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University of Natural Resources and Life Sciences, Vienna

ENVIRONMENTAL ASSESSMENT OF WOOD ASH USE IN FOREST ROAD CONSTRUCTION

Master thesis to obtain the academic degree of an environmental engineer

submitted by
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Abstract

The growing generation of ash from wood and woody biomass requires alternative recycling applications to the common practice of landfill disposal. The aim of this master thesis was to assess the environmental risks on groundwater, surface water and soil associated with the use of wood ash in forest road construction. In a full-scale field experiment we tested runoff water, leachate water and the soil layer underneath the experimental forest road sections, with and without wood ash incorporated into the road base layer, for elevated element concentrations. Additionally, a wood ash leaching experiment, to reveal the main characteristical differences in the leachate composition of the grate ash and fluidized-bed ash, and a soil column experiment, to investigate the behavior (filtration, buffering, dilution and mobilization processes) of different soils when exposed to the application of leachate from pure ash, were conducted in the laboratory. The wood ash leaching experiment and the full-scale field experiment revealed the general decrease of ash impact over time, however, some potentially critical characteristics (pH, EC, DOC, AI, As, B, Fe, Mn, Ni, NO_2) have been identified in the leachates of the full-scale field experiment. The soil column experiment proofed alkaline soils with a high content of fine soil particles to be most effective in the reduction of the ash impacts. Given the small proportion of forest roads that would be constructed using wood ash, the single application during the lifetime of the road and the seepage section through underlaying soil layers the utilization of wood ash in forest road construction can be evaluated as ecologically safe if appropriate ash and soil requirements are met.

Zusammenfassung

Die vermehrte Nutzung von Holz und hölzerner Biomasse als Energieträger und der daraus resultierende erhöhte Holzascheanfall erfordert alternative Nutzungsmöglichkeiten zur herkömmlichen Ablagerung in Abfalldeponien. Das Ziel dieser Arbeit war die Abschätzung möglicher Umweltrisiken bezüglich Grundwasser, Oberflächenwasser und Böden im Zusammenhang mit der Nutzung von Holzasche im Forstwegebau. In einem Feldversuch wurde eine mit Holzasche angelegte Forststraße auf erhöhte Schadstoffkonzentrationen im Sickerwasser. Oberflächenwasser und Boden analysiert, Zusätzlich wurden im Labor ein Sickerwasserversuch mit reiner Holzasche sowie ein Bodensäulenversuch durchgeführt. Charakteristische Unterschiede im Auslaugungsverhalten von Rostaschen und Wirbelschichtaschen wurden im Sickerwasserversuch gezeigt. Im Zuae des Bodensäulenversuchs wurden die Sickerwässer der Holzaschen auf unterschiedliche Böden aufgebracht um deren Einfluss (Filter-, Puffer-, Verdünnung- und Mobilisierungseffekte) auf die Elementkonzentrationen zu untersuchen. Der Feldversuch sowie der Sickerwasserversuch mit reiner Holzasche zeigte eine generelle Abnahme des Ascheeinflusses über die Zeit. Im Sickerwasser des Feldversuchs konnten potentiell kritische pH und EC Werte sowie Al, As, B, Fe, Mn, Ni, NO₂⁻ Konzentrationen nachgewiesen werden. Im Bodensäulenversuch zeigte der basische Boden mit hohem Anteil an feinen Bodenpartikeln den geringsten Ascheeinfluss. In Anbetracht des einmaligen Holzascheeintrags während der Lebensdauer einer Forststraße und der puffernden Wirkung der Sickerwasserstrecke unterhalb der Straße kann die Nutzung von Holzasche im Forstwegebau als ökologisch sicher bewertet werden. Auf eine geeignete Asche-Boden Kombination, hinsichtlich potentiell kritischer Charakteristika, ist jedoch unbedingt zu achten.

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List of abbreviations

AAEV	Austrian General Wastewater Directive
AEVD	Austrian Wastewater Directive on landfill leachates
CCE	Calcium carbonate equivalent
CEC	Cation exchange capacity
DOC	Dissolved organic carbon
DW	Austrian Drinking Water Regulation
EC	Electrical conductivity
FBA	Fluidized-bed ash used in the laboratory experiments
FBA-W	Fluidized-bed ash used in the full-scale field experiment
	(Weyregg forest road)
GW	Quality Target Ordinance – Groundwater
GA	Grate ash used in the laboratory experiments
GA-W	Grate ash used in the full-scale field experiment (Weyregg
	forest road)
IC	lon chromatography
ICP-MS	Inductive coupled plasma mass spectrometry
ICP-OES	Inductive coupled plasma optical emission spectrometry
LOI	loss-on-ignition method
n	Sample size/number of replicates
ÖNORM	Austrian norms
PE	Polyethylen
S1	First experimental soil (Acidic cambisol)
S2	Second experimental soil (Neutral cambisol)
S3	Third experimental soil (Alkaline chernozem)
SD	Standard deviation
SE	Standard error of the mean
SOM	Soil organic matter
W	Weyregg forest soil

1. Introduction

Growing global demand for renewable energy has led to an increased production of ash from biomass incineration. Biomass combusted in power plants include residues from forests and agriculture.

According to Siddique (2012) wood ash is the solid residue generated from the combustion of wood and wood products (chips, saw dust, bark, etc.).

The global production of forest residues with potential energy application are estimated to about 3 billion tonnes per year (Heinimö & Junginger, 2009). Wood and wood products have a lower ash yield than other types of biomasses. The mean ash yield for woody biomass can be estimated to be 3.5 %, while pointing out the big differences between wood and bark. Spruce has a relatively low ash yield with 0.5 % and 3.2 % for wood and bark, respectively (Vassilev, et al., 2010; Table 5). Hence, the global potential for wood ash production can be estimated to be around 105 Mt/yr.

The potential use as soil amendment, construction material and sorbents underline the recycling incentives of wood ash (Vassilev, et al., 2013b). A large proportion of the generated wood ash is currently landfilled at growing costs, caused by changed landfill regulations and scarcity of appropriate sites (Demeyer, et al., 2001; Kuba, et al., 2008). The pozzolanic self-hardening properties comparable to cement (Steenari & Lindqvist, 1997), the positive liming effect and the input of nutrients to forests from wood ash application (Vassilev, et al., 2013b) show the big potential of wood ash use in forest road construction. However, beside changes in the biogeochemistry of soils, leaching and runoff of various potentially harmful substances contained in wood ash may pose environmental risks associated with its application in vulnerable ecosystems, like forests.

In 2010, 128000 tonnes of straw- and wood ash were produced as a by-product of thermal utilization in Austria. 38 % (49000 t) of this volume were landfilled at high disposal costs (Umweltbundesamt, 2012). Bohrn & Stampfer (2014) report average disposal costs of 100 €/t in Austrian landfills. The big potential for the energetic use of wood and woody biomass in the densely-wooded parts of Austria and the ambitious goal to increase the share of renewable energy up to 34 % in 2020 (EEA, 2013) highlights the importance of sustainable ash reuse. The local incineration and the return of the wood ash back into a nearby forest would imply short transportation distances and the need of only small storage volumes.

Beside the monetary interests of avoiding disposal costs, the sustainable and environmental unproblematic reuse of wood ash by closing biogeochemical nutrient cycles is of special importance.

1.1 Properties of wood ash

Wood ash is a complex mixture of inorganic and organic phases from different origins. The chemical composition of wood ash depends highly on the composition of the burnt fuel (influenced by tree species, part of the tree, soil type and climate), combustion techniques and temperatures and is likely to change during the aging processes (transport and storage), when being in contact with air and/or water (Vassilev, et al., 2013a).

The two main combustion systems used in biomass power plants are grate firings and fluidized bed combustion systems. Generally, fluidized bed combustion systems operate at a slightly lower temperature and result in lower CO_2 and NO_x emissions than grate firings (Obernberger, 1997).

The three most important properties of wood ash for application in roading are the high pH value, pozzolanic properties and the positive input of nutrients into forests. However, wood ash also contains potentially toxic substances demonstrating the need for environmental assessment of the possible impacts.

High pH value (Liming properties)

The high pH value of wood ash (9-13.5) depends on the concentrations of oxides, hydroxides and carbonates of Ca, K and Mg (Etiégni & Campbell, 1991) and can be explained by high Ca and generally low S and Cl concentrations in comparison to other biomass ash or coal ash (Vassilev, et al., 2013a).

The acid-neutralizing power (liming effect), expressed by the calcium carbonate equivalent (CCE) varies between 13.2 % and 92.4 % with a median value of 48.1 % (Vance, 1996). Wood ash can increase soil pH faster, but only for a shorter time, than pure limestone. K_2CO_3 and MgCO₃ are more soluble than CaCO₃ and can therefore contribute to a high soil pH only for a limited time (Demeyer, et al., 2001).

The rise of soil pH after ash application is caused by the neutralization of H^+ cations during the reaction of oxides, hydroxides and carbonates of Ca, K and Mg (McLaren & Cameron, 1990, pp. 175-176).

CaO is the most abundant constituent, concentrations of about 430 g kg⁻¹ are reported in the literature (Obernberger, et al., 1997; Vassilev, et al., 2013a).

Pozzolanic properties

Due to the high contents of CaO and to a lower extent K_2O and MgO wood ash can be used as a substitute for burnt lime as a binding material for soil stabilisation, demonstrating the recycling potential as a construction material for forest roads. The contents of oxides of Ca, K and Mg increase with increasing combustion temperatures (Pitman, 2006). The hydration of CaO to Ca(OH)₂ and the subsequent formation of calcium-carbonate is the main reaction of the hardening process. The resulting hydrophilic properties of wood ash arise from the hydration of oxides and additional capillary absorption processes (Steenari & Lindqvist, 1997).

To ensure effective transformation processes, essential for the mechanical properties of the forest road, low organic carbon levels in the ash are of major importance (Steenari, et al., 1999a). Carbon concentrations > 20 % are reported to inhibit the self-hardening processes (Etiégni & Campbell, 1991). Additional chemical reactions of the hardening process include the formation of gypsum, ettringite and hydrated silicate and aluminium-silicate phases (Steenari & Lindqvist, 1997).

Fertilizer properties

The input wood ash into managed forests can be evaluated as a sustainable practice to bring withdrawn plant nutrients back into the natural system and enables partly closures of nutrient cycles.

Wood ash contains major (O, H, Ca, K), minor (S, Mg, P, Cl, Na) plant nutrients and essential trace elements (B, Cu, Zn), making it a potential fertilizer (Vassilev, et al., 2013b). Carbon and N are only present in marginal concentrations, since they are fully oxidized in a complete combustion process (Demeyer, et al., 2001). Improved plant growth can be mainly attributed to increased plant availability of K, P, Mg and Ca and improved N supply (organic soils) due to intensified nitrification processes (Nkana, et al., 1998). In the long term intensified nitrification and plant uptake may lead to decreased total N concentrations in the soil resulting in additional N-fertilization demand (Kahl, et al., 1996). In comparison to ash from softwood, hardwood ash is higher in K and P, but lower in Ca and Si contents (Pitman, 2006).

The fertilizer properties of wood ash can be described with the N:P:K formula of 0:1:3 (Górecka, et al., 2006). Positive impact on biomass production after wood ash application was confirmed in the reviewed literature (Arshad, et al., 2012; Augusto, et al., 2008; Nkana, et al., 1998; Pitman, 2006).

