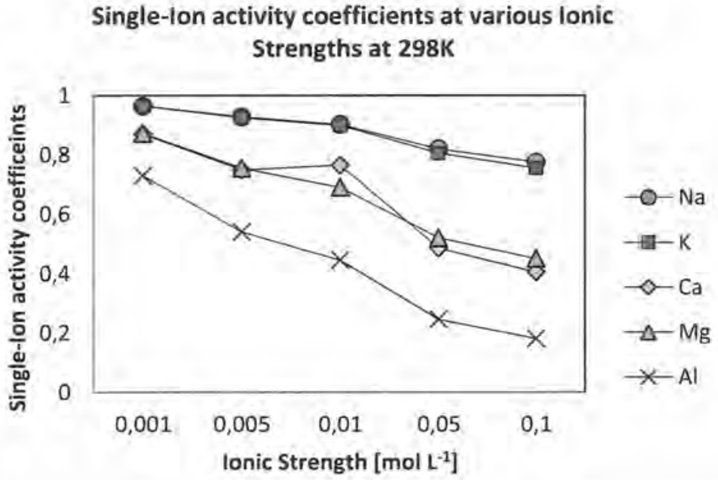


Figure 38 Decrease of Single-Ion activity coefficients at increasing Ionic strength (Sparks 2003).

There is no input of organic matter with the ashes, however wood ash application will influence the concentration of soluble organic carbon (DOC). As the displacement of divalent by monovalent cations in organic binding sites increases, a destabilisation of humus will occur and DOC concentrations will rise. In addition adsorbed DOC might be displaced by anions input at positively charged binding sites and go into solution. Increase of free DOC in soil solution will lead to exchange reactions on anion binding sites and ligand exchange reactions on complexes. This might cause desorption of anionic elements such as As, P, V, Mo or Se. Moreover, various complexation reactions of metals (such as Pb and Cd) by the functional groups of the organic molecules will occur. This can lead to increased solubility of trace metals, Fe and Al (Scheffer, Blume et al. 2010).

High soluble concentrations of Cl^- and SO_4^{2-} in the ash will lead to anion exchange reactions on positively charged binding sites. Especially SO_4^{2-} and DOC compete for the same binding sites (Evans 1986). A large portion of SO_4^{2-} is likely to be leached especially in alkaline soils, as SO_4^{2-} sorption mainly takes place at lower pH. Soils of high clay and Al and Fe (oxy)hydroxide contents are expected to retain more of the SO_4^{2-} (Tabatabai and Sparks 2005). As the two ashes used in our experiments differ clearly in their water extractable Cl^- and SO_4^{2-} concentrations (Table 4), these characteristics will be especially of concern in cases, where GA and FBA application led to different leaching behaviour. Concentrations of NO_2^- and NO_3^- after ash application might also rise due to increased nitrification at higher pH (Scheffer, Blume et al. 2010).

Depending on the soil-ash combination, in most cases ash application is unlikely to directly increase Al and Fe concentrations considerably (only Mn concentrations might increase by direct input) as these compounds occur in natural high amounts in the soil (similar total concentrations in wood ashes and soils, Table 3Table 5). Nevertheless, the soil chemistry will change as Al, Fe and Mn solubility is highly affected by soil pH, redox potential and complexing substances in solution. The ash-driven increase in pH will generally lead to a decrease in soluble Al, Fe and Mn mainly due to precipitation of these metals as oxides (Scheffer, Blume et al. 2010) However, these precipitation reactions can be counterbalanced by complexation reactions with increased DOC or SO_4^{2-} concentrations, keeping the complexed metals in solution. Moreover, free $Al(H_2O)_6^{3+}$ is stepwise hydrolysed at increasing pH. Between pH 4.7 and 7.5 solubility of Al reaches its minimum and at 7.5 most of the Al in solution is present as $Al(H_2O)_3(OH)_3^0$. However, at pH higher than 7.5 solubility is rapidly increasing and the $Al(H_2O)_2(OH)_4^-$ species predominates (Sparks, 2003). Fe and Mn are both very sensitive to redox conditions of the soil, they become more solubilised under decreasing redox potential. A change in redox potential by influence of ash application is hard to predict. At constant redox conditions Mn solubility would be expected to decrease with increasing pH (Scheffer, Blume et al. 2010). Fe(III) solubility similar to Al will decrease up to pH 7.5, will show minimum between pH 7.5 and 8.5, where the $Fe(OH)_3^0$ hydrolysis species is predominant and will increase from pH 8.5 on with rising $Fe(OH)_4^-$ concentration (Lindsay 1979) Additionally the type of oxides present in the wood ashes and soils will play a role in how easily Al, Fe and Mn will be solubilised (eg. share of poor crystalline Fe oxides) (Scheffer, Blume et al. 2010). Thus, change in Al, Fe and Mn solubility in response to ash application depends on the interaction and extent of pH increase, presence of complexation substances and redox conditions, but also individual soil properties. It is expected that in our experiments changes in Al, Fe and Mn solubility will primarily depend on initial soil pH and pH change after ash input.

Particularly Fe and Al, but also Mn (oxy)hydroxides are variably charged secondary minerals whose surface potential and therefore sorption capacity is highly affected by pH. With a zero-point of charge at pH 5-9 (Al oxides) or pH 7-10 (Fe oxides) the surfaces of these metal oxides generally carry a positive surface charge within the typical pH range in soils rendering them the main sorption sites for anionic species (Scheffer, Blume et al. 2010). However an increase in pH will decrease the positive surface potential weakening the anionic sorption capacity. At decrease of redox potential (as a possible effect of road compaction and predominant wet conditions) reductive dissolution of Fe and Mn oxides might occur, which could lead to co-dissolution of adsorbed substances, such as As, Mo, Cd, Pb, Cu, Zn, Ni (Scheffer, Blume et al. 2010).

5.1.2 Expected reactions of polluting elements

Out of the large number of elements investigated in this work, As and Ni, representing anionic and cationic pollutants respectively, will be discussed here in detail due to their environmental toxicity (Adriano 2001).

Arsenic is a highly toxic metalloid, particularly problematic due to its chemical similarity with P. In aerobic soil solutions, As is mainly found as arsenate (AsO_4^{3-}) under oxic conditions, while it is present in its reduced form arsenic acid ($H_3AsO_3^0$) under anoxic conditions. The main sorbents of As are Fe(oxy)hydroxides (Alloway 2012). Due to its large specific surface, the poorly crystalline Fe oxide ferrihydrite has a high sorption capacity for As (Scheffer, Blume et al. 2010). Arsenate is deprotonated from $H_2AsO_4^-$ to $HAsO_4^{2-}$ at pH > 7. At the same time soil constituent surfaces are more negatively charged at increasing pH. This combination of effects is expected to lead to increased repulsion of arsenate from surfaces causing enhanced mobilisation of As into solution at pH > 7 (Fitz and Wenzel 2002). It has been shown that arsenate has sorption maxima on Fe (oxy)hydroxides between 3 and 7 (Adriano 2001). However, at low presence of Fe (oxy)hydroxides in soil, solubility of As is less pH dependent (Fitz and Wenzel 2002). Moreover, studies have shown that increase in ionic strength can lead to decrease in arsenate adsorption (Alloway 2012). Arsenic acid is more toxic and more mobile than arsenate probably due to being uncharged as $H_3AsO_3^0$ at pH<9, however adsorption increases with increasing pH in soils. Yet another important factor for solubility of As are anions that compete for the same binding sites, most importantly PO_4^{3-} and DOC (Fitz and Wenzel 2002).

The combination of wood-ash-driven increases in soil pH, ionic strength and DOC together with a significant direct input of competing anions and As itself can potentially lead to leaching of soil-born (secondary mobilization) as well as ash-born As (weakly buffered, direct input). However, the soils are expected to buffer the inputs depending on their content in Fe (oxy)hydroxides. Occurrence of arsenic acid might only be of concern in the column experiment, where high water flow rate might lead to reduced conditions.

Nickel is essential to organisms in trace amounts being a component in some important enzymes. However, in higher concentrations it is toxic (Adriano 2001). Ni occurs in soil in various forms, however in solution if not as part of a complex it is present as free ion Ni^{2+}. Ni is relatively insensitive to changes in redox conditions. But it shows high affinity to form complexes with different organic or inorganic soil compounds (Adriano 2001). It is attracted to sorb to negatively charged clay mineral and (oxy)hydroxide surfaces. But the bonding is mostly weak and thus Ni is easily mobilized in contrast to Cu and Pb, which are also mostly present as divalent cations but reveal comparatively strong adsorption (Adriano 2001, Scheffer, Blume et al. 2010). Solubility of Ni is decreased at increasing pH, as surface potential becomes more negative and thus more binding sites are available. However, other divalent cations, such as Ca and Mg, can compete with Ni for the same binding sites (Maderova, Dawson et al. 2010). In addition inorganic (Cl^-, SO_4^{2-}) anions and DOC can increase Ni mobility by formation of soluble complexes (Adriano 2001).

Therefore ash application is expected to have several effects on Ni concentrations in the leachates. On the one hand, high input of Ni (by GA) might be buffered well in soils of high CEC, additionally supported by pH increase. On the other hand ash-driven increase in competing Ca^{2+} as well as complexing agents especially Cl^-, SO_4^{2-} and DOC will counteract this effect and might even lead to release of pedogenic Ni.

5.2 Comparison of results to the conceptual model

5.2.1 pH

As seen in the readsorption experiment and the water extracts of the column experiment, the high input of pH generally led to initial changes in soil solution but was buffered by the soils with time and with increased contact with pure soil and soil horizons beneath the ash-soil layer, respectively (Figure 32, Figure 27; SI-Fig. 23 and 31).

However, in the field experiment leachates only small pH effects could be observed. It seems that the buffer reactions of the soils managed to maintain the pH of the leaching water. Only at the acidic site in Kobernausserwald a slight initial ash-driven pH increase in the first sampling period could be seen, but the difference was not significant (Figure 8, SI-Fig. 1).

In the column experiment the ability of the pure soils to buffer the pH impact was confirmed. The neutral soil (S2) showed the weakest pH buffer capacity and the pH of the leachate water increased by about one pH unit (Figure 20, SI-Fig. 15).We attribute the low pH buffer capacity of this soil to its low CEC, SOM and particularly metal (oxy)hydroxide content (Table 5). Interestingly even a reduction in pH in the leaching water of the ash-treated soil compared to the control was observed for the alkaline soil, however water extractions of the soil at the end of the soil showed no significant pH change compared to the control soil (Figure 20, SI-Fig. 15).

5.2.2 EC, Ca, Mg, K and Na

Similar to pH, the readsorption experiment and the column experiment water extracts generally confirmed the ionic strength (as indicated by EC) was buffered by the soils, depending on their properties (Figure 32, Figure 27; SI-Fig. 23 and 31). A difference in salt buffer capacity of the soils could be seen in the field experiment, where increased EC and Ca, Mg, K, Na were found in the leachates of the ash-treated sites in Kobernausserwald forest, where the soil is more sandy and has a lower CEC than the soil in Weyregg (Figure 8, Figure 9; SI-Fig. 1 and 2).

In the column experiment poor buffering of EC, Ca, Mg and K was found in the neutral S2 soil due to its low CEC. All soils used in the column experiment showed a soil specific EC peak in the leachate water followed by a decline towards the end of the experimental period, clearly demonstrating that the salt effect of a one-time ash application will level off with time (Figure 20, Figure 21; SI-Fig. 15 and 16).

Interestingly, the Na concentrations were initially clearly reduced in the column leachates of all soils by ash application (Figure 22; SI-Fig. 15). This is in line with the expectation, that monovalent cations displace divalent cation and are thus better retained at high ionic strength (Scheffer, Blume et al. 2010). In Table 15 the ionic strengths calculated from the relation between EC and Ionic strength in soil extracts according to Simon et al. (1999) (Equ 2) are shown.

Table 15 Ionic strengths in mmol L^{-1} for the water extracts fo the pure soils and the soil-ash mixtures calculated by use of EC according to Simon et al. (1999).

Soil-ash mixtures	Pure ash	Ko	We	S1	S2	S3
Pure soil		0. 3	1	1	2	2
GA	115	3	8	3	5	21
FBA	130	3	8	4	10	25

The concentration ratios of monovalent to bivalent cations in the water extracts of the pure soils and the soil-ash mixtures were compared in Table 16.

Table 16 ratio of monovalent (K,Na) to divalent (Ca,Mg) cation charges in the water extract solutions comparing the pure soils and the soils mixed with ashes GA and FBA.

Soil-ash mixtures	Pure ash	Ko	We	S1	S2	S3
Pure soil		0.56	0.06	0.43	0.87	0.15
GA	0.26	0.20	0.11	0.14	0.59	0.16
FBA	0.06	0.06	0.04	0.05	0.29	0.07

The charge concentrations of the monovalent and divalent cations of the pure ashes are in average 30 and 70-fold higher than in the extracts of the pure soil, respectively (Table 4Table 6). Thus assuming the mixing of ash and soil would not lead to any exchange reactions, we would expect mono-to-divalent cation ratios in the ash-soil mixtures similar to those in the pure ashes. However, in most of the cases we see a reduction of monovalent compared to divalent cation charges in the extraction solution when comparing the pure ash with the soil-ash mixture (Table 16). This indicates, that in line with our hypothesis mixing of soil and ash triggers exchange reactions with a shift towards more divalent cations in solution. Only mixing Ko and S3 with FBA resulted in ratios similar to the pure FBA. Interestingly mixing S2 with ash led to increased ratios for both ashes. Here the low CEC and the naturally high concentrations of exchangeable K might play a role.

5.2.3 Dissolved organic carbon

In the water extracts of the soil-ash mixtures, the expected increase in DOC concentration was observed in the soils Ko, We and S1, which were the highest in SOM content and at the same time the highest in total Al and Fe concentration (Figure 32, Figure 34, Figure 35; SI-Fig. 31 and 33). This complies with the assumption that DOC is released by hydrolysis reactions of humus with OH^- or destabilisation of humus by Na^+ and by displacement from positively charged binding sites by competing anions such as SO_4^{2-}. In the second extraction step, K and S1 proofed to be able to buffer the impact. In contrast S2 was initially very high in DOC and ash application even lowers DOC. Concurrently and in contrast to the other investigated soils, a significant decrease in soluble Fe and Al was observed. This suggests that pH-driven precipitation of Fe and Al oxides lead to increased binding of DOC in this soil. In the second extraction step pH decreased to a significant extent resulting in DOC and Fe re-solubilisation.

Also the increased DOC and Fe concentration in the column eluates from S2 highlight the effect of Fe solubility in DOC concentrations (Figure 20, Figure 24; SI-Fig. 15 and 17). Furthermore the distinct difference between ash treatments in this case indicates that anion exchange reactions particularly with ash-born SO_4^{2-} contributed to the increase in DOC. The second concentration peak in the FBA treatment of S2 might have been caused by the high input of SO_4^{2-} through this ash, as seen in the SO_4^{2-} concentration curves of the experiment, displacing DOC from binding sites and causing ligand exchange reactions (Figure 26; SI-Fig. 22).

In the field experiment slightly increased DOC concentrations were found on the GA-treated sites in Kobernausserwald in accordance with the findings in the water extracts (Figure 8; SI-Fig. 1). A reason for the difference between the forest soils might be the high SOM content of the Ko soil.

5.2.4 Al, Fe, Mn

Manganese concentrations were initially decreased in the extracts of the soil-ash-mixtures compared to the pure soils, indicating that the high pH caused precipitation of Mn (oxy)hydroxides. Subsequently Mn was mostly re-solubilised at lower pH in the second extraction step (SI-Fig. 33). Solubility of Al was expected to increase along with a pH increase above 7.5. This effect was seen clearly on Ko, We and S1 soils. Here initial pH of 5.5, 7.7 and 5.6, respectively were increased to above 8.5 causing increased formation of soluble $Al(OH)_4^-$. Due to their high initial pH and their comparably low content in Al oxides (Table 5) S2 and S3 showed no or little increase of extractable Al after wood ash application. For Al concentrations as well, the decrease in pH in the second extraction step diminished the ash impact (Figure 34; SI-Fig. 33). At stable redox conditions, Fe solubility is expected to decrease with increasing pH up to pH 7.5 and increase at higher pH. However, the observed changes in Fe extractability were not in accordance with the respective pH shifts. In contrast, the Fe solubility seems to rather go along with increase in DOC concentrations, especially on K and S1, where Fe concentration was initially rather low and clearly increased after ash application (Figure 35Figure 32; SI-Fig. 31 and 33). This observation is supported by the fact that Ko and S1 have the highest concentrations in amorphous (AAO extractable) and thus labile Fe, which can be easily solubilised by complexation (Table 5).

In the field, the initial flush of Fe, Al and Mn found in Kobernausserwald treated with GA (due to its higher input of all three metals compared to FBA) might have been buffered in Weyregg because of its higher pH (Figure 10; SI-Fig. 3).

In the column experiment, Al leaching reflects the findings in the water extracts of the soil-ash mixtures: High and significantly increased leaching on S1, no change on S2 and low concentrations, but significant increase due to ash application on S3. However, the only soil, where pH was increased to above 7.5 after ash application was S2. This is contradicting the expectations that solubility of Al is increased at pH above 7.5 (Figure 23; SI-Fig. 17). Additionally on this soil highest increase in DOC solubility was found, which was expected to foster Al solubility (Figure 20; SI-Fig. 15). S2 contains little oxalate extractable, and thus labile Al. This means that despite pH increase above 7.5 and increased DOC, there might not have been enough labile Al present to be solubilised and cause significant increase in Al leaching. Similarly Fe leaching in the column experiment contradicted the expected effect of pH influence. Solubility of Fe was not constant along with pH shift from 7 to 8 on S2, but in contrast increased to a larger extent compared to the other soils (Figure 24; SI-Fig. 17). Here, similarly to the water extracts of the soil-ash mixtures, the DOC solubility is expected to have a major influence on Fe leaching, as DOC solubility is immensely increased after ash application on S2. In addition also increased concentrations of SO_4^{2-} on this soil might have caused dissolution of Fe by complexation (Figure 26; SI-Fig. 22). Manganese showed similar pattern to Al concentrations. But here the Mn input by the ashes is likely to have caused increased concentrations in the eluates in S3, while it was precipitated on S2, where pH was significantly increased. On S1 Mn leaching on the control column alone was comparably high, ash input did thus not lead to significant changes (Figure 25; SI-Fig. 17).

5.2.5 As

The As concentrations in the water extracts of the soil-ash mixtures are closely related to the DOC, PO_4^{3-} and Fe concentrations (Figure 34Figure 35; SI-Fig. 34 and 33). As expected, the ash-deriving As input and the increase in pH and competing DOC initially caused increased extractability in the water extracts of the soil-ash mixtures of As in most soils. However, similarly to DOC this was not the case on S2 and S3. Here the extractability of As was initially decreased which is contradicting the expectation that As will be adsorbed little due to their low content in Al and Fe (oxy)hydroxides (Table 5). However, the pattern shows similarity to DOC behaviour. And at least for S2 Fe precipitation can be assumed due to decreased extractability which might have enhanced sorption capacity for As. The expected release of As was then seen in the second extraction step.

Also in the soil column experiment As showed a similar behaviour to DOC (Figure 26, Figure 20; SI-Fig. 18 and 15). Again in the S2 soil columns a high As release was observed alongside with high releases of DOC, Fe, SO_4^{2-} and PO_4^{3-}. It seems that the pH-driven reduction in sorption sites (particularly Fe (oxy)hydroxides) and at the same time increased dissolution of Fe by DOC and SO_4^{2-} in the ash treatments triggered a strong competition of anions for sorption sites causing the high solubility of anions.

In the field experiment an initial flush in Kobernausserwald confirms the expectation, that As is more easily leaching in soils of coarser texture, as the delayed flush in Weyregg was much less pronounced (Figure 11; SI-Fig. 4). In Kobernausserwald the buffer capacity was not high enough to alleviate the initial input of As, the competing anions such as Cl^- and SO_4^{2-} and the increase in pH at the same time. The association of As to (oxy)hydroxides might have taken place at a later stage, as extractability of As, Al, Fe and DOC in the soil beneath the road were closely related (Figure 19; SI-Fig. 13). This relationship could be an effect of formation of DOC complexes leading to increased solubility of Fe and Al and at the same time ligand exchange reactions, when DOC is displacing As causing its release.

5.2.6. Ni

In the water extracts of the soil-ash mixes it is clear that addition of ash leads to an increase of extractable Ni on all soils (Figure 36; SI-Fig. 36). Except for the Weyregg forest soil, the soils seem not to have the capacity to re-adsorb the released Ni. While the extractable amount of the pure soils is similar, the extractable amount after adding the ash rises from S1<S2<S3. This is in accordance with rising total concentrations of Ni in the soils as well as rising clay and silt content (Table 5). This suggests that Ni is mainly fixed (however non-specificly) to cation exchange sites in the soils. Hence, the large input of competing cations by the ashes is likely to play an important role in the release of Ni from soils overruling the effect of increased pH. But also complexation to anions, such as DOC, might have led to Ni mobilisation. The fact, that the two different ashes with different Ni contents (GA>>FBA) influence the soils similarly in this experiment indicates that changes in Ni solubility by the ash are rather secondary through other ash-related properties (high EC, pH, complexing anions) than through direct Ni input. In the case of Ni, the water extracts and re-adsorption test fit the observations of the column experiment (Figure 24; SI-Fig 20). The highest increase of Ni leaching was found on the alkaline soil S3, probably due to the reasons mentioned above: highest pedogenic contents of Ni in S3 may be replaced by high loads of Ca and released by formation of complexes with ash-derived Cl^- and SO_4^{2-}, and increased concentrations of DOC.

Interestingly in the field experiment the leaching behaviour was similar to As (Figure 11; SI-Fig. 4 and 6). This is surprising, as their chemical reactions in soils are expected to be different. An explanation could be that due to the direct sampling underneath the ash/soil layer in the field experiment increased As and Ni leaching is due to direct input by the ashes, while in the column experiments it is more influenced by the soil properties in the layer underneath the ash-soil mixture. The same pattern in the forest road leachates is also found for Co, Cu, Mo and V (SI-Fig. 5 and 7). However, Co and Cu similarly to Ni are usually present in soil solution as divalent cations, while Mo and V similarly to As are rather found as oxyanions (Scheffer, Blume et al. 2010). Despite their different chemical behaviour, they all might have reacted similarly to increased dissolution of organic matter. The cations might have been released into solution by complexation with DOC, while the anions might have been mobilised by ligand exchange from (oxy)hydroxide binding sites. But all of these elements are considerably high in the GA, which is an indication for a direct input by the ashes. Generally the Weyregg soil performed better in retaining this direct input likely due to its higher clay and silt content.

5.2.7 NO_2^-, NO_3^-

No NO_2^- and NO_3^- should remain in the ashes after complete combustion (Demeyer, Nkana et al. 2001). This is confirmed by the finding, that NO_3^- extractability was not elevated in the soil-ash mixtures compared to the pure soils and NO_2^- was elevated only little on the acidic soils K and S1 (SI-Fig. 38). Also in the column ash eluates application did not lead to significant increase in leaching of NO_3^- or NO_2^- (SI-Fig. 22). Nevertheless, NO_3^- and NO_2^- concentrations were leaching in the field experiment (SI-Fig. 8; Table 11 Table 12). High values of NO_2^- and NO_3^- were especially found on the GA-treated sampling site of Kobernausserwald (SI-Fig. 8). This soil is particularly high in SOM. In addition GA application caused increase in DOC concentrations. Thus, here organic matter was better available for microorganisms. Long term changes in soil chemistry by impact of the ash might have shifted to conditions promoting increase in soil nitrification. The pH of pure soil in Kobernausserwald (5.5) is right at the border of pH range that initiates nitrification (5.5 – 8) (Scheffer, Blume et al. 2010). This means even a slight increase in pH could lead to considerable increase in first (production of NO_2^-) and second step (production of NO_3^-) of nitrification. As the pH of the leaching water of the GA treated site in Kobernausserwald is slightly increased (Figure 8; SI-Fig. 1) an increased soil pH on this site at the same time is likely. This could be an explanation for increased concentration of NO_2^- at first and related increase of NO_3^-.

5.3 Comparison of the soils

In the field, we observed on the acidic site Kobernausserwald a high initial flush of element leaching in the first sampling period in response to ash application. This was found for Fe, Mn and Al accompanied by As, B, Cd, Co, Cu, Mo, Ni, NO_2^- and V (Table 11 Table 12). As this happened mainly at the treatment with GA, which contains generally higher amounts of these compounds than the FBA (Table 3), their leaching is attributed mostly to the direct input by the ash rather than secondary mobilisation from the soil. The Weyregg soil apparently performs much better in buffering this input. The concentrations of relevant elements in the leachates were mostly much lower. An explanation could be the combination of finer soil texture, higher CEC and higher soil pH, all factors which generally mean better retention of metal cations (Scheffer, Blume et al. 2010).

Initial flush events similar to those found in the Kobernausserwald leachates did not occur on the column experiment. Here the soil layer that the eluent had to pass after the ash-soil mixture layer had a significant influence on the leaching behaviour. Interestingly, the differences in soils were more important than the differences in the two ashes. The leaching behaviour of the GA and FBA treated columns were mostly very similar. The curve patterns differed clearly between the different soils. On the acidic soil the eluate concentrations often followed peaking curves. Especially the cations Al, Cd, Pb, Co, and Zn were leaching in high concentrations compared to the other soils and significantly higher from the ash treated column compared to the control. Here the low pH and low CEC is probably the reason for poor retention properties. But also significant elevations in As, Ni and Cr loads should be mentioned. The alkaline soil resulted in comparably lower concentrations of most elements than the other soils. Only for

Ni the highest leaching after ash application was found here. This was probably caused by cation exchange reactions which mobilized Ni from the soil that had the highest total Ni content as described above. The concentration curves from this soil were often flat or increasing, as seen for Mn, Co, Mo or Ni. Maybe here the concentration peak was about to come. Especially interesting were the findings of the S2-soil. Here the differences between ash-treatments and control were the highest. This was prominent for the macro elements Ca, K and Mg and for the parameters mostly present in their anionic form DOC, As, Mo and PO_4^{3-} in particular. Here the high increase DOC and comparably little presence of Fe and Al (oxy)hydroxides which could serve as binding sites for anions might be of importance. Low SOM and CEC were probably the reason for poor retention of Ca, K and Mg.

Overall we observed a tendency of increased leaching of harmful substances from soils with lower pH and a coarser soil texture. However, the contents of SOM and Al/Fe (oxy)hydroxides play an important role for a soils capacity to buffer the ash impact as well.

In Figure 39 the main results and their relation to the single soil features are depicted to provide an overview on the possible interactions and soil constituents that support the buffer capacities of a soil.

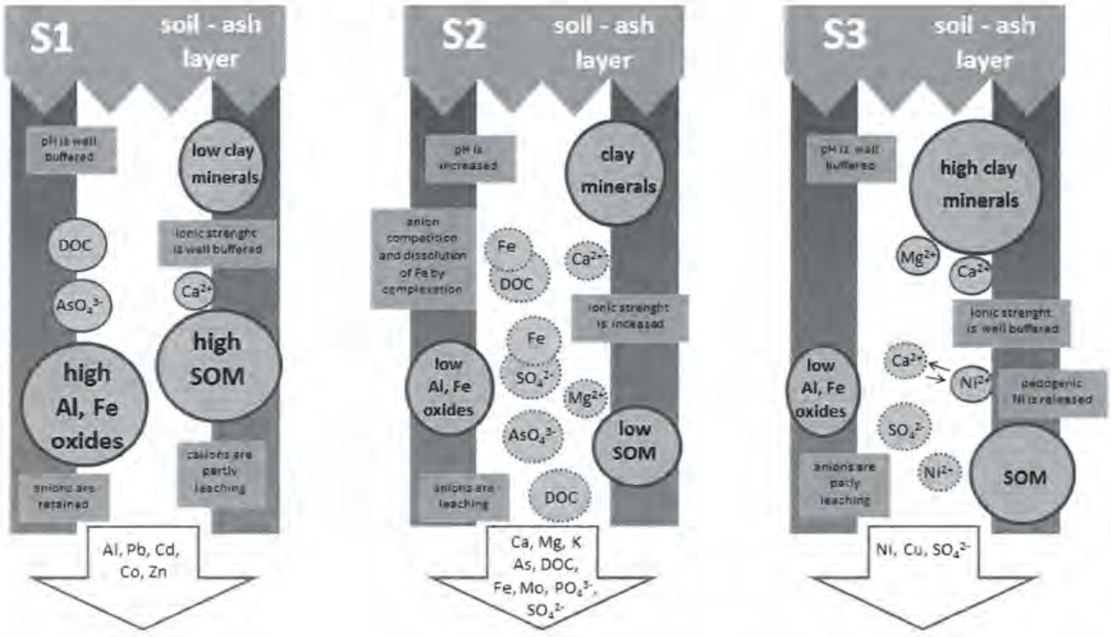


Figure 39 Schematic of the three test soils and their characteristics in relation to the results of the column experiment. S1 is the most acidic and most sandy soil. Here mainly cations are leaching. However, due to its high content in Al and Fe (oxy)hydroxides, anions are well retained and pH and Ionic strength are well buffered. S2 is neutral to slightly alkaline and with moderate clay content. At the same time it contains small amounts of Al/Fe (oxy)hydroxides and SOM. This leads to leaching of Ca, Mg and K. Due to a combination of high DOC concentration, little sorption sites for anions, complexation reactions and sorption competition likely lead to increased leaching of anionic substances on this soil. S3 is the most alkaline and has the highest clay content. Here most substances are well retained. However, pedogenic Ni is leaching due to sorption competition with bivalent cations. Due to few Al/Fe (oxy)hydroxides anions such as SO_4^{2-} are partly leaching.

5.4 Comparison of the ashes

As observed in the field experiment, it is clear that the two ashes differ in their impact on leachate chemistry, when collected beneath the soil-ash mixture layer. GA showed the higher impact on the leaching water concentration of many elements than FBA. If a significant difference between the ashes was found, leached concentrations in the GA treatments were always higher than in the FBA treated sections. A reason for this might be the "dilution" of the raw FBA by burnt lime. Hence, this modification might benefit the ash`s suitability for application.

However, this clear difference is not seen for the column eluates. Here the two ash-treatments mostly follow similar curves in contrast to the control columns. Only SO_4^{2-} loads were clearly higher on the FBA-treated columns of S2 and S3 (Figure 26) and DOC loads showed different curve pattern and were significantly higher on the FBA-treated column of S2 (Figure 20). Even though the two experiments are not easy to compare, this result indicates in general, that the influence of differences in the type of ashes is decreasing, when the leachate passes the layer of pure soil. An explanation could be, that the changes in leachate composition in the field experiment might be caused by primary impact of the ashes, e.g. high input of As, Co or Ni resulting in initial flush events on the Kobernausserwald soil. In contrast the similarity of the curves of the different ashes in the column experiment indicate, that here general characteristics of the ash, like high pH, or high Ca, K and Mg input might make the difference to the control by secondary effects. For example, high input of Ca might lead to release of Ni from cationic binding sites in the S3 soil (Figure 24). This means, that after passing the soil layer, the leachate composition is more influenced by the difference in soils than by the difference in ashes.

6 Conclusion

The results of the field experiment indicate that wood ash application in forest roads is generally environmentally acceptable under the given conditions. The surface runoff water was not influenced by ash application. Sub-road soil samples complied with all thresholds for excavated soils. As hardly any LSW and GSW thresholds were exceeded in the leachates taken at the point before entering the pure soil layer, no threat for groundwater quality is expected.

However, application of wood ash to a soil in the ratio of 15:85 has an impact on the chemistry of the leaching waters, as seen in the results of all experiments. Flush events (Al, As, Fe, Mn, Ni, Co, Cu, Mo, pH und NO_2^-) were only found in the field experiment for GA applied in Kobenausserwald. By influence of the soil layer beneath the ash-soil mixture layer, primary entry of contaminants was buffered well by the soils, as seen in the column experiment. However general ash characteristics, like high pH, high ionic strength and high input of Ca, K, Mg and Na cations as well as anions, such as SO_4^{2-} and Cl^- can change the soil chemistry. Mainly changes in surface potential, ion exchange reactions and complexation reactions led to shift in ion balances and mobilisation or immobilisation of substances. For instance, in soils of little Fe and Al (oxy)hydroxide content and thus poor retention capacity of Anions, there is a higher risk of anionic contaminants leaching, as seen for instance for As on S2. Poor buffer capacity for cations was seen on soils of lower CEC (S1, S2). Also high natural soil contents of a harmful substance might be mobilised by impact of ash application, as seen for Ni on S3.

Hence, a broad variety of buffer capacities was found for the different soils depending on their individual characteristics. Generally soils of higher pH, higher silt and clay content with higher CEC and higher amount of sorption sites for anions performed better in buffering the ash impact. Therefore it is important that future thresholds for wood ash application on forest roads will be set low enough to ensure feasibility of wood ash application on a wide range of soils including those of low buffer capacity. It is also suggested to avoid wood ash application on soils of high pedogenic content of potential contaminants that could be released due to ash influence. Finally an appropriate security buffer layer of pure soil between soil-ash-mixture layer and ground water should be ensured to secure groundwater quality.

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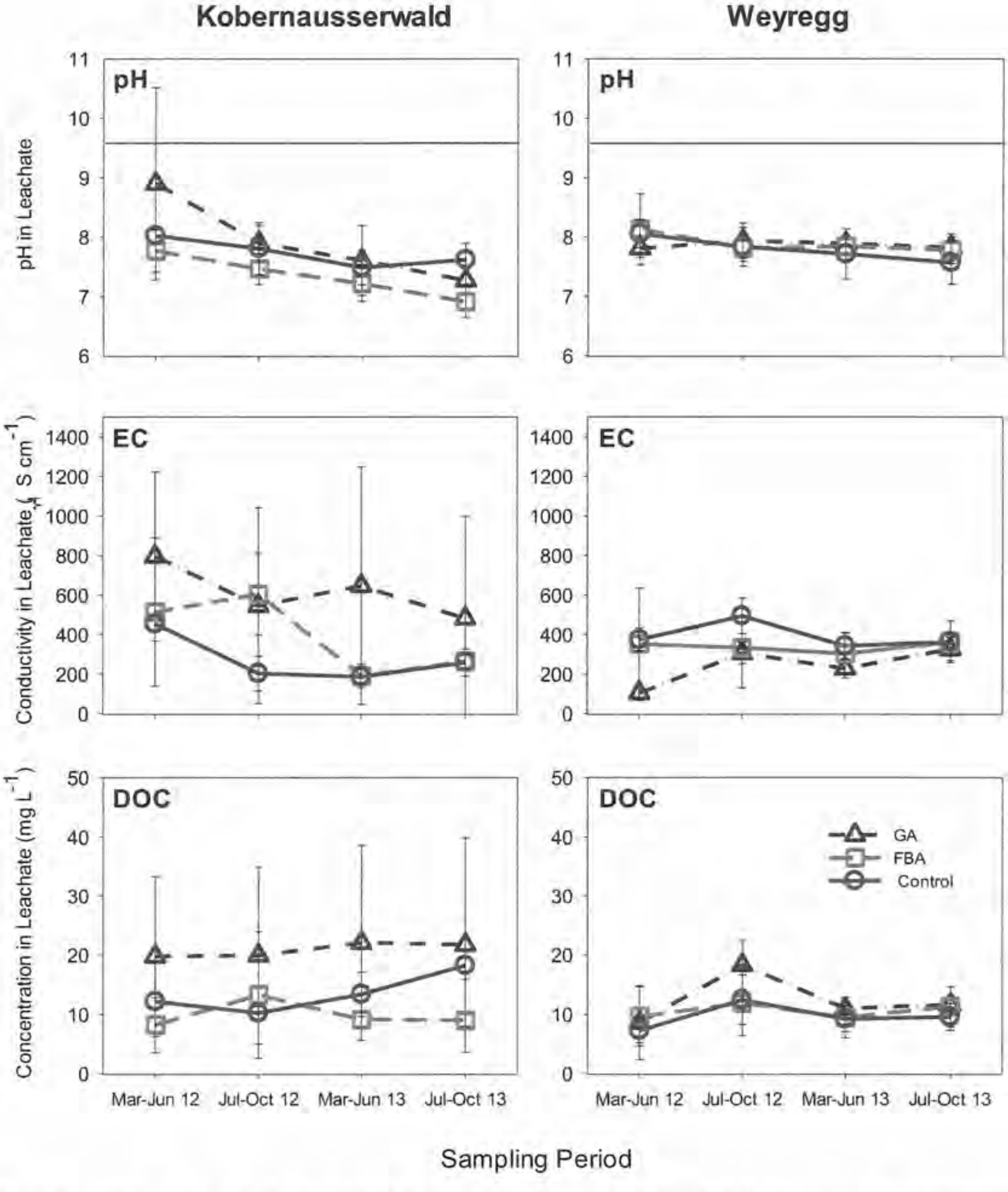
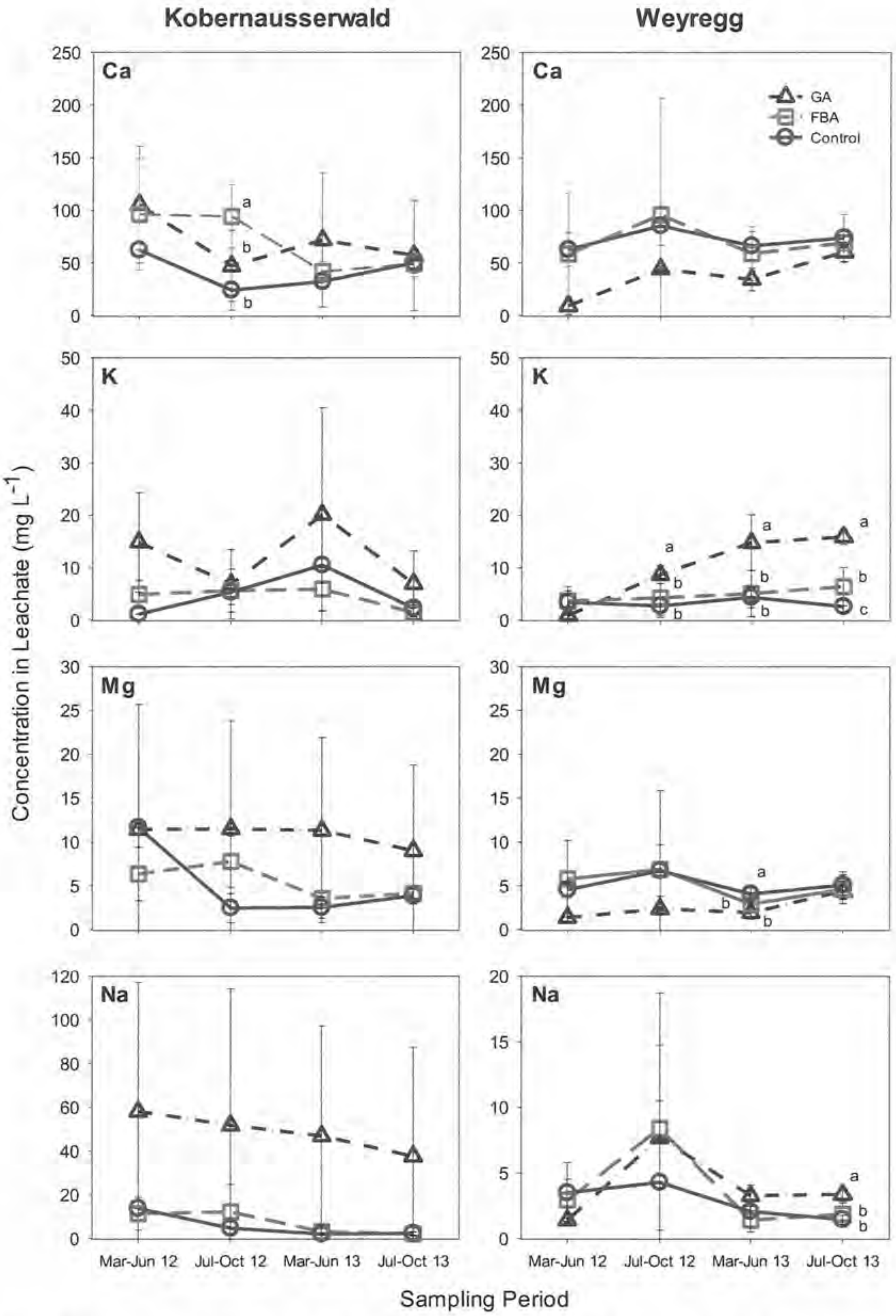
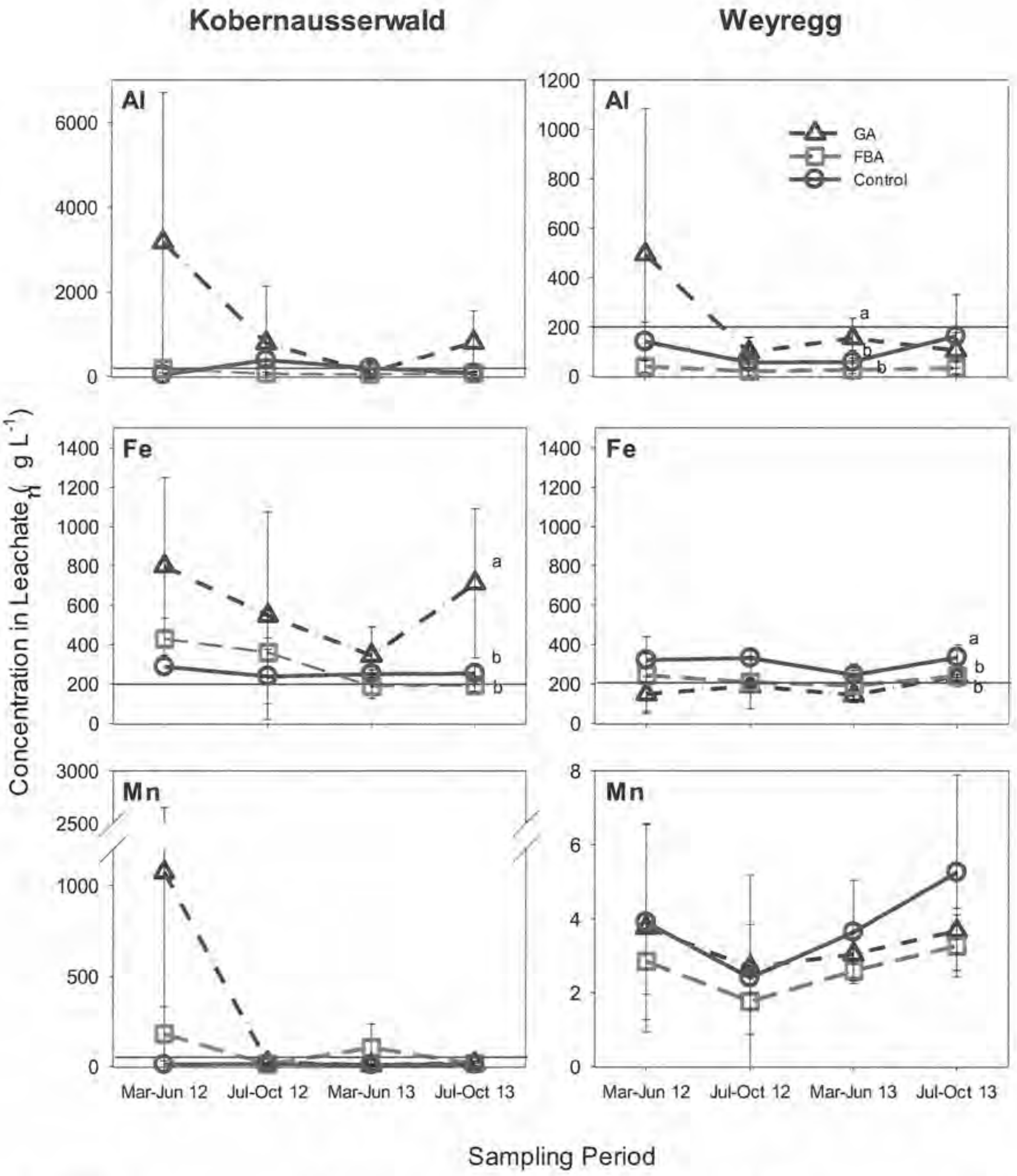
8 Supplementary Information



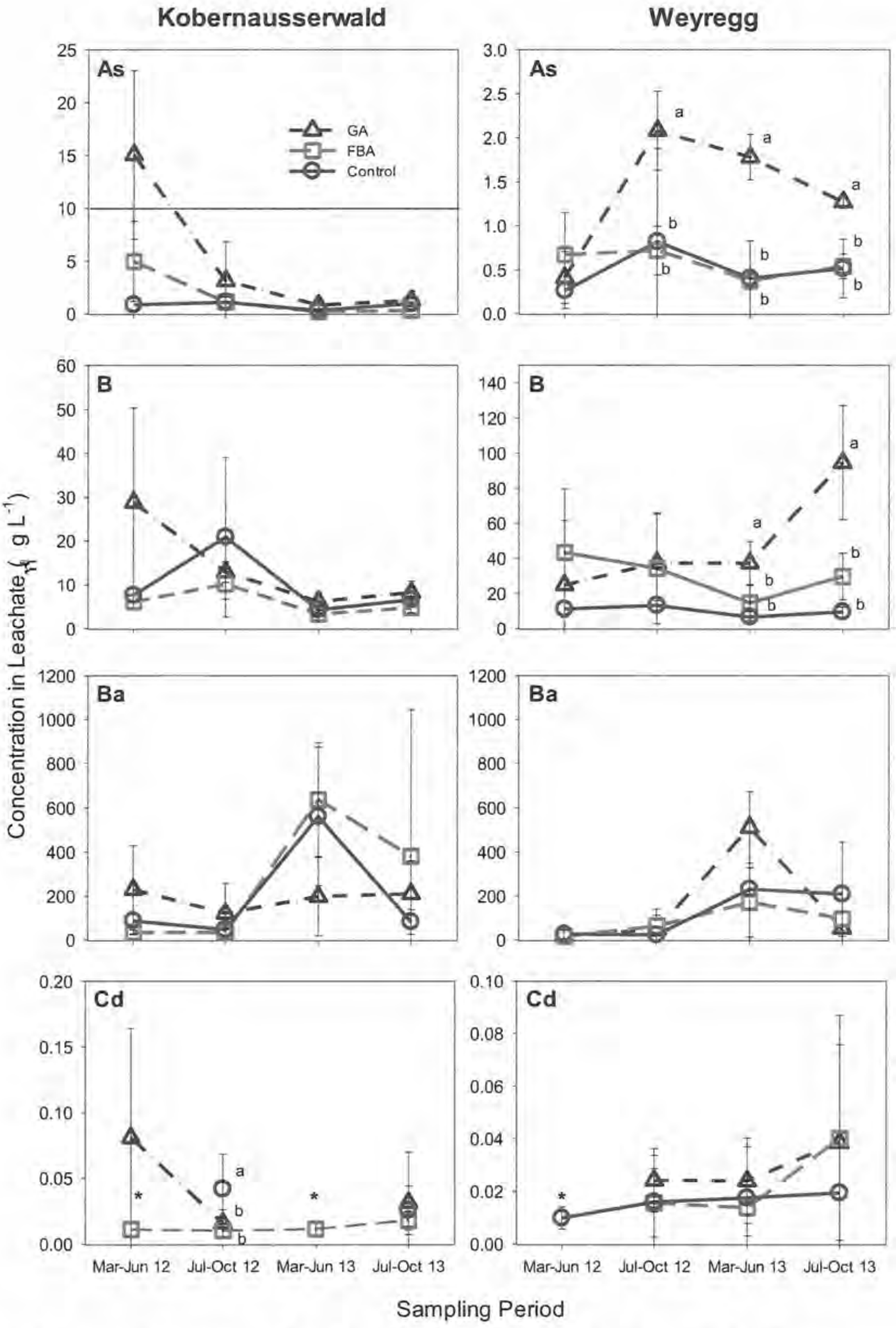
SI-Figure 1 Leachate values of pH, EC and DOC from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period (p < 0.05). The red line indicates the threshold in Austrian ordinance fort Drinking Water.