Contaminants in wood ash

Potential hazardous elements contained in wood ash are Ag, As, B, Ba, Cd, Cl, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Se, Sn, U, V and Zn (Vassilev, et al., 2013b) and toxic organic compounds (Someshwar, 1996). Their concentrations depend on the burnt fuel, combustion process and ash fraction. The four ash fractions produced in the combustion process are bottom ash, cyclone fly-ash, filter fly-ash and flue dust. Bottom ash includes coarse mineral impurities contained in the fuel, namely, sand, stones, earth and sintered ash particles, while fly-ash consists of finer particles containing more volatile elements. Due to the enrichment of volatile Cd, Zn and Pb, filter fly-ash should be separately treated from bottom ash and cyclone fly-ash, if these ashes are intended to be recycled and used in forest road construction (or other land application). Based on the high nutrient and low content of toxic elements the mixture of bottom ash and cyclone fly-ash can be regarded suitable for ash recycling. Flue dust is emitted together with the flue gas (Obernberger, et al., 1997).

In general metal concentrations in wood ash increase with combustion temperature, except Zn which showed decreasing trends at high temperatures (Etiégni & Campbell, 1991). Someshwar (1996) concludes that organic pollutants (PAHs, chlorobenzenes, chlorophenols, PCBs) only appear in negligible concentrations and PCDD/Fs are only of concern if Cl-enriched wood is burnt. Ash from the combustion of contaminated wood may be highly enriched in As, Cr, Cu and B (CCA/CCB wood preservatives) (Pohlandt, et al., 1993) and Pb, Ti and Zn (paint, binders, glue) (Siddique, 2012). Such ashes should be excluded from reuse and disposed separately.

Most of the literature stresses the highly variable and heterogeneous character of wood ash and concludes that generalizations about chemical composition and behaviour in the environment must be made with caution.

1.2 Wood ash use in forest road construction

An estimated proportion of 1-5 % of managed forest area is covered by forest roads, dependent on terrain, harvesting techniques and external factors (Enache, et al., 2011; Miller & Sirois, 1986). In forest roads ash has been primary used for the construction of the road base layer with an ash content of about 10-50 %, which was then covered by an additional gravel layer (Lind, et al., 2008). A 0.5m thick road base layer (Hjelmar, et al., 2007), hence results in an ash use in the range of 0.038 to 0.19 tonnes per square meter of road (bulk density of compacted wood ash equals 760 kg m⁻³) (Abdullahi, 2006).

Consequently, the input of wood ash into forests can roughly be estimated to be in the range of 3.8 to 95 t ha⁻¹. In the lower range this amount is comparable to land application rates for fertilization (Augusto, et al., 2008; Kahl, et al., 1996; Pitman, 2006). However, the concentrated input of ash is likely to show strong differences in its environmental behaviour compared to equally distributed ash application for fertilization and liming. Moreover, Pitman (2006) concluded that potential toxic effects can be expected at application rates greater than 10 t ha⁻¹. The concentrated wood ash input (equal to 0.11 to 0.57 tonnes per meter of forest road (3 m wide)) may cause the exceedance of the soil buffer capacity and thus result in adverse environmental effects beneath and in the immediate surroundings of the road.

1.3 Legal situation of wood ash recycling in Austria

The only legal framework directly covering ash recycling in Austria is the Austrian compost ordinance, which allows the use of biomass ash as an additive in the composting industry.

In Austria no legal regulation for the use of biomass ash on agricultural and forest land exists, however, in 2011 a guideline was established by the Austrian Ministry of Agriculture, Forest, Environment and Water (BMLFUW, 2011). The guideline gives qualitative and quantitative limits for ash utilization. Ash recycling in compliance of the guideline does not disagree with Austrian forest law. The incomplete forest and soil preservation laws, with respect to ash recycling and the classification of biomass ash as a waste material present an unsatisfactory legal situation.

This situation results in big uncertainties for the power plant operators and local forest authorities and presents a major barrier for large-scale ash recycling into Austrian forests (Obernberger, & Supancic, 2009).

2. Research Objective

Based on the great potential for ash reuse and the unclear legal situation in Austria, a legal framework for wood ash utilization in forest road construction is required. The present master thesis is part of a project that helps to provide the scientific basis of the technical feasibility and the environmental risks, associated with the use of wood ash in forest road construction.

The technical feasibility was examined at the Institute of Forest Engineering, University of Natural Resources and Life Sciences Vienna. Therefore, a full-scale experimental forest road, constructed with different ashes and different ash mixture ratios, was tested for its load bearing capacity.

The present master thesis was carried out at the Institute of Soil Research, University of Natural Resources and Life Sciences Vienna. In order to evaluate potential environmental risks the full-scale experimental forest road was tested for potentially hazardous substances in the surface runoff, leachate water and soil samples from underneath the soil-ash layer of the road.

Additionally to the full-scale field experiment I conducted a wood ash leaching experiment and a soil column experiment in the laboratory.

The wood ash leaching experiment is deemed to provide information about the leaching potential of fresh wood ash, whereas the purpose of the soil column experiment was to derive information about the response (buffering, filtering and mobilization processes) of different soils when exposed to the application of wood ash leachate.

In the absence of thresholds for potentially toxic elements and other characteristics (e.g. pH, EC) in the leachates from wood-ash-containing road base layers, the results of the experiments were compared to existing drinking water standards (plus additional thresholds) of the Austrian legislation for the assessment of the environmental impacts.

The outcome of the study should provide a scientific basis for the establishment of a legal framework for the ultilization of wood ash in forest road construction and thus facilitate sustainable wood ash recycling in Austria.

3. Material and Methods

If not noted differently, the experiments, sample preparation and sample analysis were conducted in the laboratories of the Institute of Soil Research, University of Natural Resources and Life Sciences Vienna, UFT Campus Tulln. Ion chromatography was carried out in the laboratory of the same institute in Vienna.

3.1 Full-scale Field Experiment (Weyregg Forest Road)

To investigate the possible effects of wood ash used in forest road construction on soil, surface water and groundwater resources (recharge) a full-scale field experiment was installed in May 2010. Two different types of wood ash were incorporated into an existing forest road in two application rates in the course of needed renovation measures. The road is located in a mountainous region at an altitude of about 800-900 m about 5 km east of the village Weyregg, Upper Austria. The area is characterized by calcareous bedrock and receives an annual average rainfall of 1200 mm (Hydrographischer Dienst, 2011).

3.1.1 Soil

The soil from the experimental field site, further referred to as "W", has been characterized as an alkaline silty loam as shown in Table 1.

Dissolved organic carbon (DOC), pH, and electrical conductivity (EC) were measured in H_2O extracts (ÖNORM L 1092; soil-solution ratio 1:10) using the methods and instruments described in Table 7.

Soil organic matter content (SOM) was determined applying the loss-on-ignition (LOI) method, according to ÖNORM L 1079.

We assessed the cation-exchange-capacity (CEC) by barium-chloride (BaCl₂) extraction, according to ÖNORM L 1086-89.

Soil texture was determined by the grain-size distribution, applying sedimentation and wetsieving methods, according to ÖNORM L 1061-2.

Total element concentrations and water-extractable concentrations of Weyregg forest soil are displayed in SI-Table 1.

Soil characteristics	Unit	Soil "W"
pH (H₂O)	-	7.7
EC	µS cm⁻¹	58.0
DOC	mg kg⁻¹	160
SOM	g kg⁻¹	63.3
CEC	mmolc kg⁻¹	314
Sand	g kg⁻¹	172
Silt	g kg⁻¹	625
Clay	g kg⁻¹	203

Table 1: Soil characteristics of Weyregg forest soil "W" used in the full-scale field experiment

3.1.2 Ashes

Two different types of wood ash were used to identify possible differences caused by their varying element composition.

The first ash, termed "GA-W" in this thesis, is a coarse grate ash originating from a grate furnace fueled with wood chips (with attached bark) at a combustion temperature of 850°C to 875°C. The second ash, termed "FBA-W", is a fine bottom ash from a fluidized bed combustion fired with wood chips (with attached bark) at a combustion temperature of 830°C to 850°C.

The ashes were characterized for total element concentrations via HF acid digestion (ÖNORM EN 13657) which was carried out by BIOS Bioenergysysteme, Graz Austria. Water-extractable concentrations (ÖNORM S 2115) were measured at the University of Natural Resources and Life Sciences, Vienna, and analyzed by ICP-MS, before the experiment was set up.

Based on Austrian guideline values the ashes comply with the requirements for the use in agriculture and forestry (BMLFUW, 2011).

The grate ash (GA-W) exceeds the threshold value of water-extractable concentrations of construction wastes (Baurestmassen) for Cr (Deponieverordnung, 2008; Annex 1, Table 6).

Table 2: Total element concentrations and water-extractable concentrations of the two Weyregg ashes

		GA-W		FBA-W	
			Water-		Water-
Characteristics	Unit	Total	extractable	Total	extractable
рН	-	13.5		8.6	
EC	mS cm⁻¹	10.7		0.36	
TOC	mg kg ⁻¹	1000	25	1000	25
Al		21400	0.3	15800	2.2
As		3.63	0.005	1.47	0.004
В		482	9.3	515	2.4
Ва		80	28	63	3.8
Ca		333000	8361	45600	n.a.
Cd		1.18	< 0.001	0.21	0.001
Co		9.27	0.02	1.53	0.001
Cr		114	<mark>3.24</mark>	12.6	0.12
Cu		72.4	0.03	40.5	0.005
Fe	mg kg ⁻¹	15500	40	2620	n.a.
K		31800	3417	43100	n.a.
Mg		44900	n.a.	6550	n.a.
Mn		3780	0.01	1150	n.a.
Мо		1.75	0.09	0.37	n.a.
Na		2590	68.8	3150	n.a.
Ni		32.5	0.48	5.9	< 0.001
Р		5900	0.15	2140	n.a.
Pb		10.18	0.03	15.73	< 0.001
Se		0.4	0.29	< LOQ	n.a.
V		39.9	0.003	7	n.a.
Zn		111	2.60	352	0.09
CI			47		1.8
F			< 2		0.1
NO ₂ -N	mg kg⁻¹		5.56		< 0.4
NO ₃ -N			7.02		1
PO ₄ -P			8.99		< 2
SO ₄			287		920

3.1.3 Experimental Setup

In May 2010 the two ashes GA-W and FBA-W were incorporated into the existing forest road according to the layout presented in Figure 1. The ashes and original soil material were mixed in two different ratios, 15:85 and 30:70 Vol% ash:soil, up to a depth of 50 cm, using a TERRA-MIX[™] road construction milling machine (Figure 2 & 3).The control sectors were installed between the different ash sectors to act as a buffer, thus reduce the potential of interference.



Figure 1: Schematic plan of sampling points with different ash:soil ratios and controls



Figure 2 & 3: TERRA-MIX[™] milling machine

3.1.3.1 Surface Runoff and Leachate Sampling

To investigate the environmental impact of the wood ash incorporated into forest roads, the test road was equipped with lysimeters to collect surface runoff and leachate water.

The surface runoff water was collected in rain barrels, assisted by a construction of a waterproof foil and loglines (Figure 4 & 5). The rain barrels were always located on the side of the hill slope.