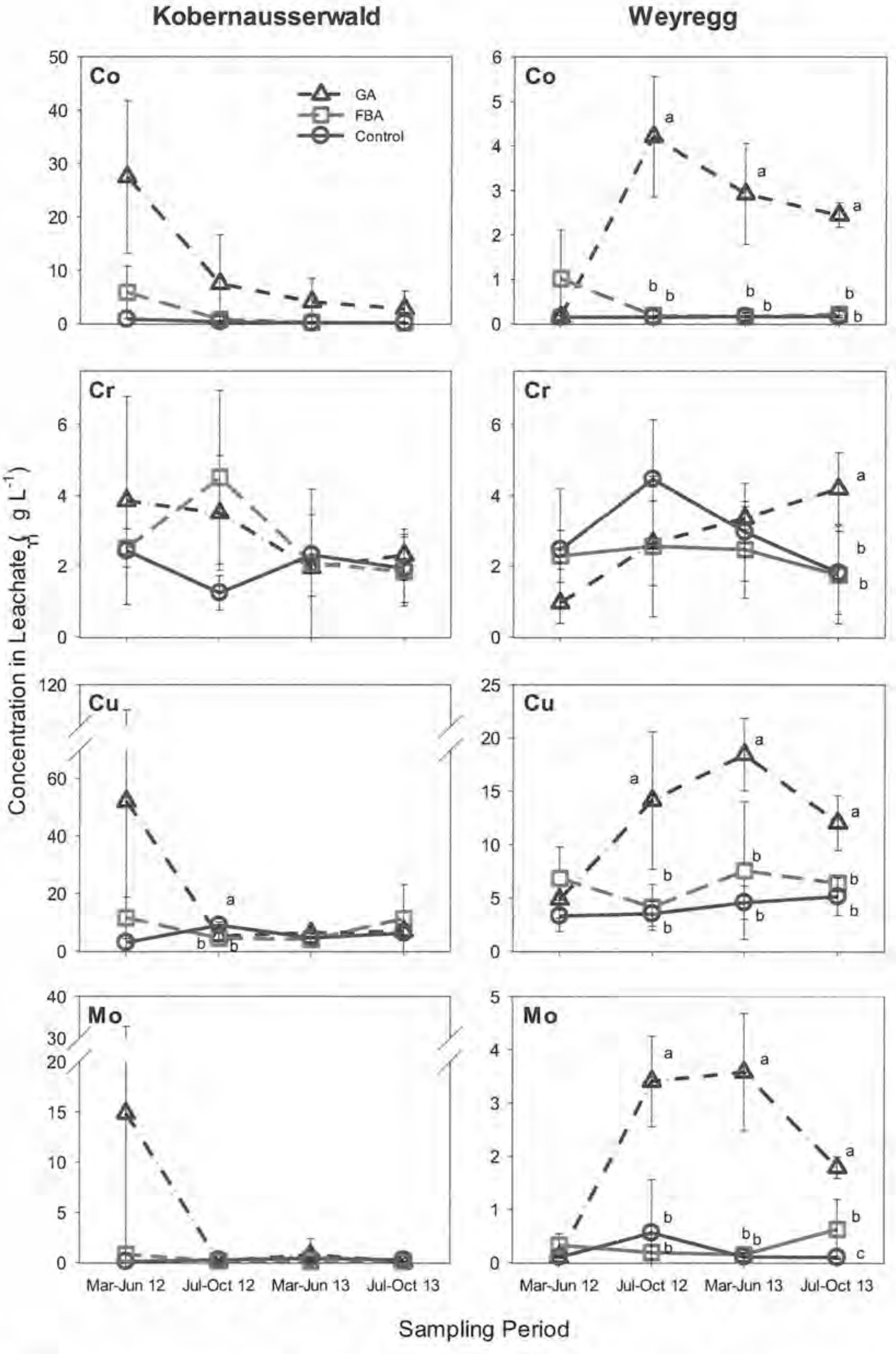
SI-Figure 2 Leachate concentrations of Ca, K, Mg and Na from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales of the Na graphs.



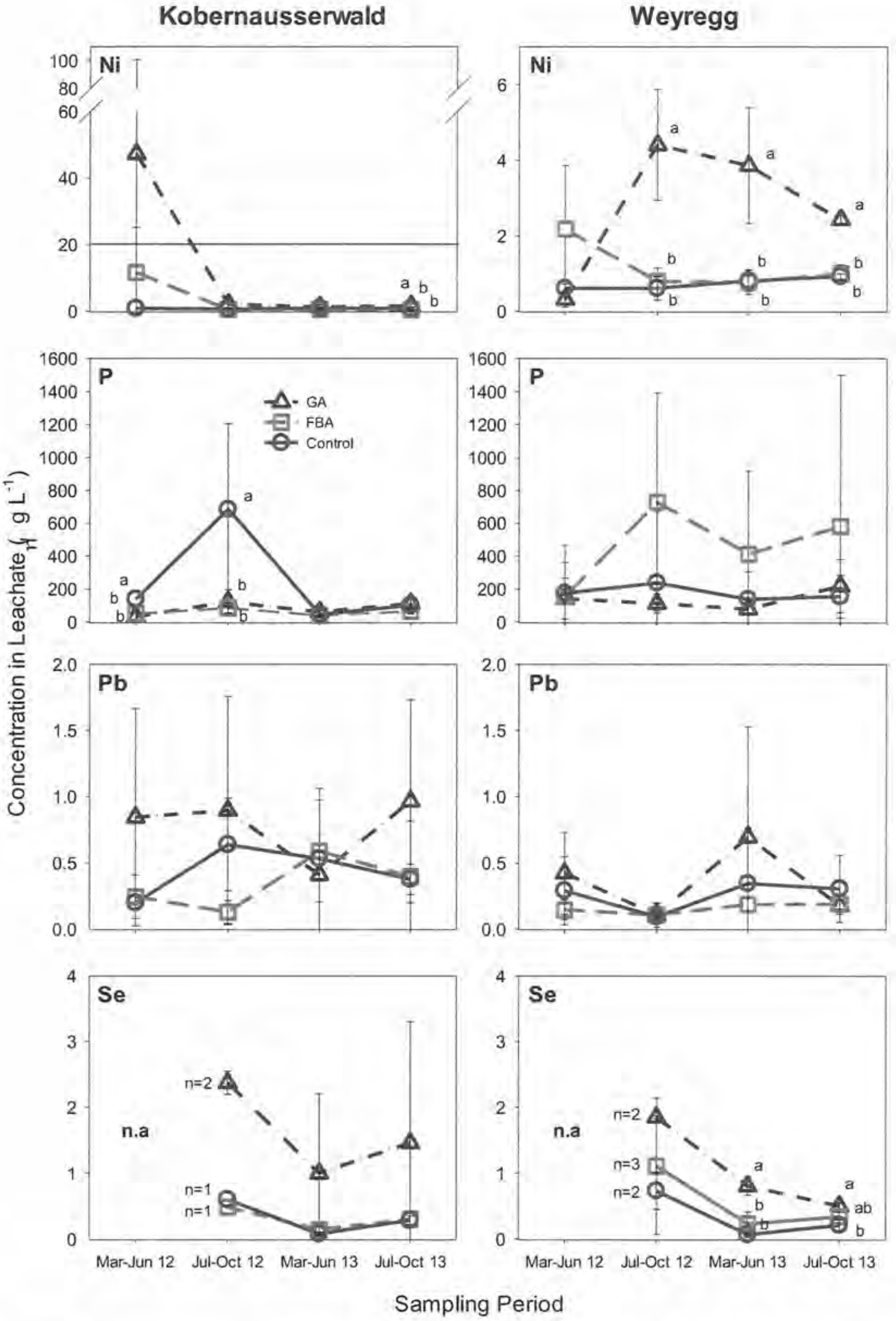
SI-Figure 3 Leachate concentrations of Al, Fe and Mg from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period (*p* < 0.05). Note the different scales of the Al and Mn graphs. The red line indicates the threshold in Austrian ordinance fort Drinking Water.



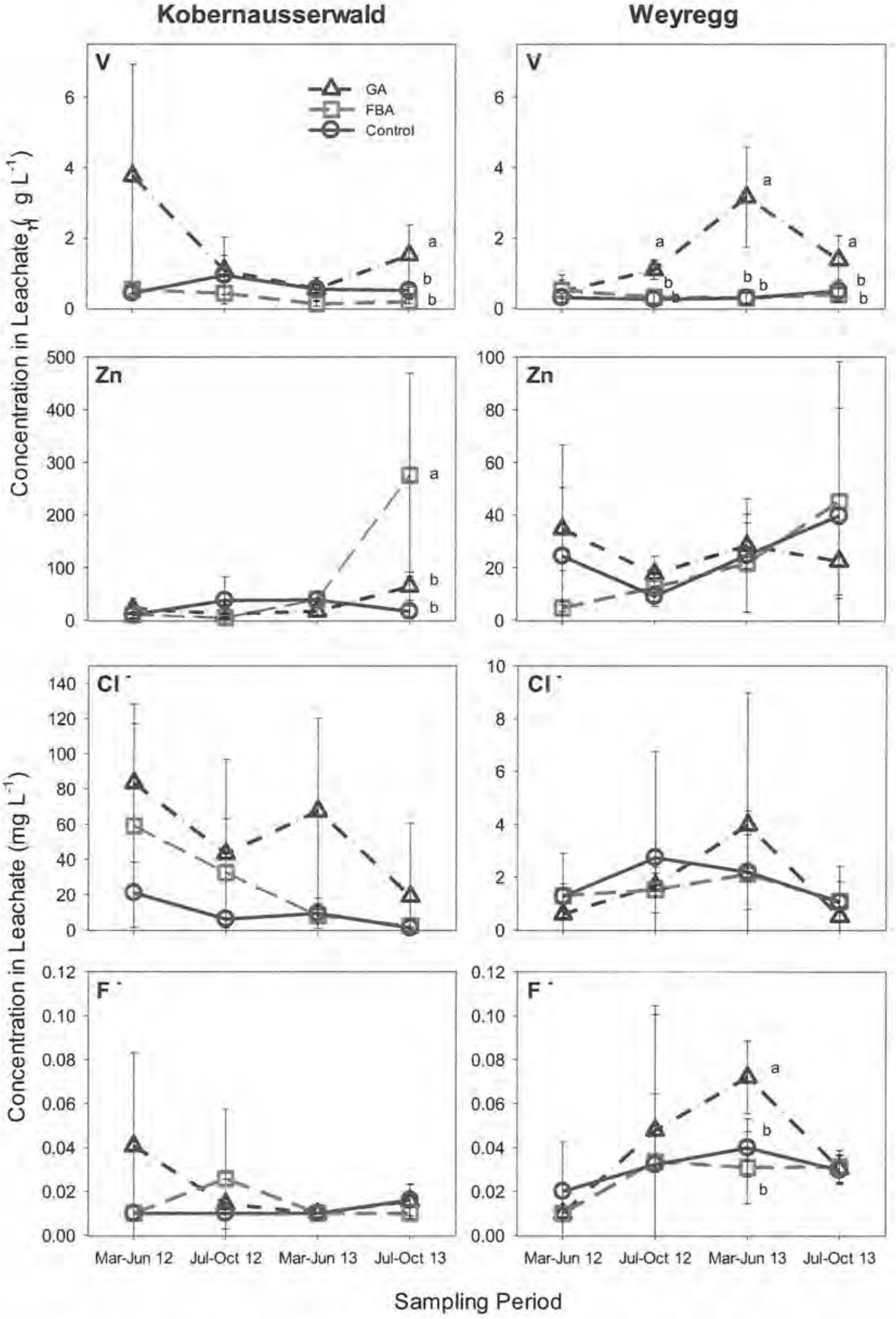
SI-Figure 4 Leachate concentrations of As, B, Ba and Cd from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales of the As, B and Cd graphs. The red line indicates the threshold in Austrian ordinance fort Drinking Water. *values below LOQ (SI-Table 1)



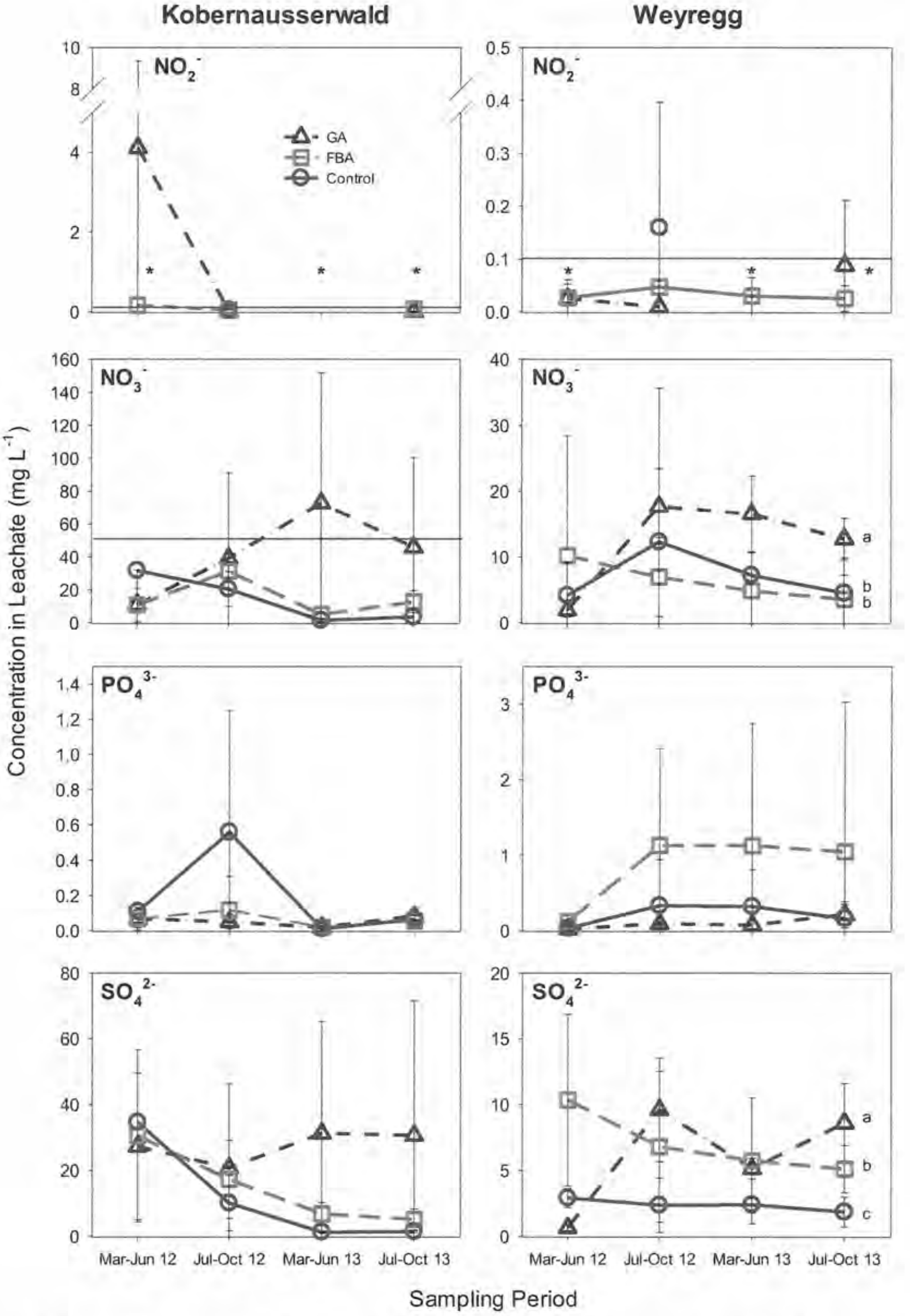
SI-Figure 5 Leachate concentrations of Co, Cr, Cu and Mo from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales of the Co, Cu and Mo graphs.



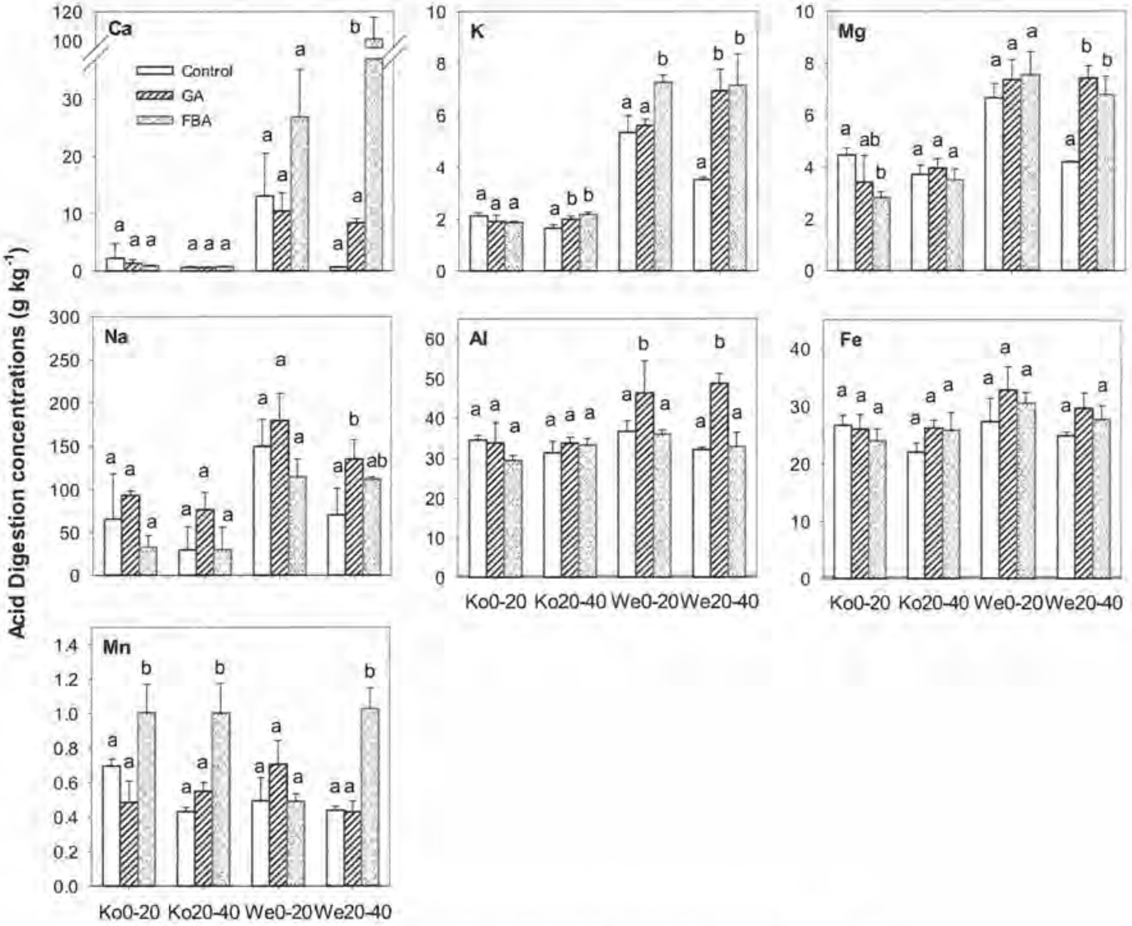
SI-Figure 6 Leachate concentrations of Ni, P, Pb and Se from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period (*p* < 0.05). Note the different scales of the Ni graphs. The red line indicates the threshold in Austrian ordinance fort Drinking Water.



SI-Figure 7 8 Leachate concentrations of V, Zn, Cl^- and F^- from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales of the Zn and Cl^- graphs.

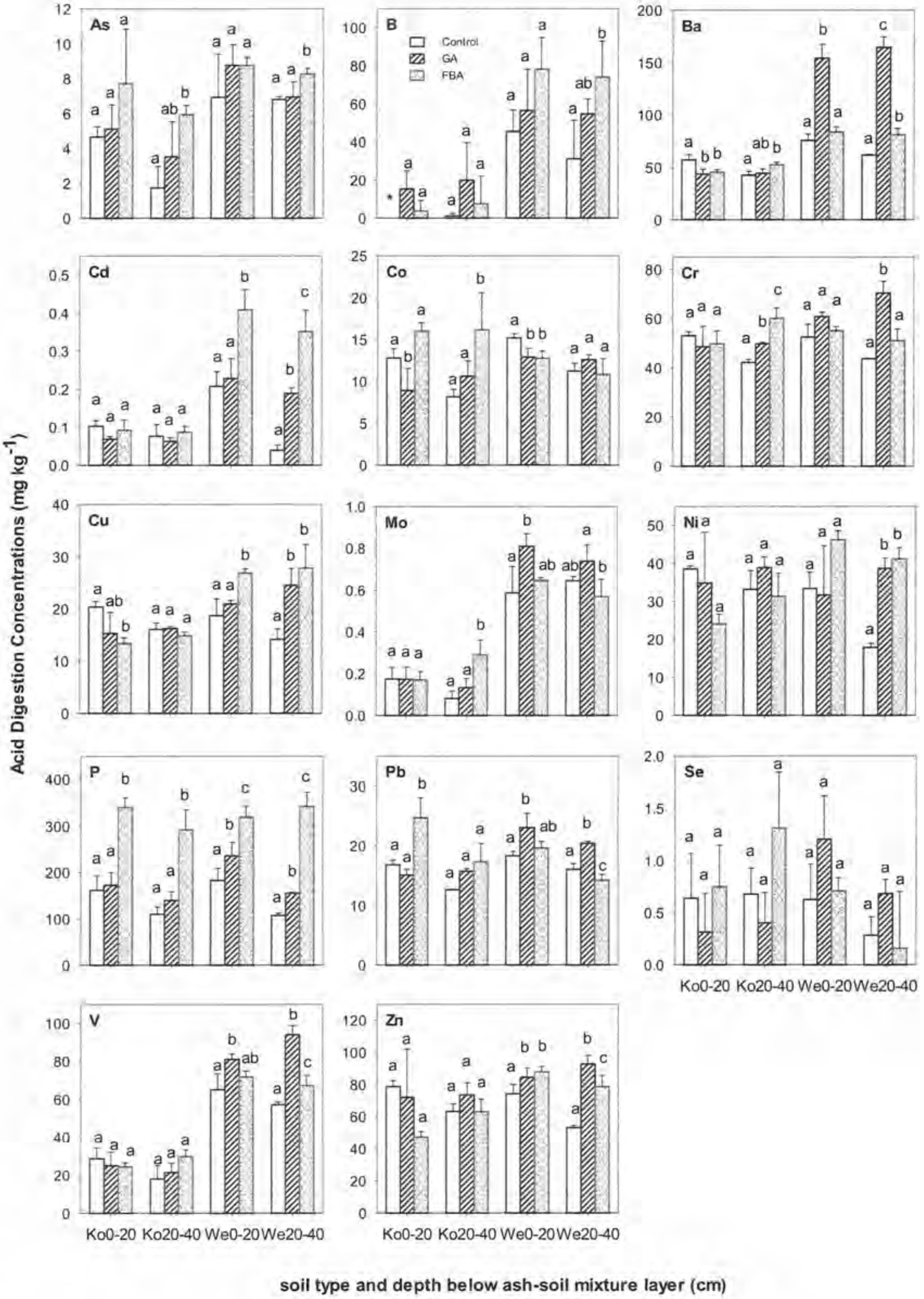


SI-Figure 9 Leachate concentrations of NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} from the forest road field sites in Kobernausserwald and Weyregg over time. Data represent averages of the four sampling periods ± standard deviations. Statistical ANOVA analysis was conducted to compare the treatments within the respective sampling period, only marked where statistical difference was found. Letters a, b, c indicate significant differences between the treatments within each sampling period ($p < 0.05$). Note the different scales of the NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} graphs. The red line indicates the threshold in Austrian ordinance fort Drinking Water. * values below LOQ (SI-Table 1)

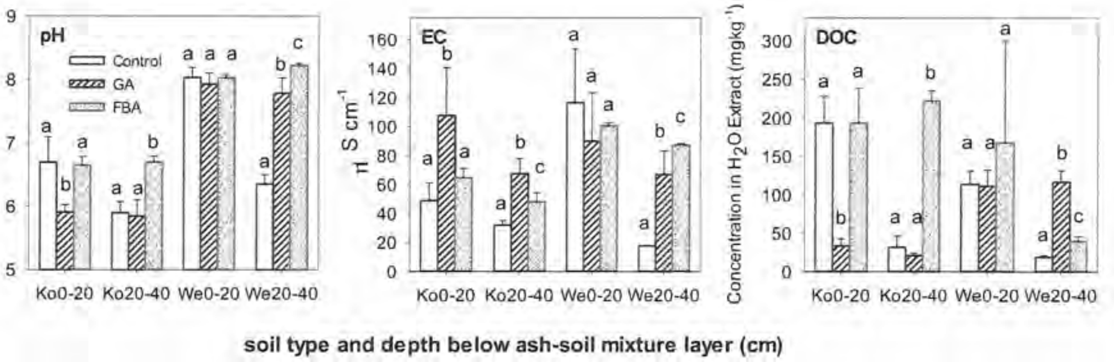


soil type and depth below ash-soil mixture layer (cm)

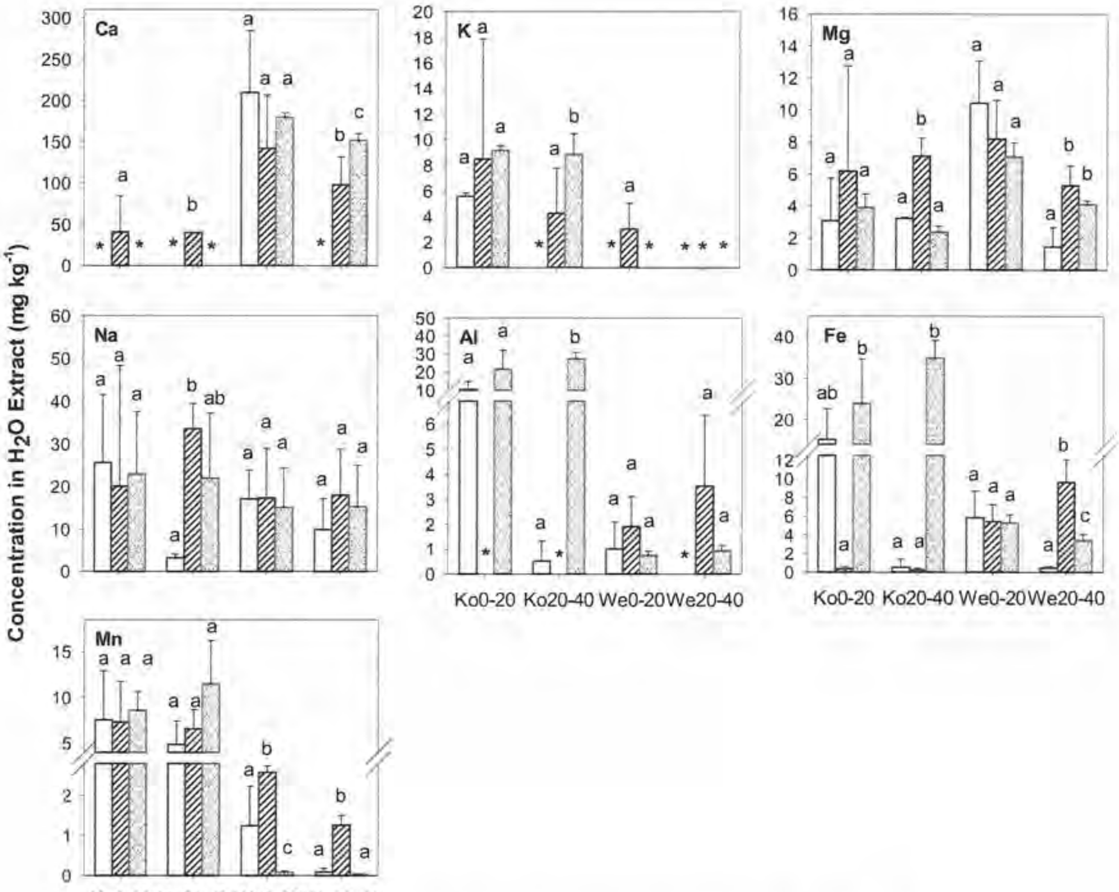
SI-Figure 10 Total Ca, K, Mg, Na, Al, Fe and Mn concentrations of the field experiment sub-road samples in the upper (0-20 cm) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest. Note the values in g kg^{-1}.



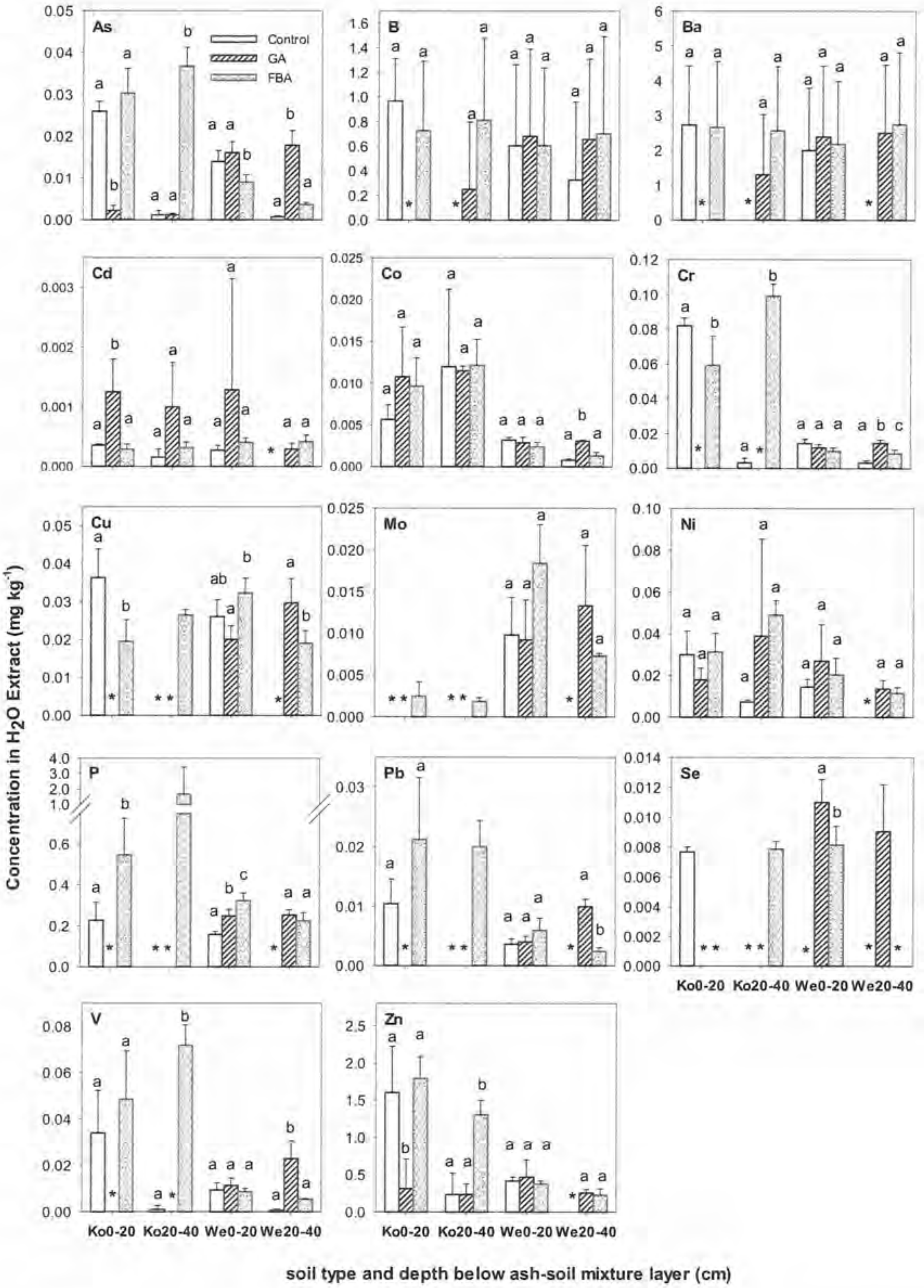
SI-Figure 11 Total As, B, Ba, Cd, Co , Cr, Cu, Mo, Ni, P, Pb, Se, V and Zn concentrations of the field experiment sub-road samples in the upper (0-20 cm) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest.



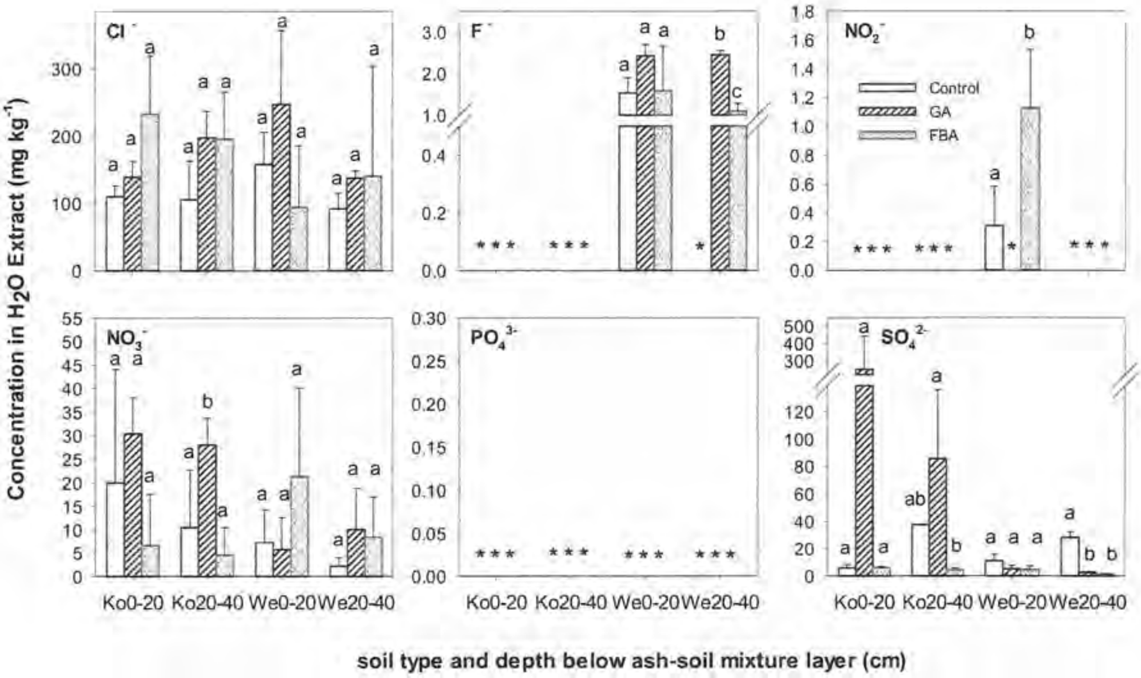
SI-Figure 12 pH, EC and DOC concentrations in the water extracts of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (Ko) and Weyregg (We). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest.



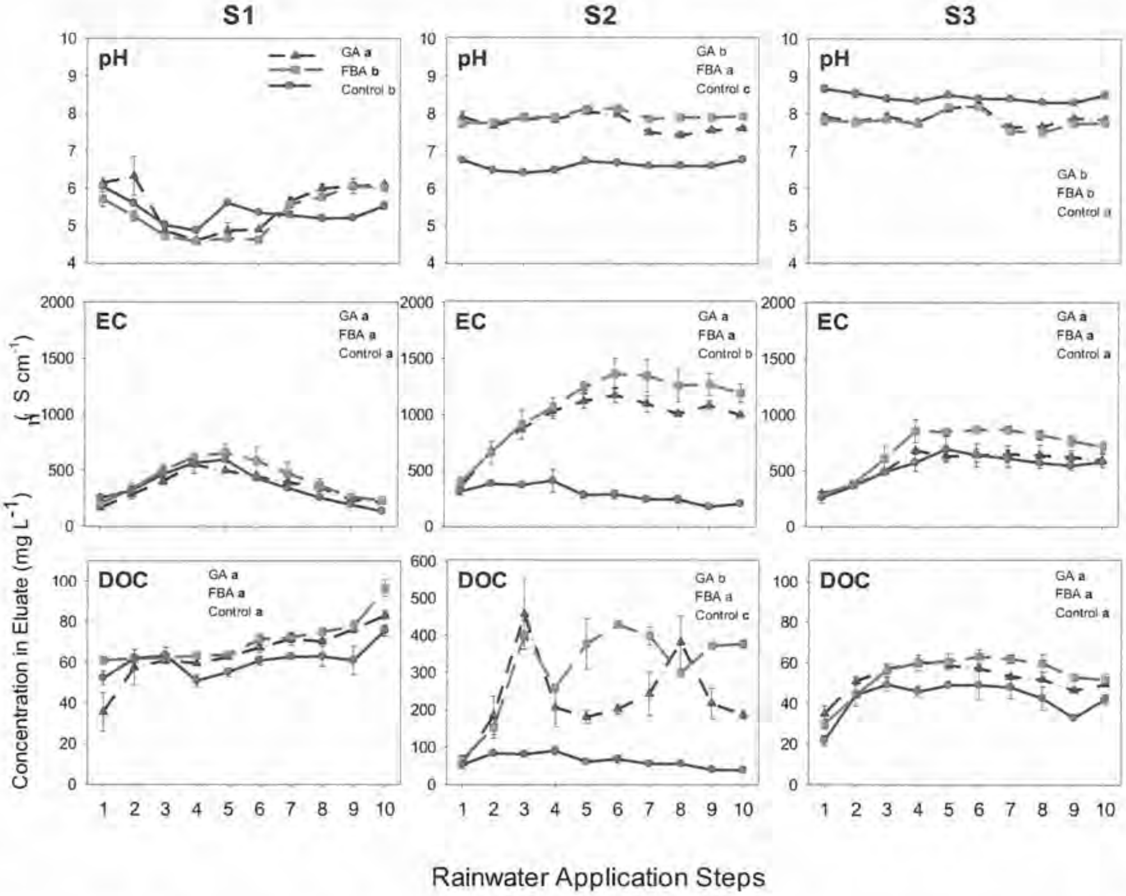
SI-Figure 13 Calcium, K, Mg, Na, Al, Fe and Mn concentration in the water extracts of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (K) and Weyregg (W). The error bars represent the standard deviations. The statistical ANOVA analysis compares the treatments within one soil layer of the respective forest. * Values below LOQ (SI-Table 1)



SI-Figure 14 Arsenic, B, Ba, Cd, Co , Cr, Cu, Mo, Ni, P, Pb, Se, V and Zn concentrations in the water extracts of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (K) and Weyregg (W). The error bars represent the standard deviations. The statistical analysis compares the treatments within one soil layer of the respective forest. * Values below LOQ (SI-Table 1)



SI-Figure 15 Chloride, F$^-$, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations in the water extracts of the field experiment sub-road samples in the upper (0-20) and lower (20-40) soil layer in Kobernausserwald (K) and Weyregg (W). The error bars represent the standard deviations. The statistical analysis compares the treatments within one soil layer of the respective forest. * Values below LOQ (SI-Table 1)



SI-Figure 16 Leaching pattern of pH, EC and DOC concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the DOC graphs.