Figure 4 & 5: Surface runoff water collection

The leachate water was collected directly underneath the soil-ash layer (similar depth in case of control point) using a 2.5m x 2.5m measuring drainage foil for leachate collection and a waterproof PE-foil for the safe water transport to a 60 liter barrel (Figure 6).



Figure 6: Leachate water collection

At the four ash and two control sections (only two of three buffers were used as experimental controls) surface runoff water and leachate water was collected during the vegetation period in 2010, 2012 and 2013. For better readability results of the individual vegetation periods were further divided in two subperiods.

The dates of water sampling are shown in Table 3.

Table 3: Dates of water sampling from full-scale field experiment

20	10	20	12	2013		
Period 1	Period 2	Period 1	Period 2	Period 1	Period 2	
29.05.2010	24.06.2010	13.04.2012	23.07.2012	27.04.2013	10.07.2013	
01.06.2010	08.07.2010	18.05.2012	20.08.2012	29.05.2013	29.08.2013	
10.06.2010	21.07.2010	25.06.2012	24.09.2012	18.06.2013	26.09.2013	
18.06.2010	04.08.2010		16.10.2012		31.10.2013	

The high sampling frequency in June 2010 is attributed to high rainfall intensities during this period.

At each sampling date, we took the sub-samples (100 ml), subsequently emptied the barrels with a submersible pump and removed the remaining water and mud (sometimes dead animal) by hand using a small container.

In the laboratory the samples were filtered through 0.45 μ m filter paper (150 mm Munktell, 14/N) and split up into aliquot subsamples for the determination of DOC, anions and macro- and microelements. We measured pH and EC in the remaining sample.

DOC samples were acidified with 1 μ L of 10% HCI (WVR Chemicals, Fontenay-sous-Bois) per mL of sample and frozen at -20°C. Anion samples were stored at 4°C. Samples for macro- and microelement determination were acidified using 10 μ L of HNO₃ (65%; Merck, Darmstadt) per mL of sample and also stored at 4°C prior to analys is.

Chemical analysis is described in chapter 3.4 together with the samples of the other conducted experiments.

3.1.3.2 Soil Sampling

To evaluate possible ecological risks in soil layers underneath the forest road, induced by overlaying ash, soil samples were collected in the six sectors according to Figure 1. Possible impacts might be attributed to the translocation of elements from the ash and/or mobilization processes caused by changes in soil chemistry.

Soil samples were taken in three replicates and two different depths (0-20cm and 20-40cm underneath the treated road layer) in July 2012 (Figure 7 & 8).



Figure 7 & 8: Weyregg Forest Road Soil sampling

In the laboratory samples were air-dried and sieved to receive a maximum particle size of 2 mm.

We analyzed the soil samples for total element concentrations and water-extractable concentrations according to Austrian Norms.

Total element concentrations were obtained by aqua-regia soil digestion (ÖNORM L1085). Airdried, homogenized and grounded soil (0.5 g) was weighed in glass tubes and 4.5 mL of HCl (37%) and 1.5 mL of HNO₃ (65%) plus one drop of octanol to inhibit foaming were added successively. After reaction over night (with attached coolers) at room temperature the soil-acid suspension was heatedfor 3 hours at 150°C. Thereaft er samples were allowed to cool down. Samples were mixed using a vortex-shaker, filtered using 0.45 μ m filter paper (150 mm Munktell, 14/N) and subsequently analyzed by ICP-MS (Elan 9000 DRCe, Perkin Elmer). For quality control an internal reference soil (Moosbierbaum) and four experimental blanks were included in the digestion procedure.

The water-extractions of the soil samples were carried out according to Austrian Norm ÖNORM L 1092-93. We weighted 4 gram of the homogenized, dry soil into 50mL centrifugal vials (Cs500, Centrifuge Tube, VWR) and added 40 mL of Milli-Q water (gravimetric soil/water ration 1:10). Samples were allowed to equilibrate for 24 hours at room temperature and then shaken for 1 hour at 20 revolutions per minute in an overhead shaker. Thereafter, the extracts were centrifuged for 10 minutes at 4000 x g (centrifugal force) and filtered through syringe filters (0.45 μ m, nylon, WhatmanTM GD/X). The samples were split up into subsamples, acidified and stored as described in chapter 3.1.3.1. Due to limited sample volume, pH and EC were measured in the DOC samples prior to acidification.

Chemical analysis see chapter 3.4.

3.2 Wood Ash Leaching Experiment

Since the full-scale field experiment, outlined above, could only examine the effects of two different ashes on one soil, additional laboratory experiments were performed.

The wood ash leaching experiment I conducted in the course of this thesis is deemed to provide information about the leaching potential of fresh wood ash.

The experiment was carried out with one ash, in addition to the master thesis of Kehrer (2012), who already performed this experiment with four different ashes. The experimental ash, termed "GA" (Grate Ash) in this thesis, is a coarse grate ash originating from a grate furnace fueled with a mixture of wood chips and bark, similar to the grate ash used in the field experiment.

To identify characteristic differences between grate ashes (GA) and fluidized-bed ashes (FBA) in their leaching potential the data of FBA, published in Kehrer (2012), was included in the results section.

As in the full-scale field experiment (see 3.1.2) the ashes were analyzed for total element concentrations and water-extractable concentrations. Based on Austrian guideline values the ashes comply with the requirements for the use in agriculture and forestry (BMLFUW, 2011).

			GA	FBA		
			Water-	Water-		
Characteristics	Unit	Total	extractable	Total	extractable	
рН	-	12.7		11.7		
EC	mS cm⁻¹	9.46		1		
TOC	mg kg⁻¹	< 500	19.4	< 500	n.a.	
AI		47700	3.56	18700	20.7	
As		11	0.004	1	< 0.6	
В		86.4	0.65	n.a.	<10	
Ba		641	12.45	n.a.	1.69	
Ca		176000	6660	43900	n.a.	
Cd		1.1	0.001	0.10	< 0.025	
Со		14.9	0.015	1.42	<0.3	
Cr		76.1	0.34	148	0.11	
Cu		70.2	0.025	30.4	< 0.125	
Fe	mg kg⁻¹	27400	31	2620	n.a.	
К		24700	2700	39300	n.a.	
Mg		21000	8.4	5800	n.a.	
Mn		3090	0.008	806	n.a.	
Мо		1.39	0.08	1.04	n.a.	
Na		5420	394	3010	n.a.	
Ni		56	0.29	4.25	< 0.125	
Р		2910	0.1	1990	n.a.	
Pb		10.1	0.022	10.3	< 0.6	
Se		0.7	0.26	n.a.	n.a.	
V		67	0.004	9.77	n.a.	
Zn		161	1.8	292	< 0.25	
CI			62		1.4	
F			0.86		<0.5	
NO ₂ -N	mg kg⁻¹		3.3		<2	
NO ₃ -N			3.7		<2	
PO ₄ -P			< 0.001		<2	
SO ₄			29		370	

Table 4: Total element concentrations and water-extractable concentrations of GA and FBA

3.2.1 Experimental Setup

Well water was applied in weekly steps between the end of September 2012 and March 2013 to pure wood ash, the leachates were subsequently collected and analyzed.

The experiment consisted of a 60 liter barrel filled with 20 kg of the experimental ash "GA" for each of the three replicates. Before the barrels were filled with ash a 5cm thick marble grit drainage layer covered by a membrane, to avoid material translocation, was placed at the bottom. The ash was then covered by a second marble grit layer (~1-2 cm) and a 5 cm thick layer of silica sand. The silica sand with a grain size of 0.5-2 mm should reduce evaporation while improving water distribution. Additionally, a plastic ring was pressed into the sand to guarantee the water percolation through the ash layer and avoid bypassing on the barrel sidewalls.

We applied 22 times 5 liters of well water (pH = 7) each, starting at the end of September 2012. For the analysis a 100ml sample was collected from every step previous to the next water application. The leachates of step 3 to 9 (in the first two steps no leachate could be recovered) were collected in a composite sample, which was used in the soil column experiment, described in chapter 3.3.

The weekly application of 5 liters on the barrels (barrel diameter = 0.35 m) corresponds to a monthly rainfall of 220 L m⁻², such high rainfall values could be reached during extraordinary wet summer months in this region (Hydrographischer Dienst Österreich, 2011).

The leachate samples were filtered through syringe filters (0.45 μ m, nylon, WhatmanTM GD/X), before they were split up into subsamples, acidified and stored for analysis (see chapter 3.1.3.1). We measured pH and EC in the remaining unfiltered sample.

Chemical analysis is described in chapter 3.4.

3.3 Soil Column Experiment

The purpose of the soil column experiment was to derive information about the response (buffering, filtering and mobilization processes) of different soils when exposed to the application of wood ash leachate.

Therefore, we applied two different wood ash leachates and artificial rainwater (as control) to three selected soils. The experiment was performed in two replicates.

Additionally to the leachate collection we sampled the soil after the experiment and determined the water-extractable element concentrations.

3.3.1 Soils

An important factor for the selection of the experimental soils was their pH value, as pH is a master variable of element solubility, (im)mobilization and buffer processes in soils.

The first soil, "S1", is an acidic Cambisol (sandy loam) with a pH of 5.6 from Siebenlinden, Lower Austria.

"S2" is a neutral Cambisol (loam) with a pH of 7.8 from Wiesen, Burgenland.

The third soil, "S3", is characterized as an alkaline Chernozem (silty loam) with a pH of 8.1 from the Marchfeld, Lower Austria.

Total element concentrations and water-extractable concentrations of the three experimental soils are displayed in SI-Table 1.

			Experimental Soils	
Soil characteristics	Unit	"S1" (acidic)	"S2" (neutral)	"S3" (alkaline)
рН	-	5.6	7.8	8.1
EC	µS cm⁻¹	55.3	160	134
DOC	mg kg⁻¹	219	725	206
SOM	g kg⁻¹	61.2	23	41.3
CEC	mmolc kg ⁻¹	109	75.2	275
sand	g kg⁻¹	713	490	236
silt	g kg⁻¹	233	421	496
clay	g kg⁻¹	53.4	88.4	268

Table 5: Characteristics of the soil column experimental soils

3.3.2 Wood ash leachates and artificial rainwater

The first wood ash leachate, here referred as "FBA", is the leachate of a fluidized bed ash, which was collected by Kehrer (2012).

As the second leachate, here referred as "GA" we used the composite sample of the wood ash leaching experiment, described in the chapter 3.2.

For the control we prepared 16 liter of artificial rainwater according to Anderson, et al. (2000).

The solution was prepared using various stock solutions and de-ionized water as given in

Table 6.

		Concentration of stock	Stock solution per L of
Chemical	Supplier	solution (mol L ⁻¹)	artificial rainwater (mL)
NaCl	Sigma-Aldrich, Steinheim	0.01	20
KCI	Sigma-Aldrich, Steinheim	0.001	10
NH ₄ Cl	Sigma-Aldrich, Seelze	0.001	10
MgCl ₂	Merck, Darmstadt	0.001	25
CaCl ₂	Merck, Darmstadt	0.001	10
NaNO ₃	Sigma-Aldrich, Steinheim	0.001	10
Na_2SO_4	Sigma-Aldrich, Seelze	0.001	25

Table 6: Composition of artificial rainwater (modified after Anderson et al., 2000; Table 1)

The chemical composition was given with (mg L^{-1}) Na⁺, 6.0; K⁺ , 0.39; NH₄⁺ , 0.18; Mg²⁺ , 0.60; Ca²⁺ , 0.40; Cl⁻ , 12; NO₃⁻ , 0.6; SO₄²⁻ , 2.4.