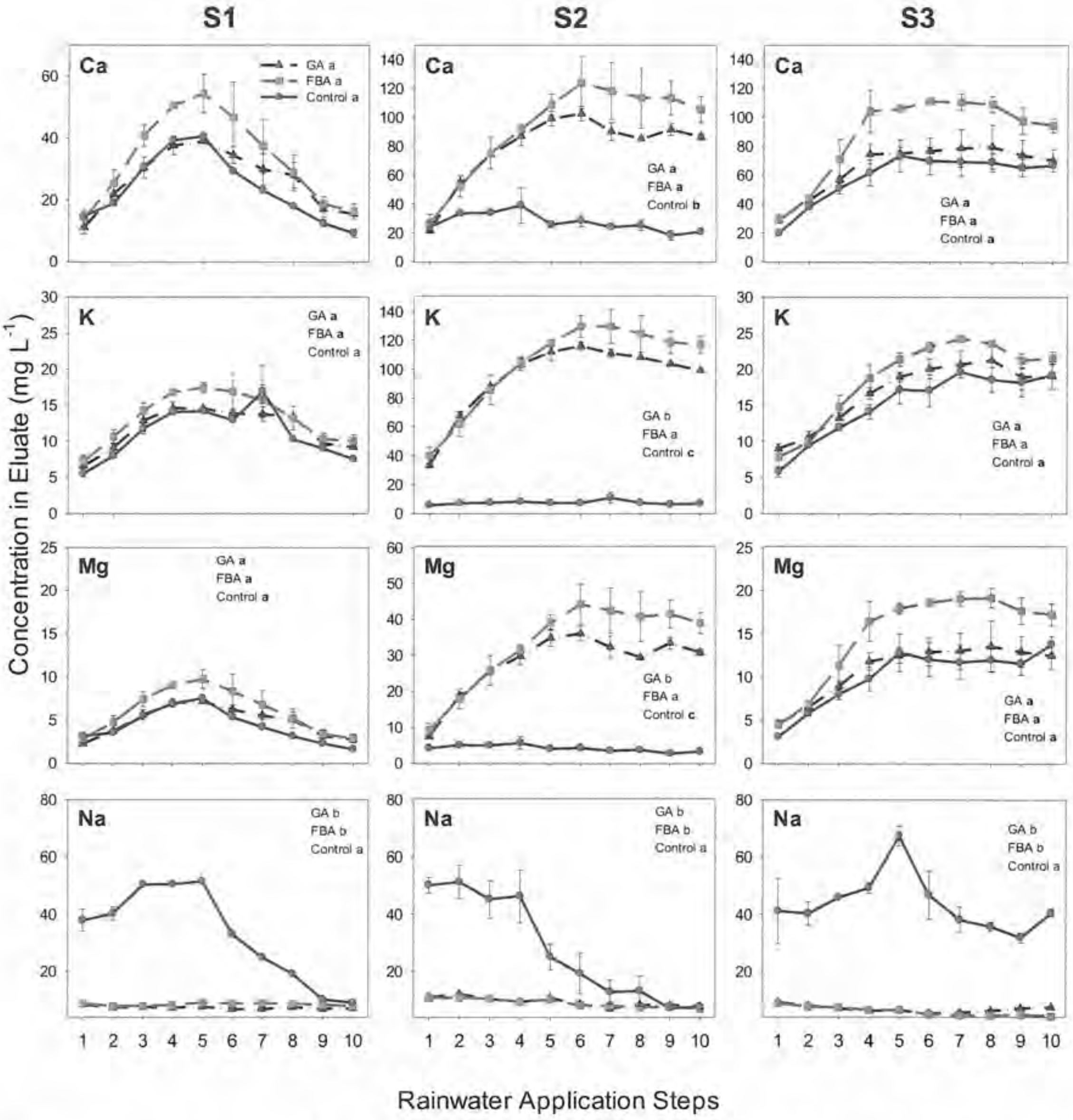
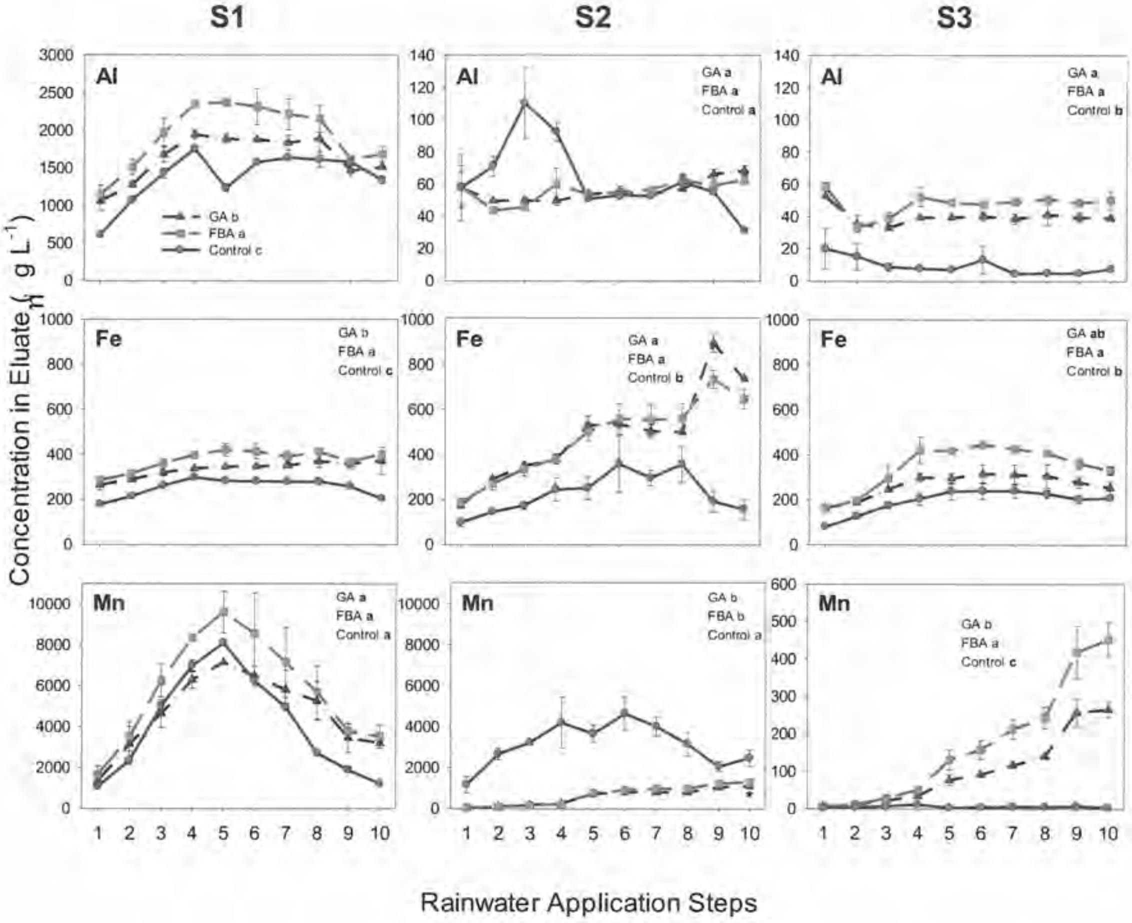
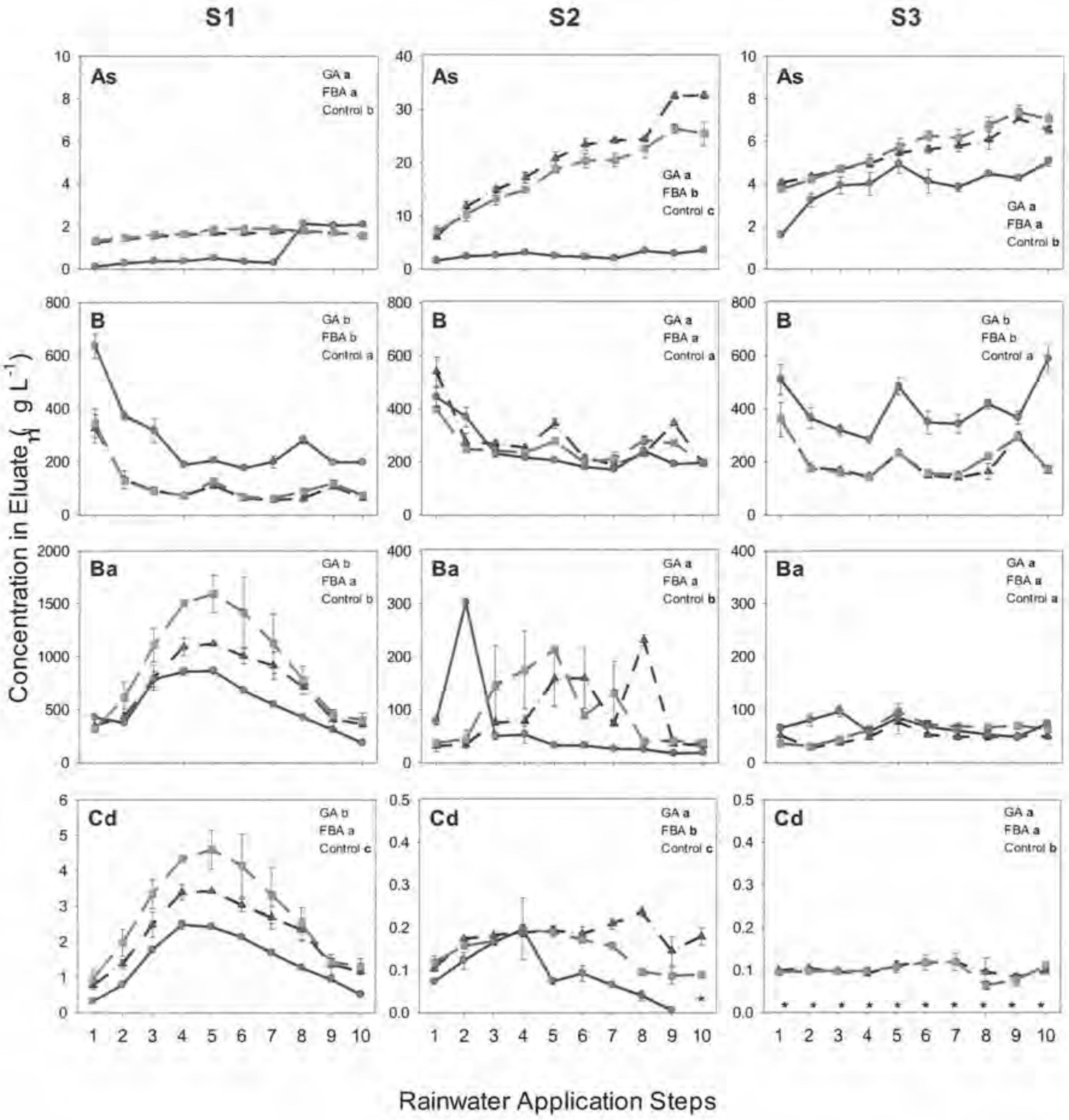


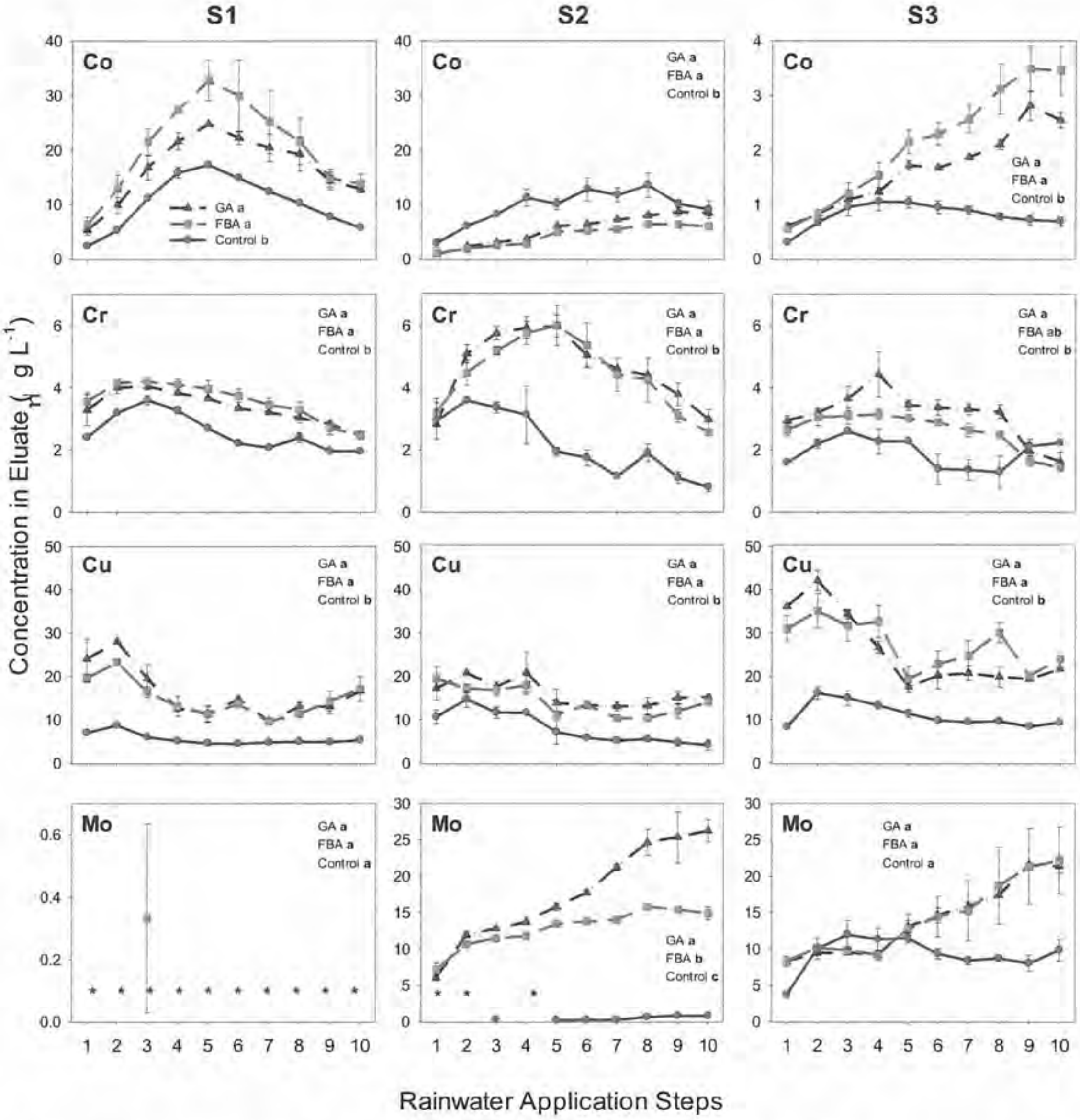
Figure 17 Leaching pattern of Ca, K, Mg and Na concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the Ca, K and Mg graphs.



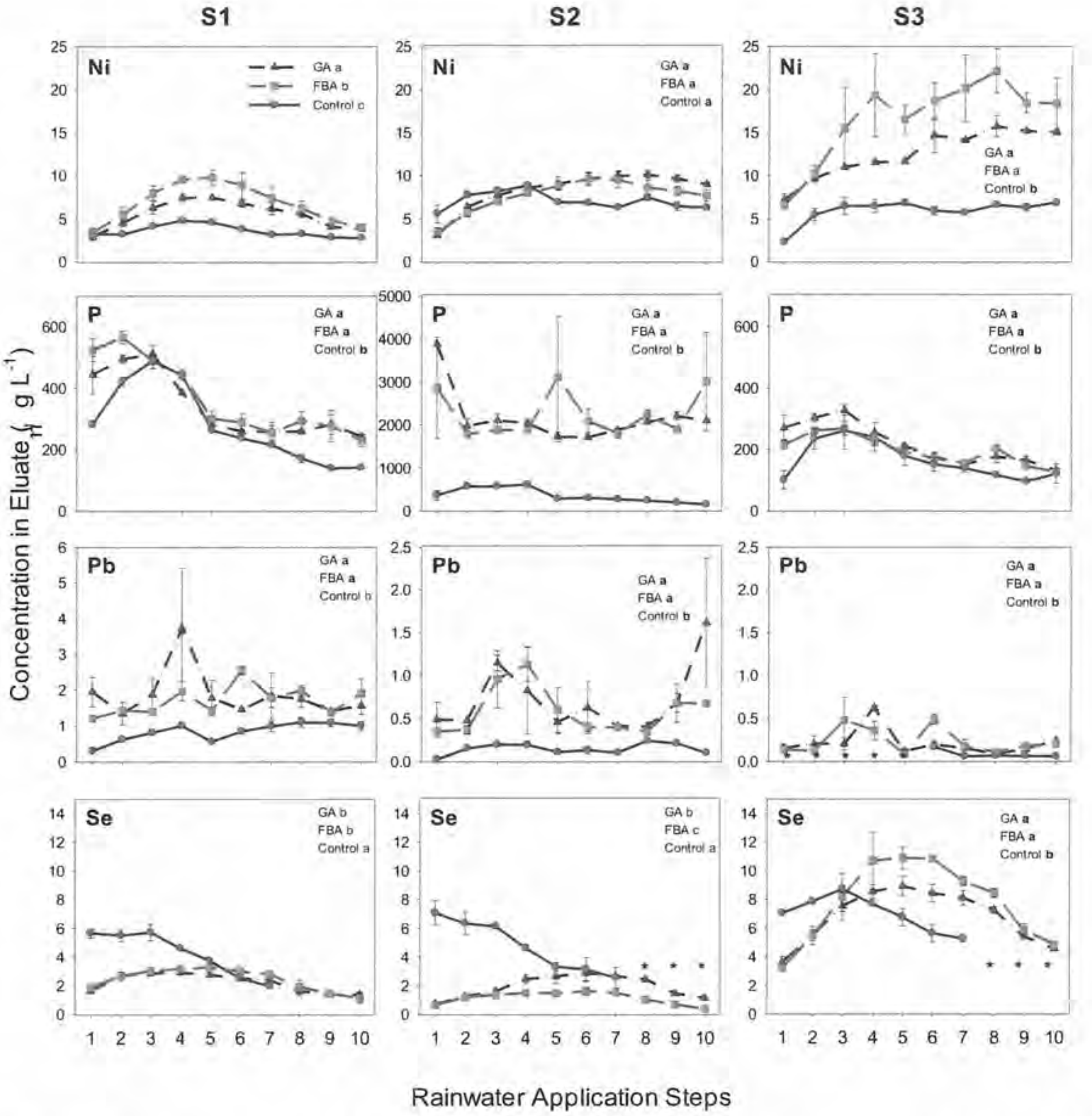
SI-Figure 18 Leaching pattern of Al, Fe and Mn concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the Al and Mn graphs.



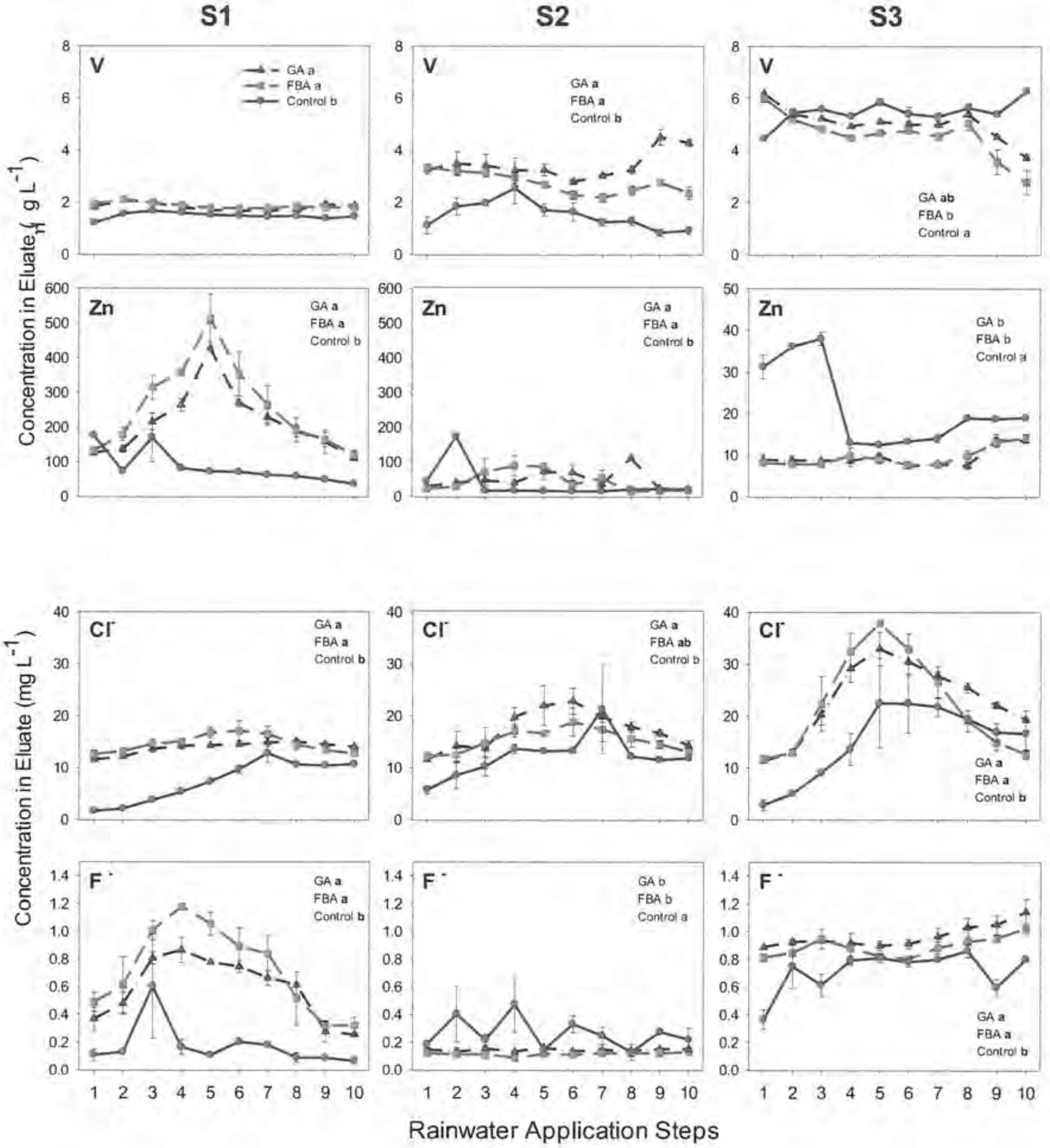
SI-Figure 19 Leaching pattern of As, B, Ba and Cd concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the As, Ba and Cd graphs. * Values below LOQ (SI-Table 1).



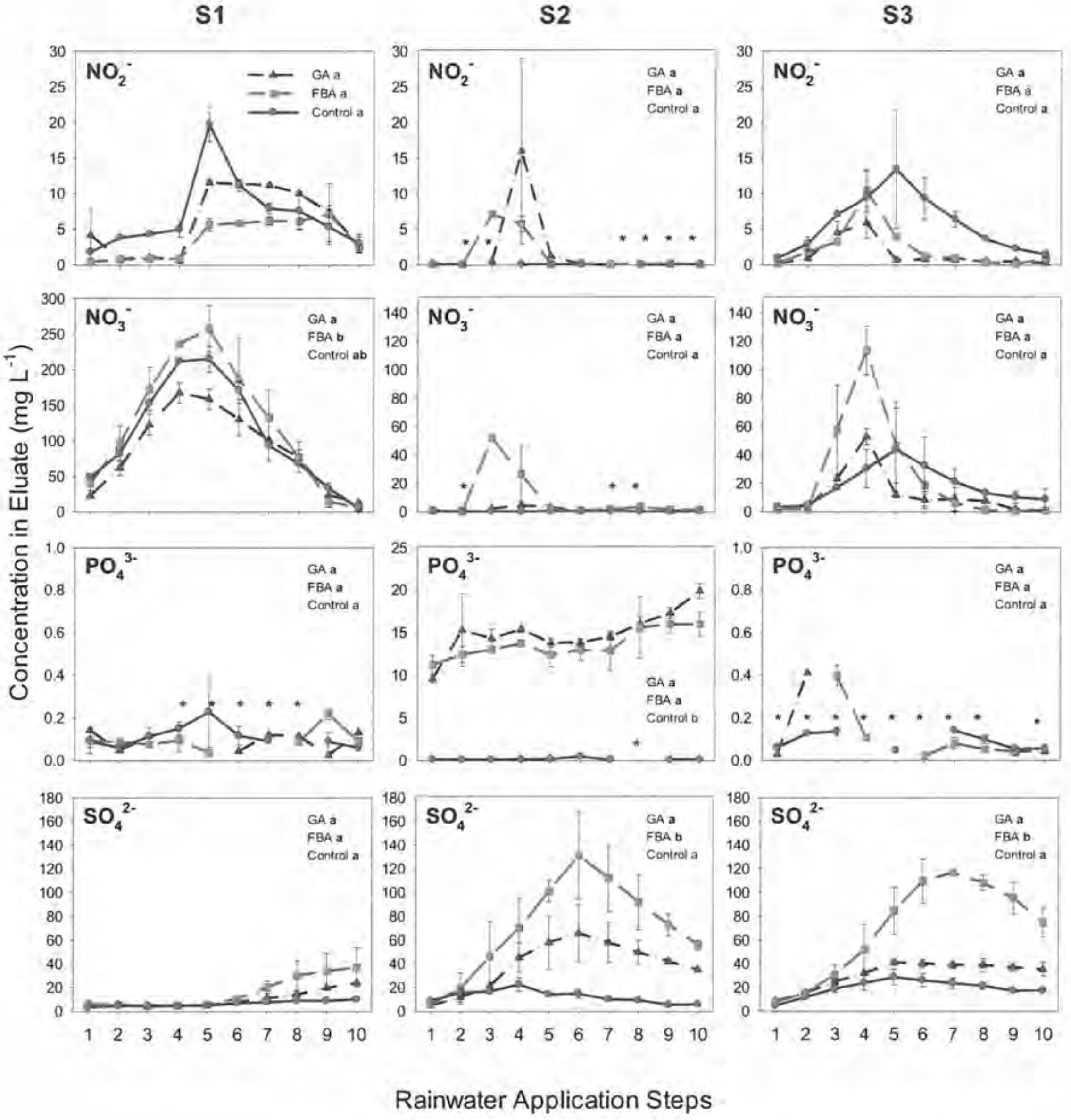
SI-Figure 20 Leaching pattern of Co, Cr, Cu and Mo concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the Co and Mo graphs. * Values below LOQ (SI-Tabel 1).



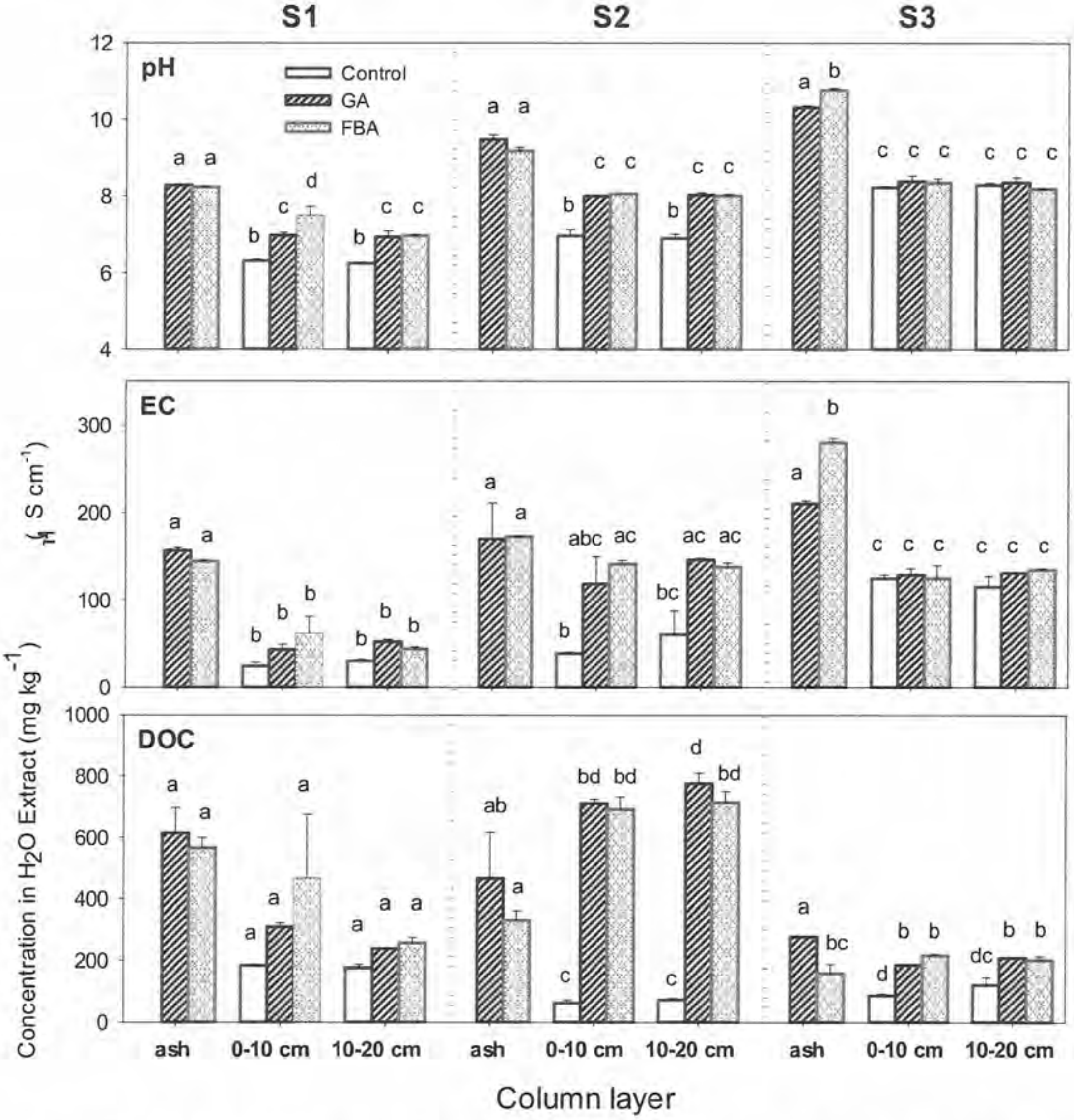
SI-Figure 21 Leaching pattern of Ni, P, Pb and Se concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the P and Pb graphs. * Values below LOQ (SI-Tabel 1).



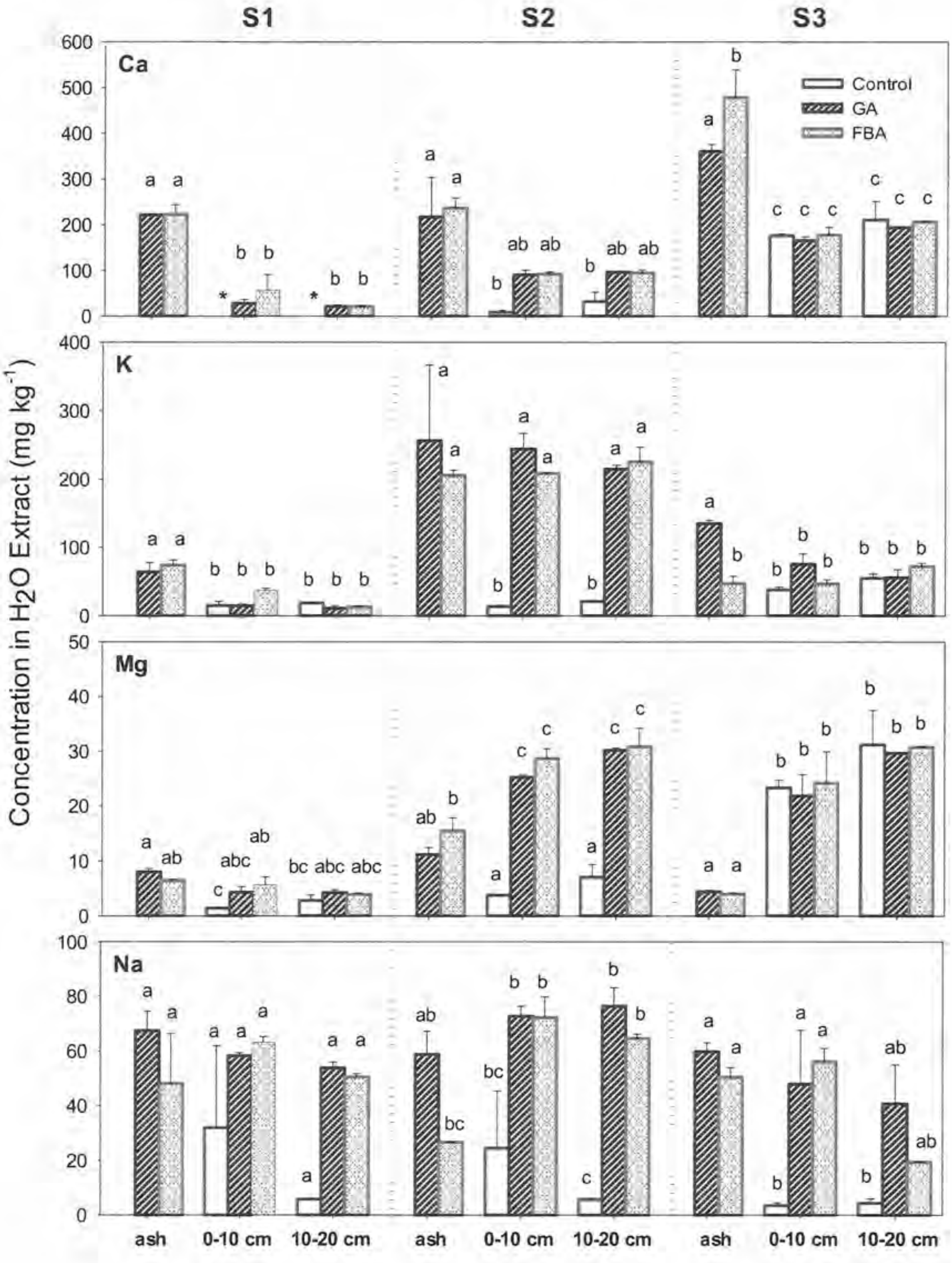
SI-Figure 22 Leaching pattern of V, Zn, Cl- and F- concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the Zn graphs.



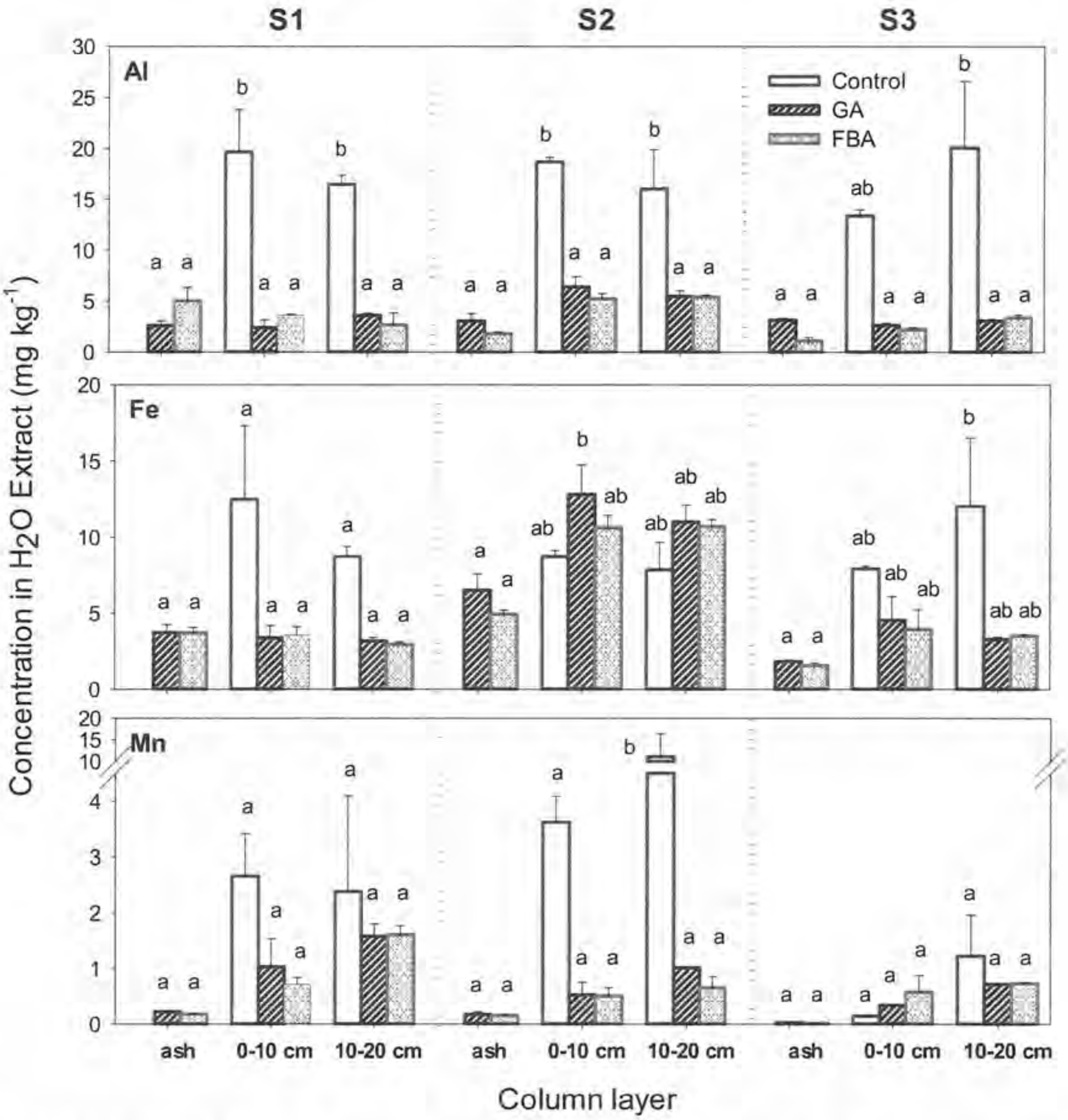
SI-Figure 23 Leaching pattern of NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations in the column eluates in response to repeated artificial rainwater applications on the three test soils S1, S2 and S3. Data represent means±SE (n=2). Letters a, b, c represent statistical differences of the cumulative load after the final rainwater application step. Note the different scales of the NO_3^- and PO_4^{3-} graphs. * Values below LOQ (SI-Tabel 1).



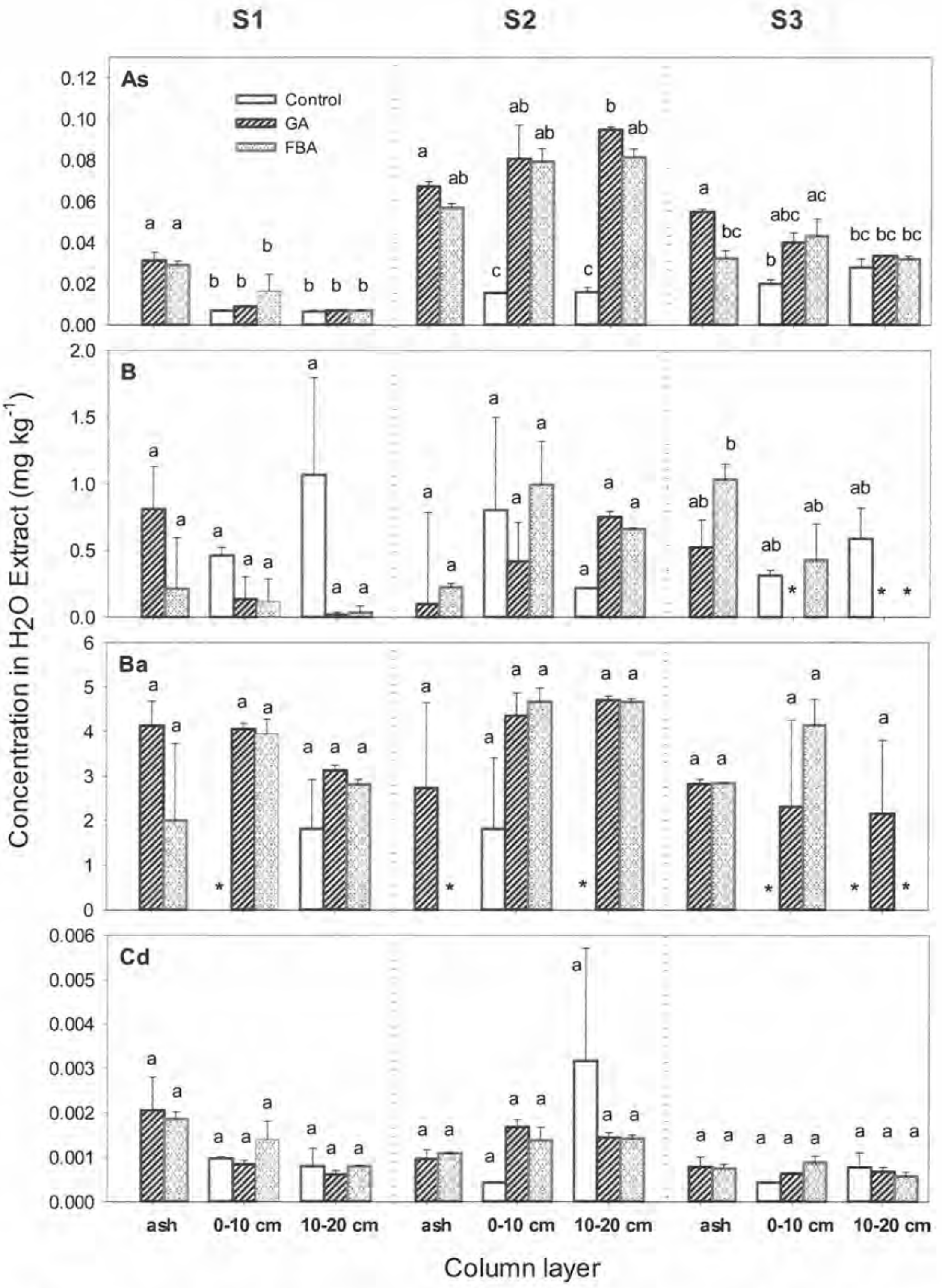
SI-Figure 24 The pH, EC and DOC concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.



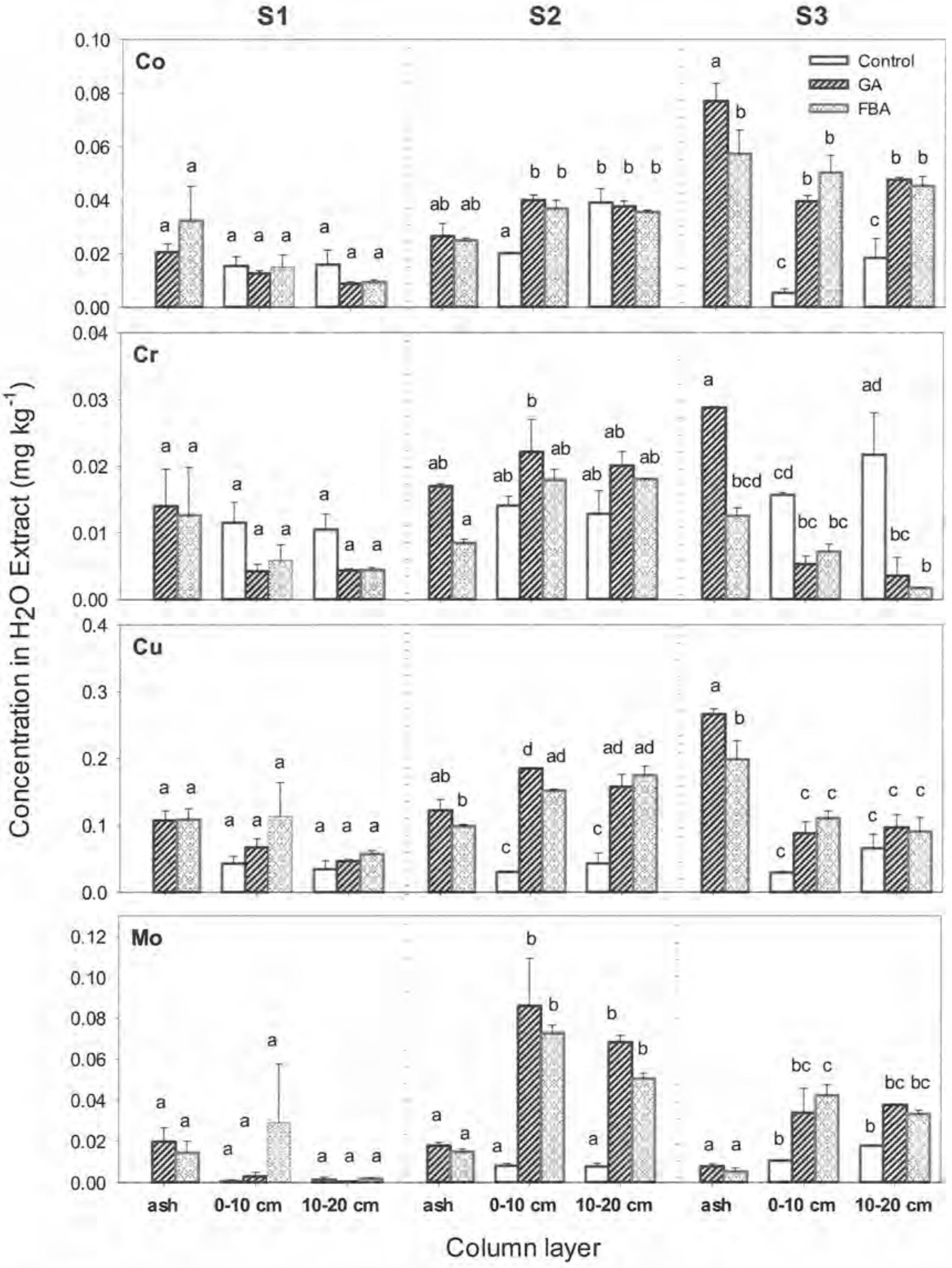
SI-Figure 25 Calcium, K, Mg and Na concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type. * Values below LOQ (SI-Tabel 1).



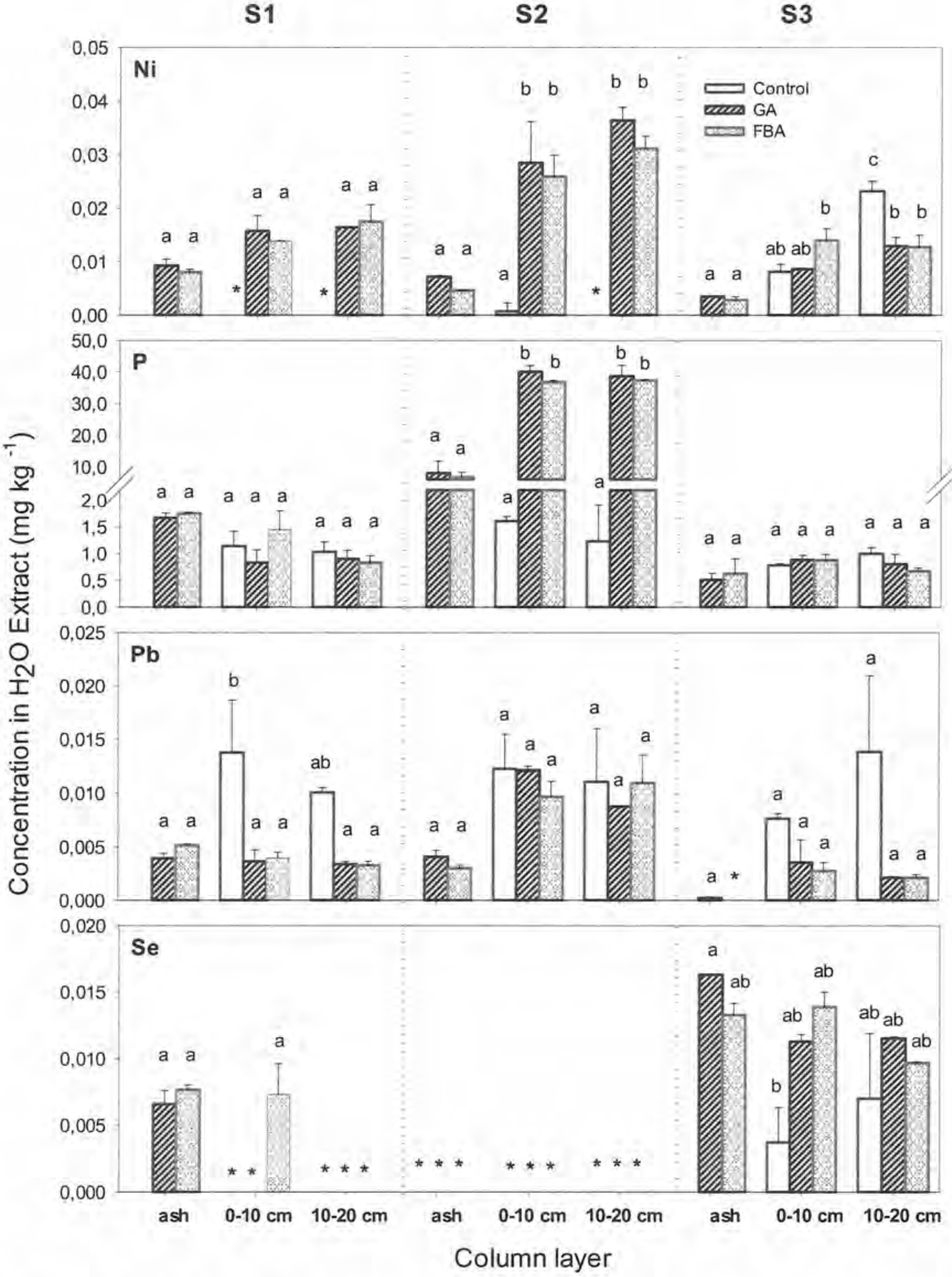
SI-Figure 26 Aluminium, Fe and Mn concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type.



SI-Figure 27 Arsenic, B, Ba and Cd concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type. * Values below LOQ (SI-Tabel 1).



SI-Figure 28 Cobalt, Cr, Cu and Mo concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type. * Values below LOQ (SI-Tabel 1).



SI-Figure 29 Nickel, P, Pb and Se concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type. * Values below LOQ (SI-Tabel 1).