The pH was adjusted to 4.44 by adding a 0.1 mol L⁻¹ HCl (WVR Chemicals, Fontenay-sous-Bois) stock solution.

3.3.3 Experimental setup

Due to organizational reasons we had to split up the soil column experiment into two sets. In August 2012 we did the experiment applying artificial rainwater on all three soils plus the "FBA" leachate on "S1" and "S3". The data for the "FBA" leachate on "S2" was taken from Kehrer (2012).

During the second set, in November 2012, the composite sample of "GA", collected in the wood ash leaching experiment, was applied on all the three soils. For "S2" the experiment had to be repeated again due to clogging of the soil columns.

Polymethyl methacrylate columns with a diameter of 12 cm were filled with 2 kg of homogenized air-dry soil (<4 mm particle size). At the bottom of each column a nylon membrane (pore size 30 μ m, SEFAR 03-30/18) and a glass wool layer (~5 cm) was installed to aid drainage and avoid material translocation. To ensure even fluid distribution over the surface and reduce evaporation a 2-3 cm thick layer of polyethylene granulate (d = 3.5 mm) was placed on top of the soil column.

Prior to fluid application the soil columns were saturated with de-ionized water from the bottom for about 15 minutes. Funnels, allowing the collection of the leachate into 250 mL vials, were attached to the prepared columns and together placed onto a, specially designed, wooden support frame for drainage (2 hours) (Figure 9).



Figure 9: Experimental setup of soil column experiment

3.3.3.1 Leachate Collection

Wood ash leachates and artificial rainwater were applied in 12 steps of 200 mL each, during 3-4 consecutive days.

This water application corresponds to 210 L m⁻², such values can only be reached during extreme rainfall events in 3-4 days (Hydrographischer Dienst Österreich, 2011).

The number of leachate samples, collected each day, is listed below. Time intervals between the application steps were 1.5 to 3 hours.

	Number of leachate samples						
	Day 1	Day 2	Day 3	Day 4			
ARW + FBA	4	5	3	-			
GA	3	5	3	1			
Rep. GA on S2	5	5	2	-			

The leachate samples were collected previous to each subsequent step of fluid application. During the course of the experiment we additionally collected five samples of each application fluid.

After filtration through syringe filters (0.45 μ m, nylon, WhatmanTM GD/X) the samples were split into aliquot subsamples, acidified and stored for analysis (see chapter 3.1.3.1)

Chemical analysis was carried out as described in chapter 3.4.

3.3.3.2 Soil Sampling

After the leaching experiment was completed, the soil columns were disassembled and the soil (still near to saturation) was sampled in two different depths (0-10 cm and 10-20 cm; measured from the top). Water-extractions and corresponding sample preparation was conducted similar to the procedure described in chapter 3.1.3.2. However, the soil was not dried prior to extraction to avoid changes of soil chemistry. A realistic water content was estimated for the calculation of the weight of wet soil, corresponding to 4 grams of dry soil. Thereafter, separate soil samples in two replicates were dried at 105°C for 48 hours for the determination of the water content, allowing the exact correction of the weight.

3.4 Chemical analysis

Table 7 gives an overview of the measured characteristics with the corresponding method and instrument.

Table 7: Overview of characteristis, methods and instruments	Table 7: Overview of	characteristis,	methods a	nd instruments
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Characteristic	Method	Instrument				
рН	pH Electrode	Ross Ultra pH/ATC Triode, Orion 3 Star				
EC	EC Electrode	Standard Conductivity Cell (LF413T-ID), Scott Instruments				
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^{-} , CI^{-} , NO_2^{-} , NO_3^{-} , $PO_4^{-3}^{-}$, $SO_4^{-2}^{-}$	lon Exchange Chromatography	881 Compact IC pro, Metrohm				

The listed characteristics were determined for all samples, except for the samples of the aquaregia soil digestion of the full-scale field experiment (see 3.1.3.2), where only the microelements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Se, V, Zn) were measured by ICP-MS.

Dissolved organic carbon (DOC) was determined by absorption of UV-light at 254 nm and the adjacent transformation of the measured values into the correspondent DOC concentration, according to the correlation found by Brandstetter, et al. (1996).

96-well plates (BRANDplates, Wertheim) with sample volumes of 300 µL were used for analysis. The original correlation was adapted to the geometry of the analytical instrument used in this study resulting in:

DOC (mg L^{-1}) = 1 + 57.56 * A (m⁻¹) at 254nm

Samples for ICP-MS analysis were diluted with 1% double-subboiled HNO₃ (if required) and ¹¹⁵In was added as internal standard.

We only used ICP-OES for the determination of the macroelements (Ca, K, Mg Na) of the wood ash leaching experiment (see 3.2).

3.5 Statistical data analysis

The analytical results of the full-scale field experiment and soil column experiment were analyzed by one-way ANOVA with a Student-Newman-Keuls Post Hoc test using the software SPSS 15.0 (SPSS Inc., Chicago, IL). The significance level of p < 0.05 was applied for all analyses.

Data from surface runoff and leachate sampling of the full-scale field experiment were merged into six sampling periods (see 3.1.3.1) and subsequently analyzed for differences between the different treatments. The analysis was separately done for each individual sampling period.

Differences between control and wood-ash sections in the forest road soil samples were compared separately within each sampling depths. The analysis was separately done for total concentrations and water-extractable concentrations.

The soil column leachates were tested for differences between control (artificial rainwater) and wood ash leachates individually for each experimental soil. Water extractions of the soil columns were tested separately for each of the three soils and each of the two sampling depths.

4. Results and Discussion

4.1 Full-scale Field Experiment (Weyregg Forest Road)

4.1.1 Surface Runoff and Leachate

To obtain an overview of the environmental impacts the element concentrations of the surface runoff and leachate were compared to legal thresholds.

Since no specific threshold values for the use of wood ash in forest road construction are established in Austrian legislation following legal frameworks were applied:

- Austrian Wastewater Directive on landfill leachates (AEVD): Threshold values for direct (AEVD_{dir}) and indirect (AEVD_{indir}) discharge (AEVD, 2003).
- Austrian General Wastewater Directive (AAEV): Threshold values for direct (AAEV_{dir}) and indirect (AAEV_{indir}) discharge (AAEV, 1996).
- Austrian Drinking Water Regulation (DW): Threshold values (DW_{th}) and indicator values (DW_{in}) (TWV, 1996).
- Quality Target Ordinance Groundwater (GW): Threshold values (GW_{th}) and values indicating a trend reversal (GW_{tr}) (QZV Chemie GW, 2010).

For Ba and Mo, the WHO guideline values (World Health Organization, 2011) were used as drinking water thresholds since in Austrian legislation solely values for wastewater are given.

A traffic light system was used to identify the potentially critical characteristics. A potentially critical characteristic was defined as a characteristic which exceeds the legal limits for at least 3 out of the 7 sampling times (2010: 8 sampling times) per vegetation period. If exceeding element concentrations were found simultaneously in the control samples and the ash treatments samples this could be attributed to a pedogenic source and was therefore not defined as a potentially critical characteristic.

Based on the reasons, described in chapter 4.1.1.2, potentially critical characteristics in the surface runoff and leachate do not necessarily mean that surface or groundwater pollution would occur.

The illustration of the different legal limits is shown in Figure 10.

No (or \leq 3) exceedance/simultaneous exceedance of control

- > 3 exceedance of DW_{in} or GW_{tr}
- > 3 exceedance of DW_{th} or GW_{th}
- > 3 exceedance of threshold values of AAEV or AEVD (dir & indir)

Figure 10: Traffic light system for the identification of potentially critical characteristics from Weyregg forest road. DW_{in}/DW_{th} : Indicator value/threshold value of Austrian Drinking Water Regulation; GW_{tr}/GW_{th} : Value indicating a trend reversal/threshold value of Quality Target Ordinance – Groundwater; AAEV/AEVD (dir & indir): Threshold value for direct and indirect discharge of Austrian General Wastewater Directive/Austrian Wastewater Directive on landfill leachates.

4.1.1.1 Surface Runoff

		Surface Runoff										
		20	10		2012				20	13		
	GA	-W	FBA	A-W	GA-W FBA-W		GA-W		FBA-W			
	15%	30%	15%	30%	15%	30%	15%	30%	15%	30%	15%	30%
рН												
EC												
DOC												
Al												
As												
В												
Fe												
Mn												
Ni												
NO2 ⁻												
PO4 ³⁻												

As seen in Figure 11 no potentially critical characteristic, except for PO_4^{3-} in the FBA samples (15% and 30%) in 2013, could be found in the surface runoff of the full-scale field experiment.

Figure 11: Potentially critical characteristics of the surface runoff from the soil-ash layer of fullscale field experiment (Weyregg forest road). The identification of the potentially critical characteristics is based on the traffic light system shown in Figure 10.

In Figure 12 the averaged concentrations of PO_4^{3-} of the surface runoff on FBA sections are displayed for the six sampling periods (see chapter 3.1.3.1). The only statistically significant difference is found for FBA 15% during the last sampling period. The elevated concentrations of FBA 15% and FBA 30% in 2013 are responsible for classifying PO_4^{3-} as a potentially critical characteristic. The high variation and high standard deviation of the data leads to the assumption that critical PO_4^{3-} concentrations are caused by punctual sources of contamination (animals, soil and plant material) in the collection barrels and/or natural variation between the sampling points.



Figure 12: Averaged period concentrations of $PO_4^{3-} \pm SD$ in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).

Figure 13 and Figure 14 show the averaged period values for pH and EC of the surface runoff on the sections built with grate ash (GA-W). Albeit, the used ash has an extraordinary high pH (pH = 13.5) and EC value (EC = 10.7 mS cm^{-1}) (Table 2) a significant effect could not be found during the experiment.

This fact approves the assumption derived above and allows us to conclude that the element concentration of the surface runoff is not affected by the ash treatment.

Surface runoff can therefore be evaluated as ecologically unproblematic and will not be discussed in further detail in this master thesis. Graphs of the mean period values for all measured elements are available in the annex (SI-Figure 1 - SI-Figure 12).



Figure 13: Averaged period values of pH \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



Figure 14: Averaged period values of EC \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).

4.1.1.2 Leachate

Figure 15 shows the potentially critical characteristics, as defined in Figure 10, of the leachates from the full-scale field experiment. A generally decreasing trend of ash impact can be observed over time. While, in the first year we found 10 characteristics to be potentially critical, 3 years after the implementation of the experiment solely pH, DOC, AI and Ni of the GA-W leachates could be classified as potentially critical characteristics. Potentially critical characteristics in the FBA-W leachates were only identified in 2010, the first year of the experiment.

	Leachate											
	2010				2012				2013			
	GA-W		FBA-W		GA-W		FBA-W		GA-W		FBA-W	
	15%	30%	15%	30%	15%	30%	15%	30%	15%	30%	15%	30%
рН												
EC												
DOC												
AI												
As												
В												
Fe												
Mn												
Ni												
NO2 ⁻												
PO4 ³⁻												

Figure 15: Potentially critical characteristics of the leachates from the soil-ash layer of full-scale field experiment (Weyregg forest road). The identification of the potentially critical characteristics is based on the traffic light system shown in Figure 10.