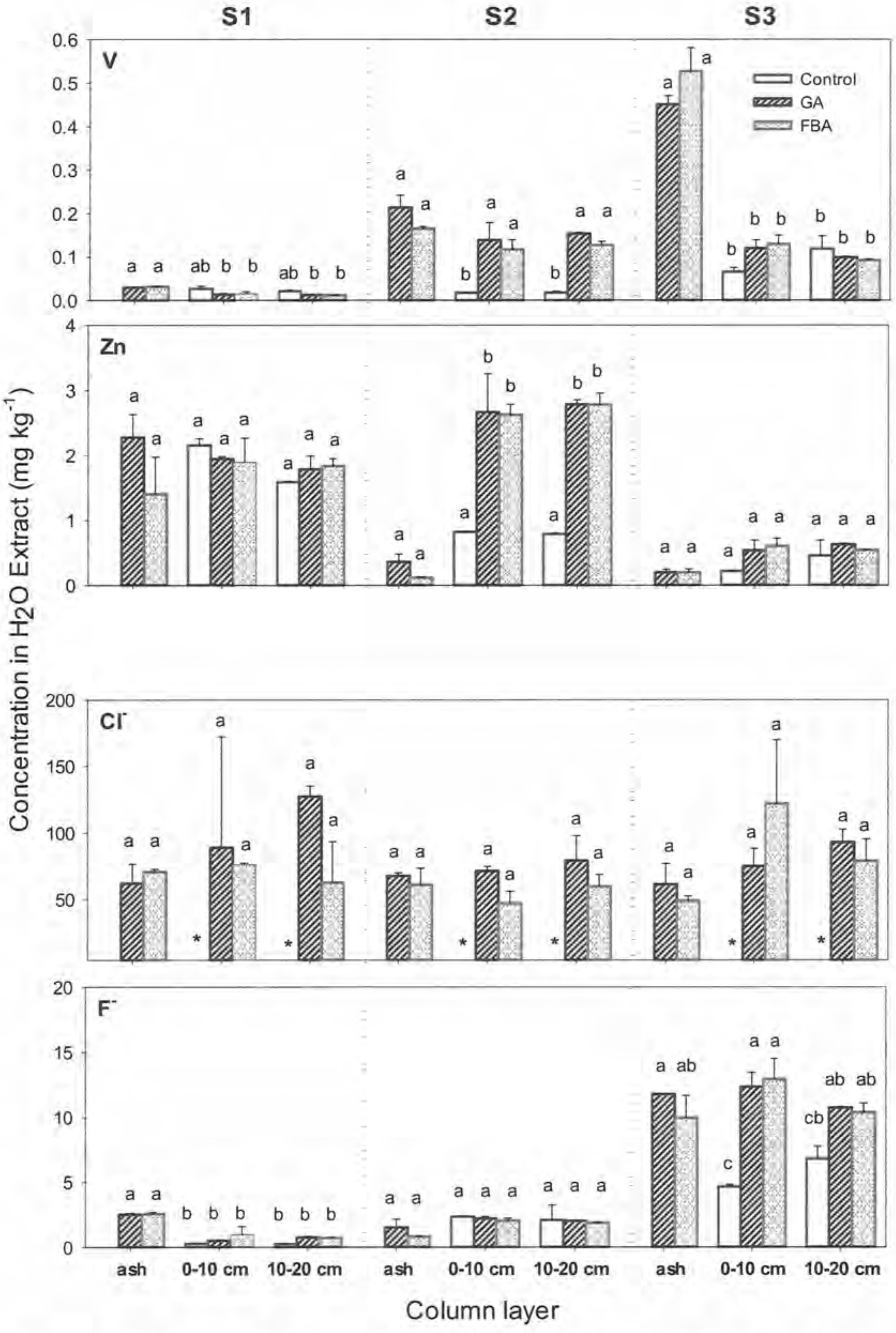
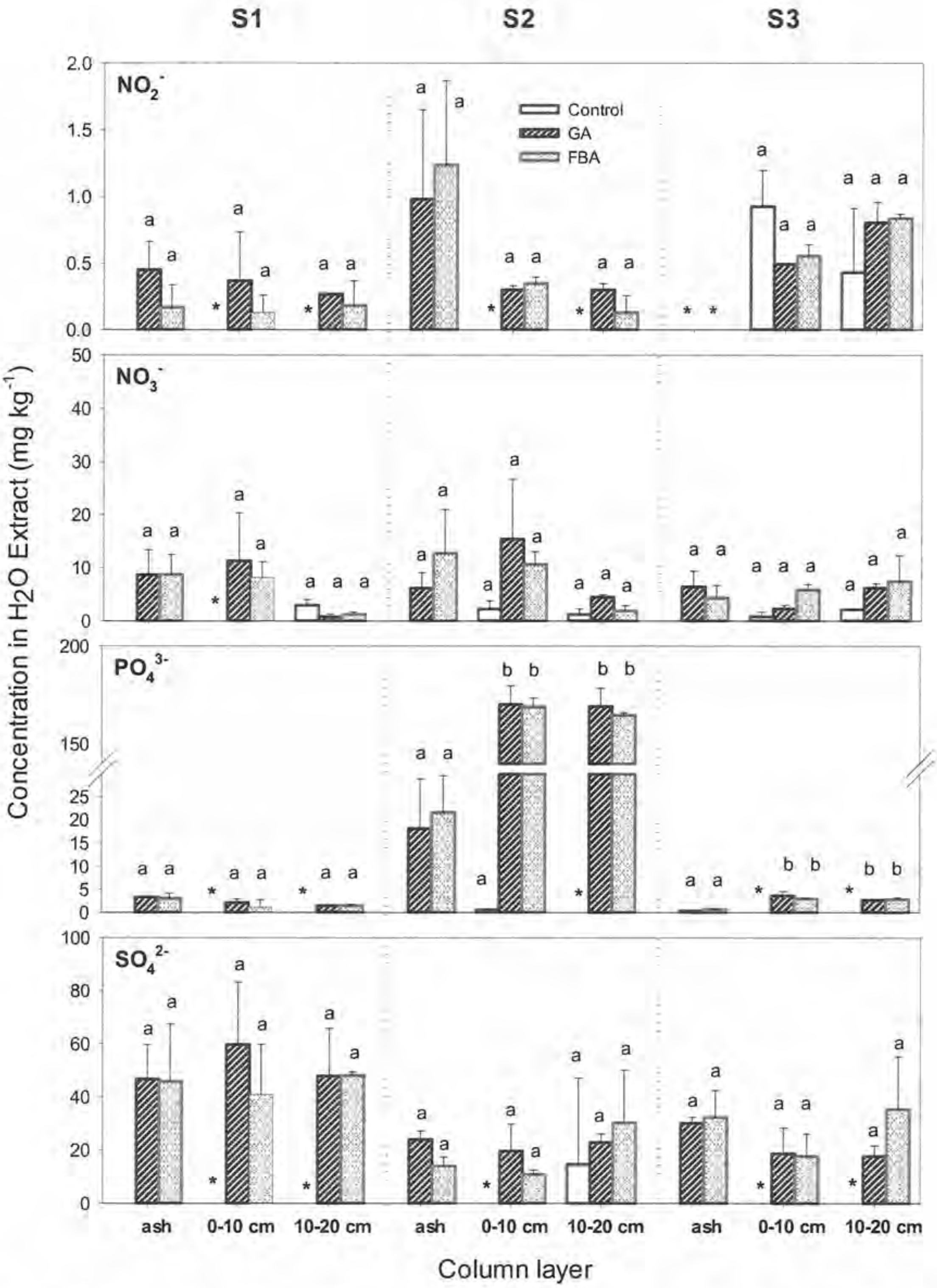
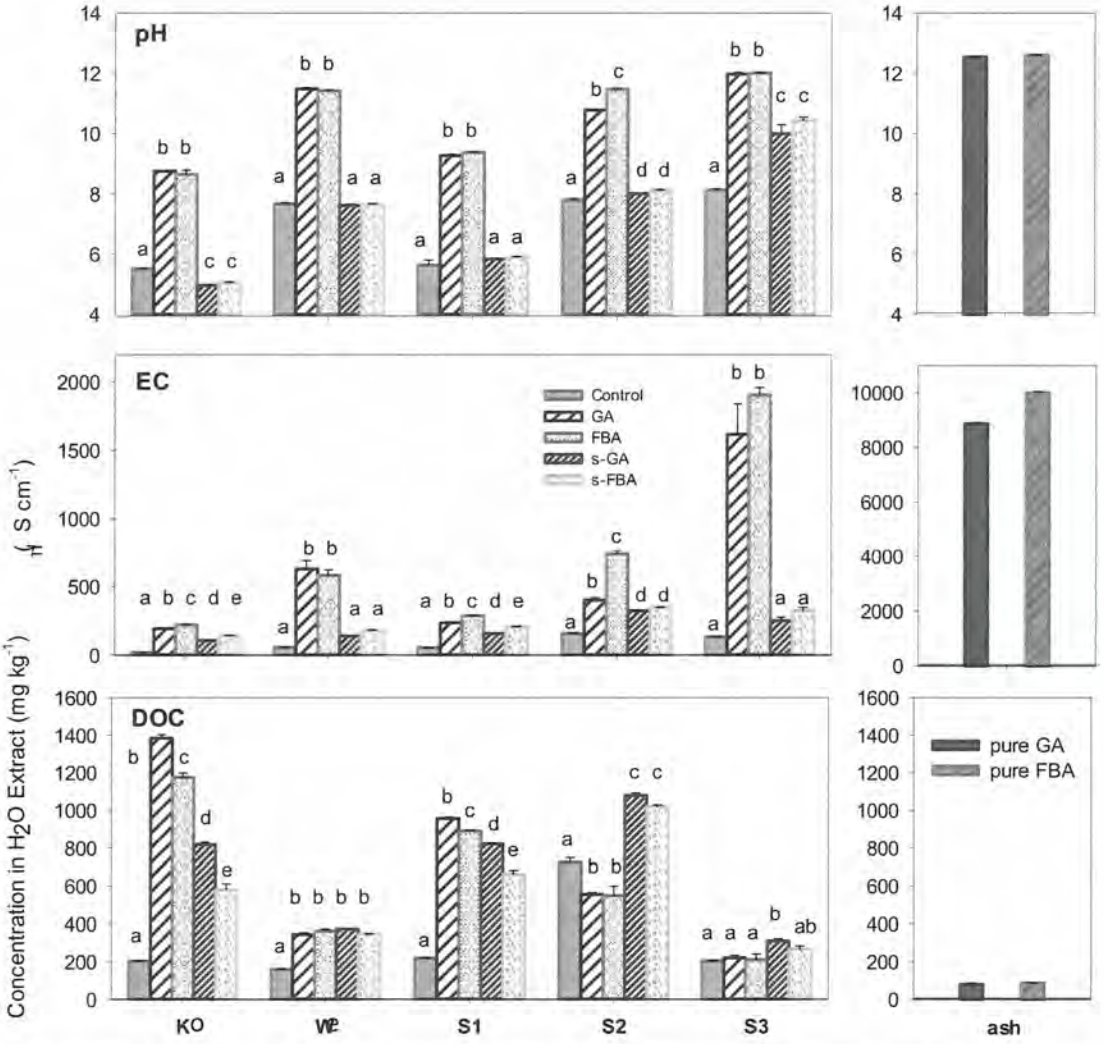


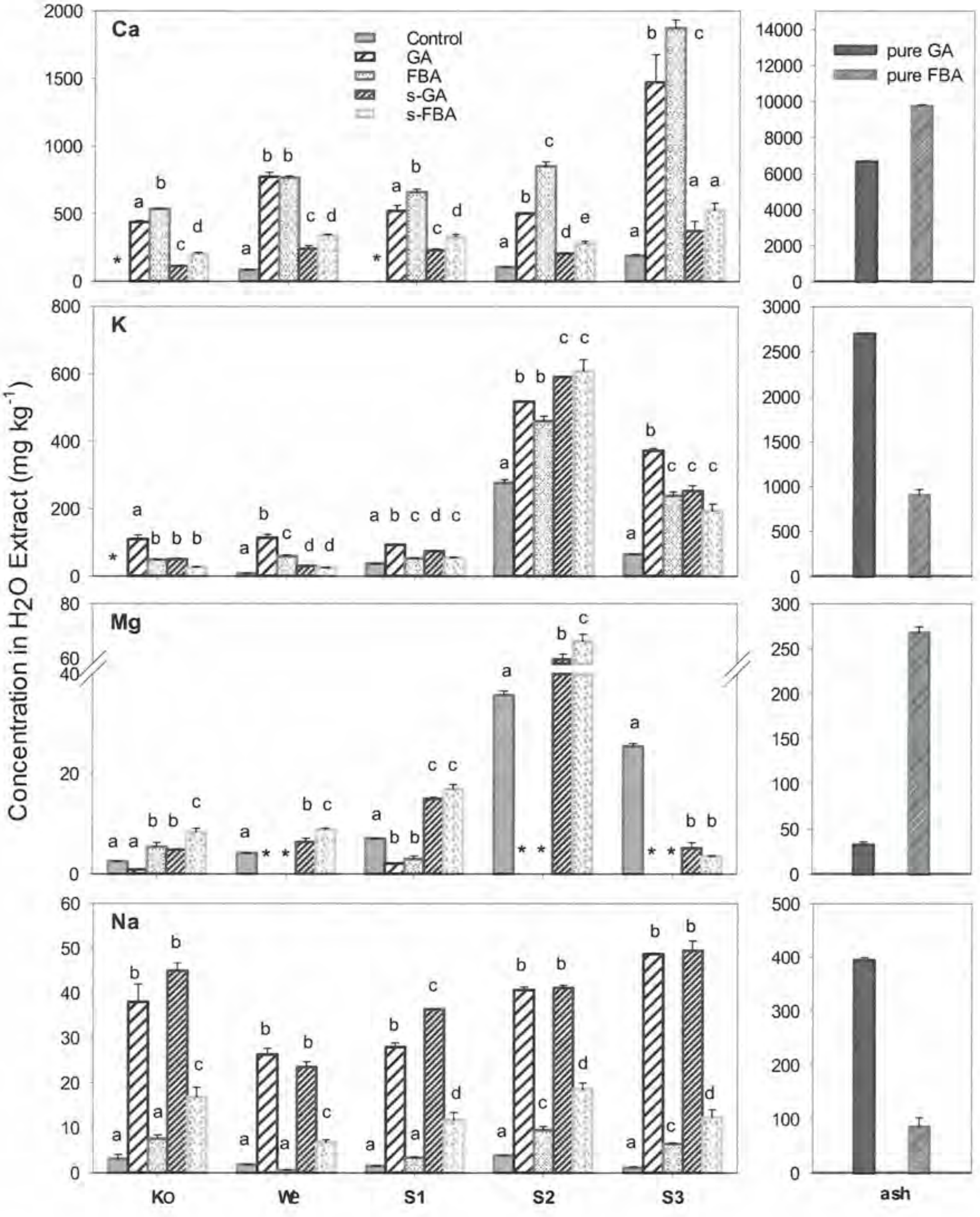
Figure 30 Vanadium, Zn, Cl⁻ and F⁻ concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type. * Values below LOQ (SI-Tabel 1).



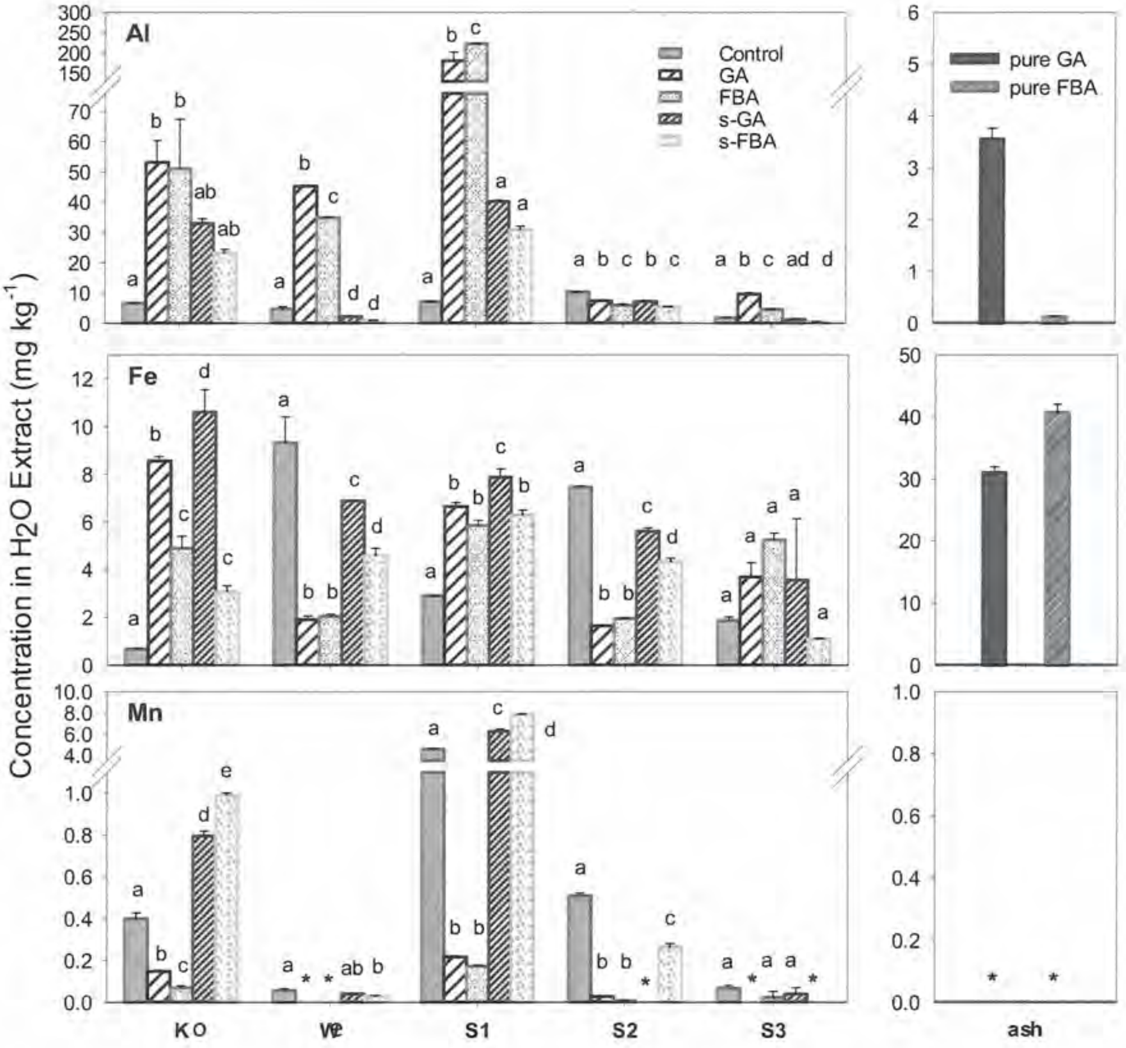
SI-Figure 31 Nitrite, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$ concentrations in water extracts taken after termination of the column experiment in the ash, the upper (0-10) and lower (10-20) soil layer on the three test soils S1, S2 and S3. The error bars represent the standard error of the mean. The statistical analysis compares the treatments and layers within one respective soil type. * Values below LOQ (SI-Tabel 1).



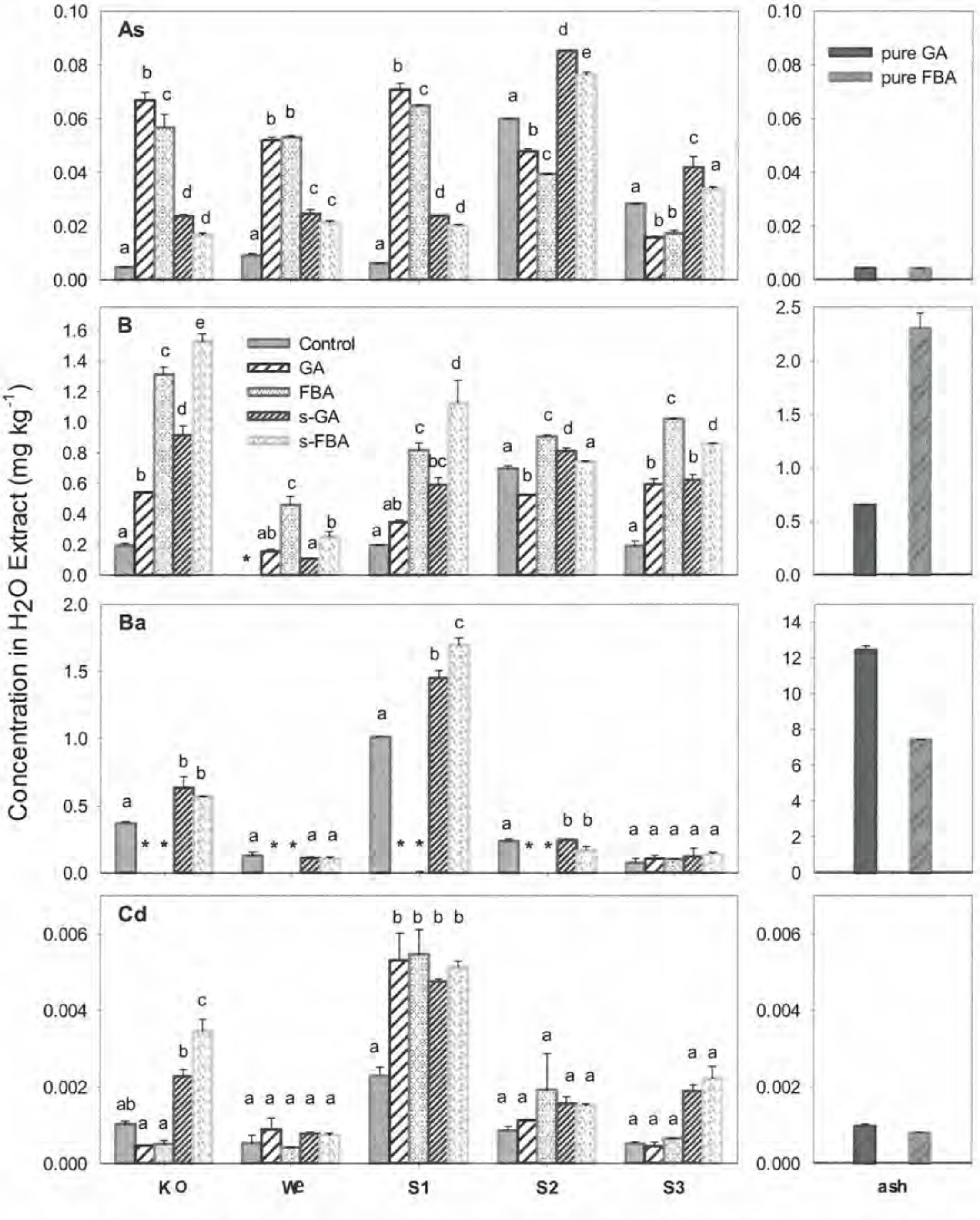
SI-Figure 32 pH, EC and DOC concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales.