For the interpretation of these results, with respect to ecological impacts, the experimental setup has to be considered. As described in chapter 3.1.3.1 the leachate was sampled directly underneath the soil-ash layer and therefore reflects the highest possible ash impact. Before reaching the groundwater body the leachate would percolate through deeper soil layers where the element concentration would be substantially lowered by filtration, buffering and dilution. Moreover, forest roads to which wood ash could be applied at a given time only cover a small proportion of watersheds.

Table 8 shows the leachate concentrations of the full-scale field experiment that are significantly affected by ash treatments. Most characteristics are significantly elevated in at least one of the ash treatments, except for P, Pb, Zn and $PO_4^{3^-}$ for which no significant differences were observed. Selinium only shows statistically significant elevation in the last sampling period with concentrations well below the legal limits and near the LOQ. Magnesium concentrations were significantly lower in the GA-W treatments and significantly higher in the FBA-W treatments compared to the control.

The most pronounced ash impact was observed for the GA-W 30% treatment, corresponding to the data presented in Figure 15.

	GA-W 15%	GA-W 30%	FBA-W 15%	FBA-W 30%
рН	+	+		
EC	+	+		
DOC	+	+	+	+
Al	+	+	+	
As	+		+	+
В	+	+	+	+
Ва		+		
Ca	+	+		
Cd		+	+	
Со	+	+	+	+
Cr	+	+		
Cu	+	+		
Fe		+	+	
К	+	+		
Mg	-	-	+	+
Mn			+	
Мо	+	+	+	+
Na		+	+	
Ni		+	+	+
Р				
Pb				
Se	+	+	+	
V	+	+	+	+
Zn				
Cl		+		
F		+	+	
NO ₂ ⁻		+		
NO ₃ ⁻			+	
PO4 ³⁻				
SO4 ²⁻		+	+	+

Table 8: List of significant differences of road leachate concentrations from control samples in one or more sampling periods (p < 0.05). "-"...significantly lower, "+"...significantly higher.

EC and pH:

EC and pH are important characteristics for the interpretation of the leachate concentrations, since they control the mobility and thus leaching behavior of most elements.

In general, an increasing pH decreases the mobility of cations and increases the mobility of anions by increasing the negative surface potential in soils (Scheffer, et al., 2010).

The pH of the two grate ash (GA-W 15% & 30%) treatments shows significantly elevated values throughout the entire period of the experiment (Figure 16). The leachates exceeded the threshold value of the Austrian drinking water regulation ($DW_{th} = 9.5$) by more than two units. In contrast the pH value of the fluidized-bed ash treatments (FBA-W 15% & 30%) was not significantly different from the control, in line with the relatively low pH of the pure ash (FBA-W) (Table 2).

The grate ash treatments caused a significant increase of the EC value of the leachate water, however, a slightly decline with time is observable (Figure 16). The increase was more pronounced for the GA-W 30% treatment, resulting in a threshold value exceedance in the majority of the sampling periods. After two sampling periods the EC value of the GA-W 15% treatment decreased below the threshold value of the Austrian drinking water regulation (DW_{th} = $2500 \,\mu\text{S cm}^{-1}$), but remained significantly higher than in the control.

Similar to the pH value a significant ash impact on the EC was not observed for the FBA-W treatments (Figure 16).

The higher pH and EC values of the grate ash treatment can be related to the high Ca (and partly Mg) contents of GA-W (Table 2).



Figure 16: Averaged period values of pH and EC \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05). The red dotted line represents legal limits given in Austrian legislation. <u>pH:</u> Indicator value of Austrian drinking water regulation DW_{in} = 6.5 - 9.5; <u>EC:</u> Indicator value of Austrian DW_{in} = 2500 μ S cm⁻¹.

DOC:

Dissolved organic carbon may form stable complexes with a number of trace elements (Co, Cu, Mn, Ni, Pb, Zn) (Adriano, 2001). High DOC concentrations may therefore be related to increased element concentrations in the leachate water.

Significantly elevated DOC concentrations were observed for all ash treatments in the first year of the experiment, exceeding the threshold value of the Austrian Wastewater Directive on landfill leachates ($AEVD_{dir}$). Highest concentrations were found for GA-W 30%.

In 2012 and 2013 the concentrations of the FBA-W samples aligned to the control and settled below the threshold value. After low concentrations in 2012, the grate ash samples increased above the threshold again in 2013 (Figure 17).



Figure 17: Averaged period concentration of DOC \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05). The red dotted line represents the threshold value for direct (AEVD_{dir} = 20 mg L⁻¹) discharge of the Austrian Wastewater Directive on landfill leachates (AEVD).

The increase of DOC in the leachate is likely to be linked to the elevated pH and accompanied mobilization of organic matter form the soil-ash layer. With increasing pH the sorption of negatively charged organic matter decreases due to the reduction of positively charged soil surfaces. Kahl, et al (1996) confirms the increased solubility of organic carbon in an acidic forest soil after the application of wood ash as a soil amendment.

This explanation only holds for the data of the grate ash treatments (GA-W 15% & GA-W 30%). Although a pH increase was not observed in the leachates of FBA-W (OH⁻ ions were buffered by soil) the moderately high pH of the ash (pH = 8.6) (Table 2) is likely to have had an effect on the mobilization of DOC in the first year of the experiment.

Fe, Mn and Al:

(Oxy)hydroxides of Fe and Mn, and to a lower extent Al, have a strong affinity in sorbing and occluding numerous trace elements (Co, Cu, Ni, Zn, Cd, Pb). Under normal conditions they retain those elements in the soil matrix, however if oxides get mobilized the inherent elements get mobilized simultaneously (Kabata-Pendias, 2011).

Leachate concentrations of Fe, Mn and Al are shown in Figure 18.



Figure 18: Averaged period concentrations of Fe, Mn and AI \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05). The red dotted line represents legal limits given in Austrian legislation. <u>Fe:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.2 mg L⁻¹; Mn: Indicator value of Austrian drinking water regulation DW_{in} = 0.05 mg L⁻¹; <u>AI:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.2 mg L⁻¹.

A steadily rising trend of the Fe concentrations in the control samples was observed throughout the experiment, resulting in the exceedance of the indicator value of the Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$) after the first half of the experiment.

The FBA-W treatments do not significantly affect Fe mobility with the exception of FBA-W 15% in the last sampling period. The leachate of the GA-W 30% treatment showed significantly higher Fe concentrations in the second, third and fifth sampling period of the experiment. During the first and the last sampling period Fe concentrations did not significantly differ from control treatment. Leachates of GA-W 15% follow this pattern, however without statistical significance.

Iron and Ca concentrations showed a similar leaching pattern (Figure 20). The Fe oxides might have been precipitated on calcium compounds and conjointly leached from the forest road (Kabata-Pendias, 2011).

The increased concentration of Fe in the leachates of grate ash can be mainly attributed the high pH of the corresponding leachates (Figure 16). Elevated Fe solubility at high pH is due to the hydrolysis of $Fe(OH)_3^0$ to $Fe(OH)_4^-$ (and $Fe(OH)_5^{2^-}$) taking place at pH values higher than 8.5 (Lindsay, 1979; Fig. 10.3). Complexation of Fe with DOC (Figure 17) might have also played a considerable role in Fe solubilization. Formation of complexes with $SO_4^{2^-}$ (Figure 23) did not affect Fe concentrations (Lindsay, 1979; Scheffer, et al., 2010).

The observed increase of Fe in FBA-W 15% leachates in the last sampling period might be caused by mobilization of Fe oxides/hydroxides due to reducing conditions in this specific sampling point (Kabata-Pendias, 2011).

Manganese concentrations in the leachates of the FBA-W 15% treatment were significantly increased solely in the first two sampling periods, resulting in the exceedance of the indicator value of the Austrian drinking water regulation ($DW_{in} = 0.05 \text{ mg L}^{-1}$). Thereafter, concentrations aligned to the control treatment and remained well below the legal limits. All other ash treatments did not result in elevated concentrations. Based on the lower Mn contents (Table 2) of FBA-W, in comparison to GA-W, this leaching behavior is unexpected and a clear explanation could not be found.

Aluminium concentrations were found to be highest in the leachates of the GA-W 15% treatment, shown by significant differences in five out of six sampling periods and a 3 - 4 fold exceedance of the indicator value of the Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$). GA-W 30% showed similar high Al-concentrations in the first year, aligning to control values in the course of the experiment.

Similar to Fe, the increased concentration of Al in the leachates of grate ash can be mainly attributed the high pH of the corresponding leachates (Figure 16). Here, the hydrolysis of $AI(OH)_3^0$ to $AI(OH)_4^-$ (and $AI(OH)_5^{2^-}$) takes place at pH values higher than 7.5 (Lindsay, 1979; Fig. 3.3) and is responsible for the elevated Al solubility. Complexation of Al with DOC (Figure 17) might have also played a considerable role in Al solubilization. As for Fe, the formation of complexes with $SO_4^{2^-}$ (Figure 23) did not affect Al concentrations (Lindsay, 1979; Scheffer, et al., 2010).

The treatment with FBA-W (15% & 30%) did not result in an increase of AI in the leachates, with the exception of FBA-W 15% in the last sampling period, which is strongly elevated and approaches the indicator value of the Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$). A clear explanation for this behavior could not be found.

Macroelements: Ca, K, Mg, Na

The concentrations of Ca, K, Mg and Na in both ashes considerably exceeded those in the soil of the experimental site. With a total concentration of 333 g kg⁻¹ and a water-extractable concentration of 8.36 g kg⁻¹ the used grate ash was especially rich in Ca (Table 2).

The leachate concentrations of Na and Ca, K, and Mg are shown in Figure 19 and Figure 20.

Sodium concentrations were significantly increased in the leachate of GA-W 30% displaying a slightly decreasing trend over time. The leachate concentration of the FBA-W 15% section showed a peak in the beginning of the second half of the experiment, however the data had high variability.



Figure 19: Averaged period concentrations of Na \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).

The Ca concentration in the leachate of GA-W 15% was elevated throughout the entire experiment, however, due to high spatiotemporal variability of the data significant differences to the control were only observed in two sampling periods. Ca concentration in the GA-W 30% leachate was increased in 2012 and 2013 showing significant differences in the first sampling period in both years. A statistically significant effect was not observed for the Ca concentration in the leachate of the fluidized bed-ash treatments (FBA-W 15% and 30%). The findings are well reflected by the high total and water-extractable Ca concentrations of GA-W.

Despite higher total K concentrations of FBA-W (Table 2) significantly elevated concentrations in the leachate water were only found for the GA-W treatments. The leachate concentration of the GA-W 30% treatment was about twice as high as for the GA-W 15% treatment.

Magnesium concentrations were found to be lower than the control in the GA-W leachates, whereas for the FBA treatment no trend in the leachate concentration could be identified.



Figure 20: Averaged period concentrations of Ca, K and Mg \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).

Trace elements: As, B and Ni

The leachate concentrations of As, B and Ni showed a strong decreasing trend over the course of the experiment (Figure 21). The three elements were identified to be potentially critical characteristics according to Figure 15. However, after the first year of the experiment most leachates complied with the legal limits and only few ash treatments exhibited significant differences to the control.

Cd, Co, Cu and Mo showed similar pattern, however their concentrations were well below the legal limits and therefore not discussed in further detail (SI-Figure 15 - SI-Figure 17).

The As concentrations in the leachate water from the road section constructed with grate ash showed initial leaching for the GA-W 30% treatment in the first experimental year. Legal limits were not exceeded. The fluidized bed-ash treatments resulted in significantly elevated As concentrations in the first year, exceeding the threshold value of Austrian drinking water regulation $DW_{th} = 0.01 \text{ mg L}^{-1}$. Thereafter they dropped well below the threshold value, however, remained significantly increased for FBA-W 15% throughout the entire experiment.

The leaching pattern of As correlates well with the leaching of CI^{-} , $SO_4^{2^-}$ (Figure 23) and DOC (Figure 17) for the GA-W and FBA-W treatment, respectively. The high input of CI^{-} and $SO_4^{2^-}$ along with the ash-induced solubilization of DOC might have caused a mobilization of As by anion competition for positively charged exchange sites (Alloway, 2012).

Boron concentrations were exclusively affected by FBA-W treatments, where they exceed the legal limit ($GW_{tr} = 0.75 \text{ mg L}^{-1}$) for both ash application rates during the first sampling period. Additionally, the FBA-W 15% treatment exceeded the legal limit in the third sampling period and generally showed higher concentrations than the FBA-30% treatment. In the last sampling period the ash effect was still statistically significant, however concentrations were well below GW_{tr} .

The GA-W 30% treatment resulted in elevated Ni concentrations in every sampling period, especially in the first year the legal limits ($DW_{th} = 0.02 \text{ mg L}^{-1}$; $GW_{th} = 0.018 \text{ mg L}^{-1}$; $GW_{tr} = 0.015 \text{ mg L}^{-1}$) were greatly exceeded. The leachate concentrations of the fluidized bed-ash samples showed significant differences to the control with the exceedance of legal limits solely in the first year of the experiment. Thereafter no significant ash effects were present. Ni might have been mobilized from the soil-ash layer by complexation with DOC (Figure 17). Additionally, complex formation with Cl⁻ and SO₄²⁻ (Figure 23) might render Ni more mobile (Adriano, 2001).

A bigger effect of FBA-15% than of FBA-30% was observable for As, B and Ni (Figure 21) (likewise for Cd and Mo (SI-Figure 15 and SI-Figure 17)). Given the higher input of trace metals with a higher ash application rate one would expect the opposite effect on the leachate concentration.



Figure 21: Averaged period concentrations of As, B and Ni \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05). The red dotted line represents legal limits given in Austrian legislation. <u>As:</u> Threshold value of Austrian drinking water regulation DW_{th} = 0.01 mg L⁻¹; <u>B</u>: Value indicating a trend reversal of the Quality Target Ordinance-Groundwater GW_{tr} = 0.075 mg L⁻¹; <u>Ni</u>: Threshold value of Austrian drinking water regulation DW_{th} = 0.02 mg L⁻¹; Threshold value (GW_{th} = 0.018 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.015 mg L⁻¹) of Quality Target Ordinance-Groundwater.
Trace elements: Ba, Cr and V

The leachate concentrations of Ba, Cr and V were elevated throughout the experiment without showing a specific pattern. The exceedance of legal limits is of no concern. Solely the leachate of the GA-W 30% marginally exceeded the WHO drinking water guideline value for Ba (0.7 mg L^{-1}) in one of the six sampling periods (Figure 22).

The Ba concentration of the grate ash treatments were elevated throughout the experiment, whilst the treatment with fluidized bed-ash only resulted in elevated concentrations during the second half of the experiment. The results, however, did not show statistical significance (SI-Figure 15).

Chromium concentrations were significantly elevated for the grate ash treatments, showing higher concentrations for the 15% ash application rate. FBA samples did not significantly differ from the control (SI-Figure 16).

Higher Ba and Cr concentrations in the leachates of the road-section, constructed with grate ash, were supported by higher total and water-extractable element concentrations of the fresh ash (Table 2).

Vanadium showed statistically elevated concentration for GA-W 30% and FBA-W 30% in the first year of the experiment aligning to the control in the following years. In contrast, the 15% ash treatments of GA-W and FBA-W were significantly increased during the last two years of the experiment (SI-Figure 19).



Figure 22: Averaged period concentrations of Ba, Cr, and V \pm SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05). The red dotted lines represent legal thresholds given in Austrian legislation. <u>Ba:</u> WHO drinking water guideline value (0.7 mg L⁻¹).

Anions: NO2⁻, Cl⁻ and SO4²⁻

The leachate concentrations for NO_2^- , Cl^- and SO_4^{-2-} exceeded the legal limits in at least one of the six sampling periods (Figure 23).

Nitrite concentrations of the control samples generally were below the threshold value of the Austrian drinking water regulation (DW_{th} = 0.1 mg L⁻¹). Only during the first sampling period in 2013 (2013 P1) DW_{th} was marginally exceeded. The ash treatments caused a strong increase in leachate concentrations, however, due to high variability of the data, differences were only significant for the GA-W 30% treatment during 2010 and 2012. In the last two sampling periods the nitrite concentrations remained below 0.1 mg L⁻¹ for most ash treatments. Solely GA-W 30% slightly exceeded the threshold value of the Austrian drinking water regulation in the very last sampling period. Elevated nitrite concentrations might be caused by increase in pH upon ash application and the induced enhanced nitrification processes (Pitman, et al., 2006).

Chloride showed a strong flush behavior only for GA-W 30% during the first year of the experiment with the exceedance of legal limits ($DW_{in} = 200 \text{ mg L}^{-1}$, $GW_{th} = 180 \text{ mg L}^{-1}$, $GW_{tr} = 150 \text{ mg L}^{-1}$) in the first sampling period. GA-W 15% and FBA treatments did not affect the Cl⁻ concentrations in the leachate water.

The sulfate concentrations in the leachate water were only marginally affected by the grate ash treatments with values well below the legal limits. In contrast, the two FBA treatments resulted in a strong flush behavior with exceedances of the legal limits ($AAEV_{indir} = 200 \text{ mg L}^{-1}$, $DW_{in} = 250 \text{ mg L}^{-1}$, $GW_{th} = 225 \text{ mg L}^{-1}$, $GW_{tr} = 187.5 \text{ mg L}^{-1}$) in the first sampling period. The effect of FBA-15% remained statistically significant throughout the entire experiment.

The strong flush behaviour of Cl^{-} and SO_4^{2-} can be attributed to their presence in the form of readily water-soluble salts (Steenari, et al., 1999b).

The anions fluoride, nitrate and phosphate were investigated as well, however they did not exceed legal limits and mostly did not show significant differences to the control (SI-Figure 22 and SI-Figure 23).

The water-extractable concentrations of the anions NO_2^- , CI^- and SO_4^{2-} in the ashes, as seen in Table 2, are in accordance with the observed results.



Figure 23: Averaged period concentrations of NO²⁻, Cl⁻ and SO₄²⁻ ± SD in leachates from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05). The red dotted lines represent legal thresholds given in Austrian legislation. <u>NO₂:</u> Threshold value of Austrian drinking water regulation DW_{th} = 0.1 mg L⁻¹; <u>Cl:</u> Indicator value of Austrian drinking water regulation DW_{in} = 200 mg L⁻¹; Threshold value (GW_{th} = 180 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 150 mg L⁻¹) of Quality Target Ordinance-Groundwater. <u>SO₄²⁻</u>: Threshold values of Austrian General Wastewater Directive (AAEV) for indirect discharge AAEV_{indir} = 200 mg L⁻¹; Indicator value of Austrian drinking water regulation DW_{in} = 250 mg L⁻¹; Threshold value (GW_{th} = 225 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 187.5 mg L⁻¹) of Quality Target Ordinance-Groundwater. Mind the different scales.

4.1.2 Assessment of element redistribution in the soil profile

4.1.2.1 Total element concentration

The undisturbed soil layers (0-20 cm & 20-40 cm) underneath the forest road were tested for the total element concentrations to assess material relocation originating directly from the ash input or, due to mobilization processes, from the soil-ash layer.

To assess the potential contamination of the sub-road soil layer we compared the total element concentrations to the legal thresholds for excavated soil given in Austrian legislation (Deponieverordnung, 2008).

All measured element concentrations in the soil layers complied with the legal limits.

Table 9 reveals significant differences of the ash treatment samples to the control. The effect of the ash treatments will be discussed in the following.

Table 9: List of significant differences of total element concentrations of the soil layer underneath the forest road from the control samples (p < 0.05). "-"...significantly lower, "+"...significantly higher.

	GA-W 15%	GA-W 30%	FBA-W 15%	FBA-W 30%
Al			+	
As				
В				
Ва				
Cd	+			
Со				
Cr				-
Cu				-
Fe				
Mn	+			
Мо	+			
Ni		-		-
Р	-	-	-	-
Pb				
Se				
V				-
Zn				-

Aluminium was significantly elevated for FBA-W 15% in the upper soil layer (0-20 cm) (SI-Figure 25). Due to comparably low Al-content in the ash (Table 2) and unaffected Al concentrations in the leachate (Figure 18) an ash effect could be excluded, pointing out the big influence of natural variability within the experimental site. Unaffected concentrations on the FBA-W 30% sampling point confirm this assumption.

The GA-W 15% sampling point showed significantly higher concentrations for Cd (20-40 cm soil layer), Mn (20-40 cm soil layer) and Mo (0-20 cm soil layer) (SI-Figure 26 and SI-Figure 28). No relevant changes in the leaching behavior of the elements were observed (SI-Figure 15 and SI-Figure 17). Total concentrations on the sampling point constructed with the higher ash application rate (GA-W 30%) remained unaffected.

Total concentrations of Cr (0-20 cm soil layer), Cu (0-20 cm soil layer), V (0-20 cm soil layer) and Zn (0-20 cm & 20-40 cm soil layer) were significantly lower on the FBA-W 30% sampling point. Again, no relevant changes in the leaching behavior of the elements were found (SI-Figure 16 and SI-Figure 19).

Total Ni concentrations were significantly lower in the lower soil layer (20-40 cm) of GA-W 30% and FBA-W 30% (Figure 24). The leachates of the ash treatments showed increased concentrations, especially in the first year of the experiment (Figure 21). Nickel leaching from the soil-ash layer, however, would increase the total element concentration in investigated soil samples, the results are therefore contradictive.



Figure 24: Averaged total concentration of Ni \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).

Despite the relatively high concentration of phosphorus in the pure ashes (Table 2) the soil samples showed significantly lower concentrations for all ash treatments in both soil depths (SI-Figure 29). Leachate data is only available for 2012 and 2013, where all ash treatment samples show lower, however not statistically significant, P-concentrations compared to the control (SI-Figure 18). The results show that the control sample has a high P concentration due to natural variability of the experimental site.

No effect of the ash treatments on the total element concentrations in the soil layer underneath the forest road could be identified for the two sampling depths. Significant higher (Al, Cd, Mn, Mo) or lower (Cr, Cu, Ni, P, V, Zn) concentrations compared to the control were solely caused by the natural variability of the different sampling points.

All element concentrations were well below the legal threshold values. It can be concluded, that with respect to total concentrations, the ash treatments did not pose a risk for contaminate the sub-road soil layer during the 3-year experiment.