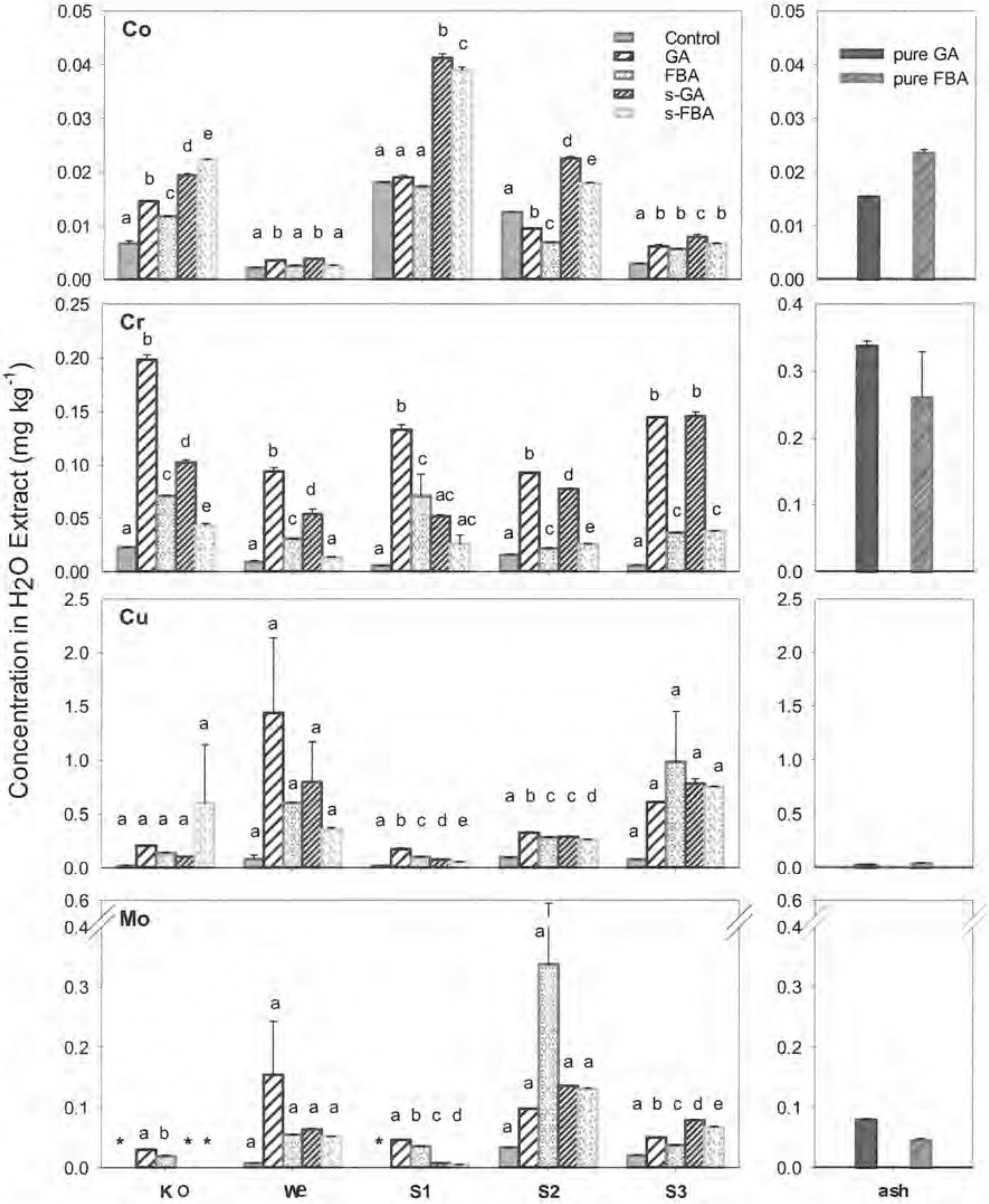
SI-Figure 33 Calcium, K, Mg and Na concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).



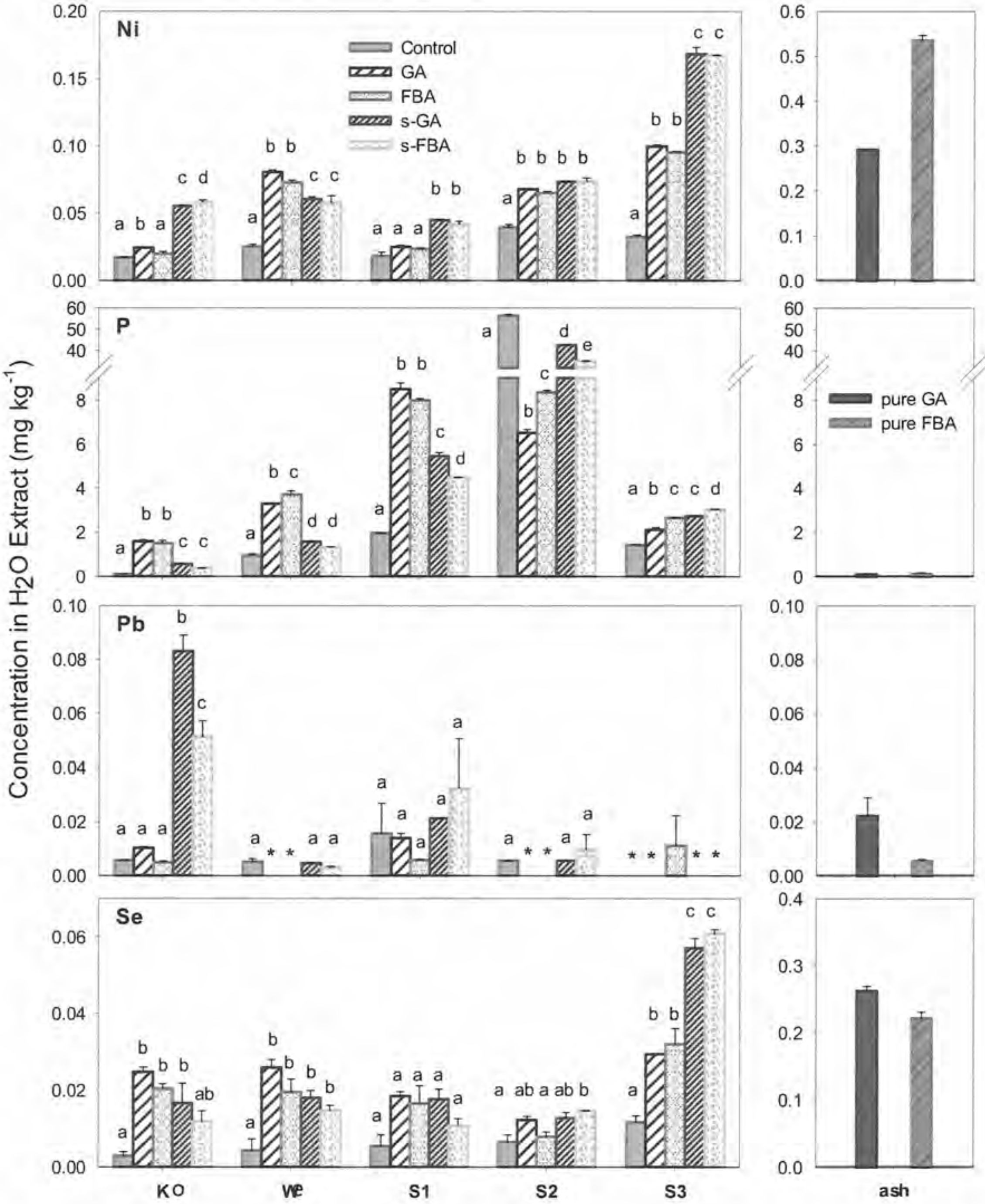
SI-Figure 34 Aluminium, Fe and Mn concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).



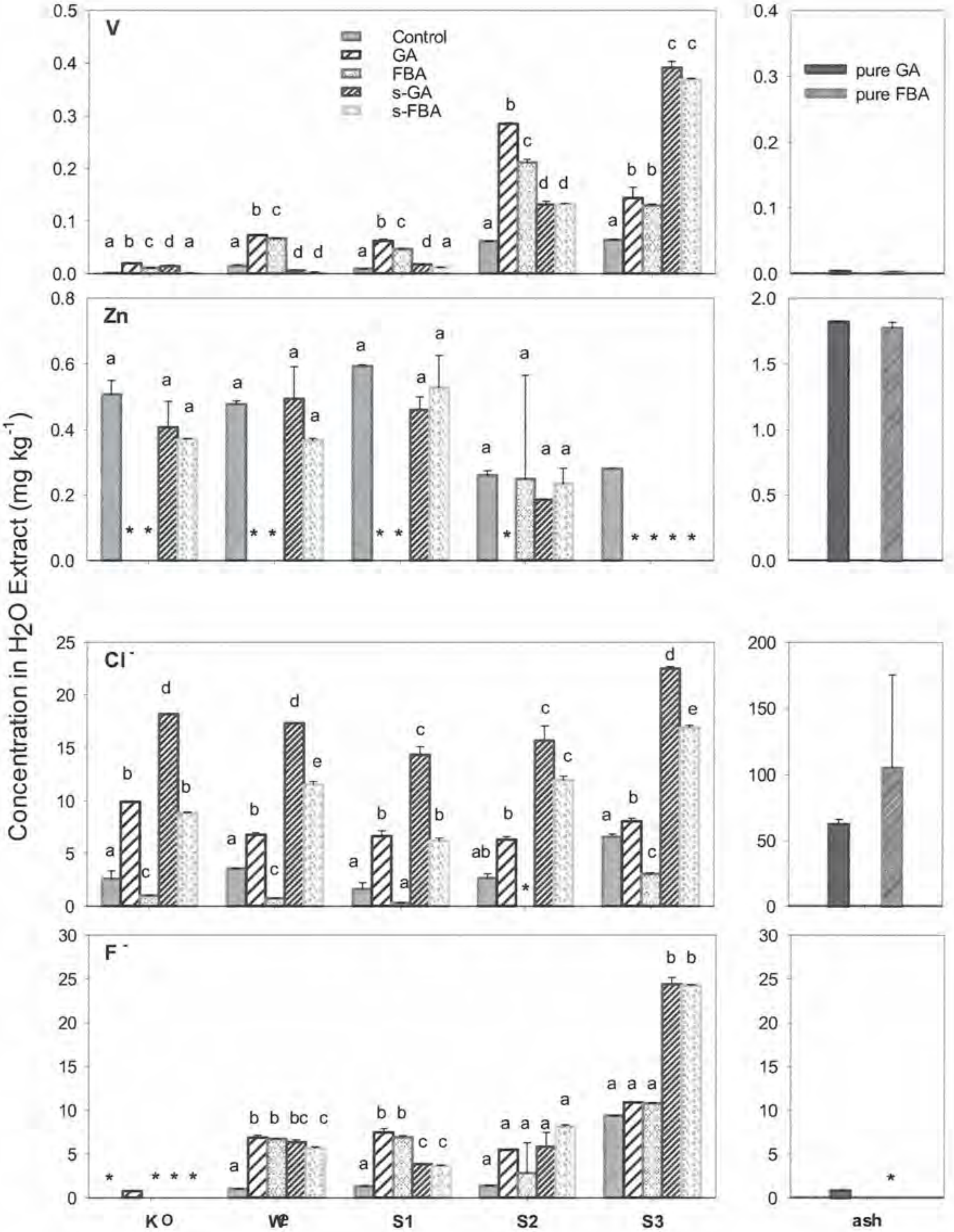
SI-Figure 35 Arsenic, B, Ba and Cd concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).



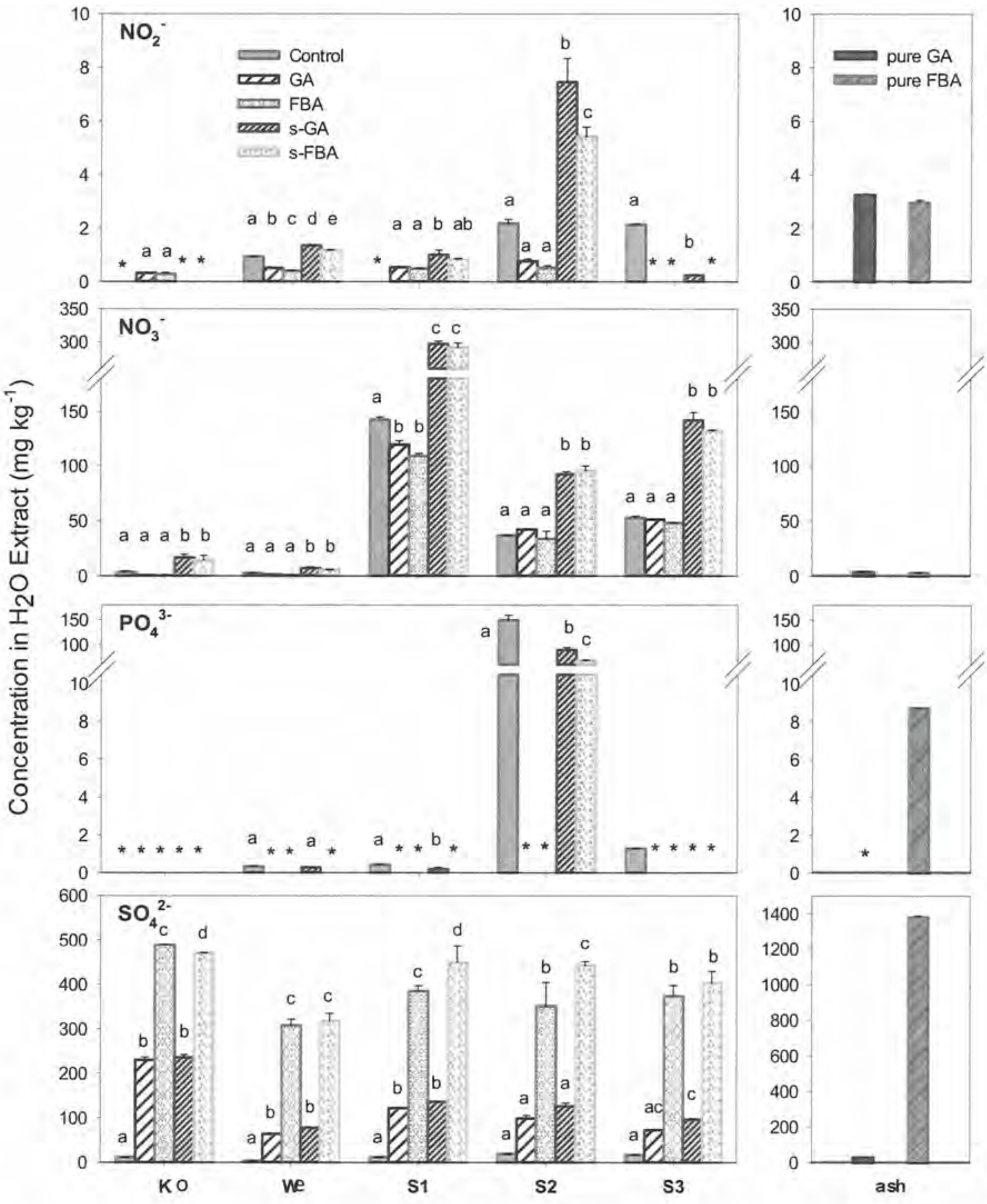
SI-Figure 36 Cobalt, Cr, Cu and Mo concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).



SI-Figure 37 Nickel, P, Pb and Se concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).



SI-Figure 38 Vanadium, Zn, Cl⁻ and F⁻ concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).



SI-Figure 39 Nitrite, NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations in the water extracts of the pure soil (Control) and the ash-soil (GA, FBA), as well as the readsorption experiment (s-GA, s-FBA). In the graph on the right site the concentrations in the water extracts of the pure ashes are shown. The error bars represent the standard error of the mean. The statistical analysis compares pure soil, ash-soil mixtures and readsorption test of one respective soil. Note the different scales. * Values below LOQ (SI-Table 1).

Table 1 LOQ concentrations for the field experiment leachates, the column eluates and the water extracts. The values for all elements, excluding the anions analysed by IC, were obtained by averaging the LOQs of 11 ICP-MS measurements.

	Field experiment[1] and column leachates [µg L^{-1}]	Water extracts [mg kg^{-1}]
Ca	4190	41.9
K	505	5.05
Mg	199	1.99
Na	623	6.23
Al	3.12	0.0312
Fe	15.7	0.157
Mn	0.16	0.0016
As	0.14	0.0014
B	3.64	0.0364
Ba	0.13	0.0013
Cd	0.016	0.0002
Co	0.007	0.0001
Cr	0.38	0.0038
Cu	0.20	0.0020
Mo	0.18	0.0018
Ni	0.39	0.0039
P	17.7	0.177
Pb	0.04	0.0004
Se	0.66	0.0066
V	0.19	0.0019
Zn	0.88	0.0088
Cl^-	20	0.2
F^-	20	0.2
NO_2^-	20	0.2
NO_3^-	20	0.2
PO_4^{-3}	20	0.2
SO_4^{-2}	20	0.2

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[1] As shown in Table 7, the concentrations of the field experiment leachates were obtained by averaging the concentrations of the respective sampling period. In case some of the values were <LOQ, the ½ LOQ was used for calculation and for statistical analysis. Only when all values were <LOQ, the average was indicated as <LOQ as well. This is the reason, why some average values are shown, even though the final values were <LOQ.

SI-Table 2 Overview on occurence of signifcant differences in all experiments for the five soils.

	Ko						We						S1						S2						S3					
	Leachates		Sub-road		2-step		Leachates		Sub-road		2-step		Eluates		C-extracts		2-step		Eluates		C-extracts		2-step		Eluates		C-extracts		2-step	
	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA	GA	FBA
pH	nd	nd	-	+	+	+	nd	nd	+	+	+	+	+	nd	+	+	+	+	+	+	+	+	+	+	-	-	nd	nd	+	+
EC	nd	nd	+	+	+	+	nd	nd	+	+	+	+	nd	nd	nd	nd	+	+	+	+	nd	+	+	+	nd	nd	nd	nd	+	+
DOC	nd	nd	-	+	+	+	nd	nd	+	+	+	+	nd	nd	nd	nd	+	+	+	+	+	+	-	-	nd	nd	+	+	nd	nd
Ca	nd	nd	nd	nd	+	+	nd	nd	+	+	+	+	nd	nd	+	+	+	+	+	+	nd	nd	+	+	nd	nd	nd	nd	+	+
K	nd	nd	nd	+	+	+	+	nd	+	+	+	+	nd	nd	nd	nd	+	+	+	+	+	+	+	+	nd	nd	nd	nd	+	+
Mg	nd	nd	nd	nd	+	+	nd	nd	+	+	-	-	nd	nd	nd	+	-	-	+	+	+	+	-	-	nd	nd	nd	nd	-	-
Na	nd	nd	nd	nd	+	nd	nd	nd	nd	nd	+	nd	-	-	nd	nd	+	nd	-	-	+	+	+	+	-	-	+	+	+	+
Al	nd	nd	nd	nd	+	+	+	nd	+	nd	+	+	+	+	-	-	+	+	nd	nd	-	-	-	-	+	+	-	-	+	+
As	nd	nd	nd	+	+	+	+	nd	nd	nd	+	+	+	+	nd	nd	+	+	+	+	+	+	-	-	+	+	nd	+	-	-
B	nd	nd	nd	nd	+	+	+	nd	nd	nd	+	+	-	-	nd	nd	nd	+	nd	nd	nd	nd	-	+	-	-	-	-	+	+
Ba	nd	nd	-	+	-	-	nd	nd	+	+	-	-	nd	+	+	+	-	-	+	+	+	+	-	-	nd	nd	+	+	nd	nd
Cd	-	-	nd	nd	nd	nd	nd	nd	+	+	nd	nd	+	+	nd	nd	+	+	+	+	nd	nd	nd	nd	+	+	nd	nd	nd	nd
Co	nd	nd	nd	nd	+	+	+	nd	nd	nd	+	nd	+	+	nd	nd	nd	nd	-	-	+	+	-	-	+	+	+	+	+	+
Cr	nd	nd	nd	+	+	+	+	nd	+	nd	+	+	+	+	nd	nd	+	+	+	+	nd	nd	+	+	+	nd	-	-	+	+
Cu	-	-	nd	-	nd	nd	+	nd	+	+	nd	nd	+	+	nd	nd	+	+	+	+	+	+	+	+	+	+	nd	nd	nd	nd
Fe	+	nd	nd	nd	+	+	-	-	nd	nd	-	-	+	+	nd	nd	+	+	+	+	nd	nd	-	-	nd	+	nd	nd	nd	nd
Mn	nd	nd	nd	nd	-	-	nd	nd	nd	nd	-	-	nd	nd	nd	nd	-	-	-	-	-	-	-	-	+	+	nd	nd	-	nd
Mo	nd	nd	nd	+	+	+	+	+	nd	nd	nd	nd	nd	nd	nd	nd	+	+	+	+	+	+	nd	nd	nd	nd	nd	+	+	+
Ni	+	nd	nd	nd	+	nd	+	nd	+	+	+	+	+	+	+	+	nd	nd	nd	nd	+	+	+	+	+	+	-	-	+	+
P	-	-	nd	+	+	+	nd	nd	+	+	+	+	+	+	nd	nd	+	+	+	+	+	+	-	-	+	+	nd	nd	+	+
Pb	nd	nd	nd	nd	nd	nd	nd	nd	+	nd	-	-	+	+	-	-	nd	nd	+	+	nd	nd	-	-	+	+	nd	nd	nd	+
Se	nd	nd	nd	nd	+	+	+	nd	nd	nd	+	+	-	-	+	+	nd	nd	-	-	+	+	nd	nd	+	+	nd	nd	+	+
V	+	nd	nd	nd	+	+	+	nd	+	nd	+	+	+	+	nd	nd	+	+	+	+	+	+	+	+	nd	-	nd	nd	+	+
Zn	+	+	nd	nd	-	-	nd	nd	+	+	-	-	+	+	nd	nd	-	-	+	+	+	+	-	nd	-	-	nd	nd	-	-
Cl^-	nd	nd	nd	nd	+	-	nd	nd	nd	nd	+	-	+	+	+	+	+	nd	+	nd	+	+	nd	-	+	+	+	+	+	-
F^-	nd	nd	nd	-	+	nd	+	nd	+	+	+	+	+	+	nd	nd	+	+	-	-	nd	nd	nd	nd	+	+	+	+	nd	nd
NO_2^-	nd	nd	nd	nd	+	+	nd	nd	-	+	-	-	nd	nd	+	+	+	+	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	-	-
NO_3^-	nd	nd	+	nd	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd	-	-	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PO_4^{3-}	nd	nd	nd	+	nd	nd	nd	nd	+	+	-	-	nd	nd	+	+	-	-	+	+	+	+	-	-	nd	nd	+	+	-	-
SO_4^{2-}	nd	nd	nd	nd	+	+	+	+	-	-	+	+	nd	nd	+	+	+	+	nd	+	+	+	nd	+	nd	+	+	+	nd	+