4.1.2.2 Water-extractable concentrations

For the assessment of ecological risks to the groundwater body the soil layer underneath the forest road was tested for its water-extractable element concentrations. The overlying ash could potentially affect the soil chemistry and thus alter the mobility of elements in the sub-soil layers. Altered element mobility and the direct element input from leaching could lead to contaminated groundwater recharge.

We compared the water-extractable concentrations to the legal thresholds for excavated soil given in Austrian legislation (Deponieverordnung, 2008).

The soil layer complied with the legal limits for all investigated elements in both soil depths.

Table 10 reveals significant differences of the ash treatment samples to the control. The effect of the ash treatments will be discussed in the following.

Table 10: List of significant differences of water-extractable element concentrations of the soil layer underneath the forest road from the control samples (p < 0.05). "-"...significantly lower, "+"...significantly higher.

	GA-W 15%	GA-W 30%	FBA-W 15%	FBA-W 30%
рН				-
EC		+	-	
DOC				+
Al			+	+
As			+	+
В			+	+
Ва			+	+
Ca			-	-
Cd				
Со			+	+
Cr			+	+
Cu				+
Fe			+	+
К				
Mg	-	+	-	-
Mn				+
Мо		+		
Na			+	+
Ni			+	+
Р				
Pb				+
Se				
V			+	+
Zn				
CI				
F				
NO ₂				
NO ₃ ⁻	+			
PO4 ³⁻				
SO4 ²⁻		+		

While the grate ash treatments only resulted in minor changes of element solubility the treatments with fluidized-bed ash, FBA-W 30% in particular, show increased solubility for most elements (especially metallic trace elements).



Figure 25: Averaged pH, EC, and DOC concentrations \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05). The red dotted lines represent legal thresholds for excavated soil given in Austrian legislation. <u>pH:</u> 6.5 – 11.

The pH value was significantly lower for FBA-W 30% in the upper soil layer (0-20 cm). GA-W 15% and FBA-W 15%, as well, resulted in a lower, yet not statistical significantly different, pH value. With a pH of 13.5 and 8.6 of GA-W and FBA-W respectively, a pH decrease cannot be attributed to the ash treatments, but solely to natural variability.

Significant differences to the control for electrical conductivity (EC) were found for GA-W 30% (higher EC) and FBA-W 15% (lower EC) in the lower soil layer (20-40 cm). The upper soil layer (0-20 cm) gives similar results, however without statistical significance (Figure 25). The high EC value of GA-W 30% can be attributed to Ca, K and Mg inputs to the subsoil. Statistical significance is only given for Mg (SI-Figure 35). The generally low EC value of the fluidized-bed ash samples is mainly associated with the significantly lower Ca concentrations. Low concentrations of K and Mg also play a considerable role.

The significantly higher concentration of Mo for GA-W 30% (SI-Figure 36) can be attributed to the high pH dependence of Mo solubility (Adriano, 2001).

The grate ash samples also showed increased solubility of NO_3^- for GA-W 15%, and SO_4^{-2-} for GA-W 30% (SI-Figure 41SI-Figure 42). The corresponding leachates of the forest road, however did not exhibit relevant increases in element concentration.

DOC was significantly higher in the FBA-W 30% sample in the upper soil layer (0-20 cm), the lower soil layer also showed higher values, yet not statistically significant (Figure 25). This finding is not explained by the increased leachate concentrations of the FBA-W samples (Figure 17), since the increased leachate concentrations of the GA-W samples did not result in higher DOC values of the corresponding sub-road samples. Furthermore, due to the low pH of FBA-W 30% sample one would anticipate lower DOC concentrations than in the sub-road sections constructed with GA-W (Kahl, et al., 1996). The result can therefore most likely be attributed to natural variability.

The water-extractable concentrations of AI and Fe were significantly higher for both application rates of FBA-W in the lower soil layer (20-40 cm). FBA-W 30% additionally showed significantly higher concentrations for Fe and considerable, yet not significantly, higher concentrations for AI in the upper soil layer (0-20 cm). Manganese concentrations were significantly higher for FBA-W 30% in both soil depths (Figure 26). The corresponding leachates of the road layer did not show relevant increases of element concentrations (Figure 18).

The higher solubility of AI, Fe and Mn is likely to be linked to the low pH of the soil sampling points (Figure 25) (Adriano, 2001).

Along with AI, Fe and Mn higher concentrations of As, B, Ba, Co, Cr, Cu, Ni, Pb and V were observed and are statistical significant in most cases (SI-Figure 32, SI-Figure 33, SI-Figure 34, SI-Figure 37, and SI-Figure 38).

Considering the fact, that the pure fluidized-bed ash (FBA-W) (Table 2) has lower total and water-extractable concentrations of all the above mentioned elements, except for Pb, than the grate ash (GA-W), higher solubility of these elements in the sub-road layer of the FBA-W treatment cannot be related to ash impacts, but rather reflect natural variability of the soil properties.

Since no legal limits were exceeded and no direct link between ash treatments and altered water-extractable element concentrations could be identified it can be concluded that in the full-scale field experiment, no environmental risk for the sub-road layer is present.



Figure 26: Averaged water-extractable concentrations of Al, Fe, and Mn \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).

4.2 Wood Ash Leaching Experiment

The wood ash leaching experiment should provide information about the leaching potential of fresh grate ash (GA) and fluidized-bed ash (FBA) and reveal the main characteristical differences in the leachate composition.

4.2.1 Comparison to legal limits

Figure 28 gives an overview of the averaged leachate concentrations for each water application step in relation to legal limits of Austrian Legislation. The same legal frameworks as defined in chapter 4.1.1 were applied. For the illustration of the legal limit exceedances the traffic light system, shown in Figure 27, was used.

- no threshold existent
- no exceedance of threshold/indicator value
- exceedance of indicator value $(DW_{in})/value$ indicating a trend reversal (GW_{tr})
- < 3 exceedance of DW_{th}/GW_{th}
- > 3 exceedance of DW_{th}/GW_{th}
- < 3 exceedance of threshold values of AAEV or AEVD (dir & indir)
- > 3 exceedance of threshold values of AAEV or AEVD (dir & indir)

Figure 27: Traffic light system for identification of legal limit exceedances for wood ash leaching experiment. DW_{in}/DW_{th} : Indicator value/threshold value of Austrian Drinking Water Regulation; GW_{tr}/GW_{th} : Value indicating a trend reversal/threshold value of Quality Target Ordinance – Groundwater; AAEV/AEVD (dir & indir): Threshold value for direct and indirect discharge of Austrian General Wastewater Directive/Austrian Wastewater Directive on landfill leachates.



Figure 28: Comparison of averaged concentrations of GA and FBA leachates (n=3) to legal limits given in Austrian Legislation. The identification of the legal limit exceedances is based on the traffic light system shown in Figure 27.

The varying number of water application steps is due to the fact that the wood ash leaching experiment for FBA was not conducted in the course of this master thesis, but for comparison taken from Kehrer (2012).

During the first two water application steps for GA and the first water application step for FBA no leachate could be recovered because the applied water was fully retained by the ash.

In Figure 28 a general decreasing trend in leachate concentration of most elements during the course of the experiments can be observed. The most evident difference between GA and FBA, concerning legal limits, are the high concentrations of Ba, Cr, Pb and Zn in the GA leachate and the high concentration of B in the FBA leachate. Selenium, F and P were not analyzed in the FBA leachates.

4.2.2 Leaching behavior

The leaching behavior of ash depends on its particle size distribution, pH, the L:S (liquid-tosolid) ratio and the temperature. Leachate concentrations are generally highest in the initial phase (Sarenbo, et al., 2009).

The test duration of the two leaching experiments was 176 and 64 days for GA and FBA, respectively. On GA a total of 110 L (L:S ratio = 5.5) and on FBA a total of 100 L (L:S ratio = 5) was applied.

The variation in test duration and L:S ratio limits the comparability of the two experiments, however should be adequate to identify general leaching trends.

A high temperature was observed during the first water application step in the barrels filled with GA caused by the exothermic reaction, taking place during the hydration of calcium oxide (see Equation 1).

EC and pH:

The pH and EC values of the different ashes as given in Table 4 are well represented in the leachates from the wood ash leaching experiment (Figure 29). A slightly decreasing trend during the course of the experiment can be observed for both ashes. The higher pH and EC value of GA is likely to be mainly caused by its higher content of Ca in the fresh ash (Table 4).

The pH value of both ashes exceeded all applied legal limits during the entire period of the experiment, indicating their persistent alkalinity after the application of about 100 liters of well water (corresponding to 1000 mm of rainfall). Similarly, the EC value of GA remained highly elevated after the water application. The EC value in the FBA leachate complied with the legal limits after the first half of the experiment.



Figure 29: Averaged pH and EC \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent legal limits given in Austrian legislation. <u>pH:</u> Indicator value of Austrian drinking water regulation DW_{in} = 6.5 - 9.5; <u>EC:</u> Indicator value of Austrian drinking water regulation DW_{in} = 2500 μ S cm⁻¹; Threshold value (GW_{th} = 2250 μ S cm⁻¹) and value indicating a trend reversal (GW_{tr} = 1875 μ S cm⁻¹) of Quality Target Ordinance-Groundwater.

DOC:

The DOC concentration in the two ash leachates showed a similar behavior and exceeded the threshold values of the Austrian Wastewater Directives ($AEVD_{dir} = 20 \text{ mg L}^{-1}$; $AAEV_{dir} = 25 \text{ mg L}^{-1}$) solely in the first collection step. Thereafter the concentration aligned to about 5 mg L⁻¹ and 3 mg L⁻¹ for GA and FBA, respectively. Based on the high pH value of the ashes the remaining DOC from the ashes was quickly leached with the application of the first 20 L of well water.



Figure 30: Averaged concentration of DOC \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent the threshold values for direct discharge of the Austrian Wastewater Directive on landfill leachates (AEVD_{dir} = 20 mg L⁻¹) and the Austrian General Wastewater Directive (AAEV_{dir} = 25 mg L⁻¹).

Macroelements: Ca, K, Mg, Na, P

Calcium, K, Mg, Na and P are important plant nutrients and abundant in wood ash (Demeyer, et al., 2001).

The Ca concentration in the wood ash leachates of GA and FBA showed dissimilar behavior. While the Ca concentration in the FBA leachate was steadily decreasing from initially 550 mg L⁻¹ to about 50 mg L⁻¹ in the last collection steps, the GA leachate showed an increasing trend of Ca concentration with repeated water application. The different pattern may be caused by the different forms of calcium present in the fresh ashes. Based on the varying combustion techniques and temperatures calcium may be present in the form of calcium oxide (CaO), portlandite (Ca(OH)₂), calcite (CaCO₃), calcium silicates and calcium aluminium silicates. Calcium oxide and portandite are the dominating species (Steenari, et al., 1999a).

The leaching behavior of GA might be explained by a high content of CaO, which needed to be hydrated in an exothermic reaction (Equation 1) before leaching as portlandite (Sarenbo, et al., 2009).

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

Equation 1: Hydration of calcium oxide

Additionally to the delayed Ca leaching from GA, the retention of the water from the first two application steps could be explained by this reaction. The observed temperature rise (up to about 60° C; estimation) of the barrels after the first water application confirms the reaction.

In contrast to GA, the leaching behavior of FBA might be explained by big proportions of Ca that were present in the form of readily leachable portlandite $(Ca(OH)_2)$ in the fresh ash. Moreover, a temperature rise during the experiment was not reported (Kehrer, 2012).

The alkalimetals, K and Na, showed a similar behavior for both ashes, however the leachate concentrations were about tenfold lower for FBA. The high initial leaching of the elements is due to their presence in the form of highly soluble species bound as sulfates and chlorides (Ulery, et al., 1993; Demeyer, et al., 2001, Sarenbo, et al., 2009). A strong correlation between the K and Na concentrations and the EC value in the ash leachates is observable.

The GA leachate exceeded the indicator value of the Austrian drinking water regulation for Na $(DW_{in} = 200 \text{ mg L}^{-1})$ during the first six application steps. The above described temperature rise was also induced by the exothermal dissolution reaction of sodium hydroxide in water.

The leachate concentrations of Mg were low for both ashes and are therefore not discussed in further detail. Phosphorus was only measured in the GA leachates, where it showed a low leaching rate (SI-Figure 45). Low leaching rates from wood ashes for Mg and P have also been reported by Steenari, et al., (1999a).



Figure 31: Averaged concentration of Ca, K, Mg and Na \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted line in the graph, showing Na, represents the indicator value of Austrian drinking water regulation DW_{in} = 200 mg L⁻¹.

Fe, Mn and Al:

Iron concentration showed dissimilar behavior in GA and FBA leachates and correlate well with the leachate concentrations of Ca for both ashes. FBA showed high initial leaching and exceedance of the threshold value of the Austrian General Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹) in the first two steps. After the application of 50 L the Fe concentration dropped below the indicator value of the Austrian drinking water regulation (DW_{in} = 0.2 mg L⁻¹). The leachates of GA, however, showed increasing Fe concentrations with repeated water application.

Similarly to Ca, Fe might be present in various different species, depending on the applied combustion technique. After water application the present iron oxides are suspected to form hydroxides, which are only slightly soluble (Steenari, et al., 1999a). The different leaching behavior can therefore be attributed to varying iron speciation.

The similar leaching pattern of Fe and Ca is likely to be based on the strong affinity of iron to precipitate on calcium compounds (Kabata-Pedias, 2011).

Aluminium, as well, showed a dissimilar leaching behavior for the two ashes. Here, in contrast to Fe however, GA showed high initial leaching and Al concentrations in the FBA leachates steadily increased over time. The indicator value of the Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$) was exceeded in most leachate samples of both ashes.

The increasing AI concentrations in FBA leachates might have been caused by the decreasing trend of pH as seen in Figure 29.

Manganese leaching rates were low and correlate well with the leachate concentrations of K and Na for both ashes. No legal limits were exceeded. The leaching rates of Mn from GA were ten-fold higher than that of FBA.



Figure 32: Averaged concentration of AI, Fe and Mn \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent legal limits given in Austrian legislation. <u>Fe:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.2 mg L⁻¹; Threshold values for direct discharge of the Austrian General Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹); <u>AI:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.2 mg L⁻¹; Threshold values for direct discharge of the Austrian General Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹); <u>AI:</u> Indicator discharge of the Austrian General Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹).

As and B:

The easily-soluble fractions of As and B leached from the GA during the first few steps of water application. Only the first collected GA leachate exceeded the legal limits for As and B. Thereafter, concentrations were very low and even dropped below the LOQ ($5.4 \times 10^{-5} \text{ mg L}^{-1}$) in case of As. The high initial leaching of As and B may be attributed to high leachate concentrations of Cl⁻ and SO₄²⁻ (Figure 36) and accompanied anion competition for positively charged exchange sites (Adriano, 2001).

Arsenic concentrations in the FBA leachates were rather stable with a concentration around 0.001 mg L^{-1} and are of no concern regarding water quality. The slight offset, observable at a water application of 60 L, is due to analytical reasons (Kehrer, 2012).

Boron concentrations in the FBA leachates exceeded the legal limits given in Austrian legislation ($DW_{th} = 1 \text{ mg } L^{-1}$, $GW_{th} = 0.9 \text{ mg } L^{-1}$, $GW_{tr} = 0.75 \text{ mg } L^{-1}$) during the entire experiment. However, with further water application their compliance would be expected. High B concentrations for FBA are in accordance with higher concentrations, measured in the fresh ash (Table 4).



Figure 33: Averaged concentration of As and B \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent legal limits given in Austrian legislation. <u>As:</u> Value indicating a trend reversal of the Quality Target Ordinance-Groundwater GW_{tr} = 0.0075 mg L⁻¹; <u>B:</u> Indicator value of Austrian drinking water regulation DW_{in} = 1 mg L⁻¹; Threshold value (GW_{th} = 0.9 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.75 mg L⁻¹) of Quality Target Ordinance-Groundwater.

Cr, Mo, Pb, Se:

Chromium, Mo, Pb and Se showed a similar pattern as the concentrations of K, Na and Mn (Figure 31 and Figure 32) in the wood ash leachates.

Cadmium, Cu and V had a similar leaching behavior, however their concentrations were not of environmental concern and therefore not discussed in further detail (SI-Figure 44 and SI-Figure 45).

Chromium concentrations exceeded the threshold values of the Austrian Wastewater Directive $(AEVD_{dir} = AEVD_{indir} = AAEV_{dir} = AAEV_{indir} = 0.5 \text{ mg L}^{-1})$ in the first two GA leachates. Thereafter, concentrations remained higher than the legal limits for drinking water and groundwater given in Austrian legislation (DW_{th} = 0.05 mg L⁻¹, GW_{th} = 0.045 mg L⁻¹, GW_{tr} = 0.0375 mg L⁻¹). In the last sampling steps they complied with water quality requirements. The leachates of FBA solely exceeded the legal limits of drinking water and groundwater in the first sampling step. Thereafter, concentrations were negligibly small.

Molybdenum showed similar concentrations for both ashes, they dropped below the WHO drinking water guideline value (0.07 mg L^{-1}) after high initial leaching.

Lead concentrations were highly elevated in the GA leachates compared to the FBA leachates. The high initial concentration of 188 mg L⁻¹ for GA dropped quickly to about 40 mg L⁻¹ and thereafter slowly decreased near to the threshold value of Austrian drinking water regulation ($DW_{th} = 0.01 \text{ mg L}^{-1}$). With further water application the compliance of water quality requirements would be expected. Lead leaching from GA may be due cation competition with K and Na for exchange sites (Figure 31) and the formation of Pb-DOC (Figure 30) complexes (Adriano, 2001). In the FBA leachates Pb was only present in negligible small concentrations near the LOQ ($1.5 * 10^{-5} \text{ mg L}^{-1}$).

Selenium was only measured in the leachates of GA. After high initial leaching it aligned to the threshold value of Austrian drinking water regulation ($DW_{th} = 0.01 \text{ mg L}^{-1}$) during the end of the experiment, however remained elevated throughout the entire test duration. Similar to Pb the compliance of water quality requirements would be expected with further water application.

The leaching pattern the oxyanions Cr Mo, and Se may be mainly attributed to anion competition with DOC (Figure 30) and SO_4^{2-} (Figure 36) (Adriano, 2001).



Figure 34: Averaged concentration of Cr, Mo, Pb and Se \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent legal limits given in Austrian legislation. <u>Cr</u>: Threshold value of Austrian drinking water regulation DW_{th} = 1 mg L⁻¹; Threshold values for direct and indirect discharge of the Austrian Wastewater Directive on landfill leachates and the Austrian General Wastewater Directive (AAEV_{dir} = AAEV_{indir} = AEVD_{dir} = AAED_{indir} = 0.05 mg L⁻¹). <u>Mo</u>: WHO guideline values for drinking–water quality = 0.7 mg L⁻¹; <u>Pb</u>: Threshold value of Austrian drinking water regulation DW_{th} = 0.01 mg L⁻¹; Threshold value (GW_{th} = 0.009 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.0075 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>Se</u>: Threshold value of Austrian drinking water regulation DW_{th} = 0.01 mg L⁻¹.

Ba, Co, Ni, Zn:

Barium, Co, Ni and Zn showed a similar pattern as the concentrations of Ca and Fe (Figure 31, Figure 32) in the corresponding leachates. Especially for GA the similarity is well pronounced.

The trace elements seemed to be sorbed by Fe oxides, which precipitated on calcium compounds and conjointly leached from the ash (Kabata-Pendias, 2011). Additionally, cation competition mainly with Ca may have played a considerable role for the leaching pattern of Ba, Co, Ni and Zn (Adriano, 2001).

The leachates of GA exceeded the threshold values of the Austrian Wastewater Directive after a strong initial increase for Ba ($AAEV_{dir} = AAEV_{indir} = 5 \text{ mg L}^{-1}$) and Zn ($AEVD_{dir} = AEVD_{indir} = 0.5 \text{ mg L}^{-1}$). Their concentrations were low for FBA and only showed a marginal exceedance of the WHO guideline value (0.7 mg L⁻¹) for Ba during step 4 to 8.

Nickel concentrations were low in the FBA leachates. In the GA leachates Ni exceeded the value, indicating a trend reversal ($GW_{tr} = 0.015 \text{ mg L}^{-1}$) in groundwater, solely in one step. Nickel concentrations remained below the threshold value of Austrian Drinking water regulation ($DW_{th} = 0.02 \text{ mg L}^{-1}$) at all times.

Cobalt was of no concern regarding water quality.



Figure 35: Averaged concentration of Ba, Ni and Zn \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent legal limits given in Austrian legislation. <u>Ba</u>: Threshold values for direct and indirect discharge of the Austrian General Wastewater Directive (AAEV_{dir} = AAEV_{indir} = 5 mg L⁻¹); WHO guideline values for drinking–water quality = 0.7 mg L⁻¹; <u>Ni</u>: Value indicating a trend reversal of Quality Target Ordinance-Groundwater GW_{tr} = 0.015 mg L⁻¹; <u>Zn</u>: Threshold values for direct and indirect discharge of the Austrian Wastewater Directive on landfill leachates (AEVD_{dir} = AAED_{indir} = 0.5 mg L⁻¹).

Anions:

Anion concentrations were rapidly decreasing in the ash leachates and complied with the legal water quality limits at the latest after a water application of 40 L. Thereafter concentrations were very low.

Nitrite, however, showed a slightly slower decrease and dropped below the threshold value of Austrian drinking water regulation ($DW_{th} = 0.1 \text{ mg L}^{-1}$) after a water application of 50 L. Despite compliance, except for one leachate step of FBA, concentrations remained near the legal limits throughout the entire test duration.

High concentrations of nitrite in the leachates were unexpected since N should be fully oxidized in a complete combustion process and only be present in the ash in negligible concentrations. Optimization of the combustion process could effectively decrease N concentrations in the ashes and thus associated nitrite leaching (Demeyer, et al., 2001).

The high initial leaching of Cl^{-} and SO_4^{2-} can be attributed to their presence in the form of readily water soluble salts (Steenari, et al., 1999b).

Expect for phosphate the anion concentrations were permanently higher in the leachates of GA.

The leaching behavior of phosphate and sulfate is in contrast to the results of the ash analysis (Table 4).



Figure 36: Averaged concentration of Cl, F, NO₃, NO₂, SO₄² and PO₄³ ± SE in GA and FBA leachates from wood ash leaching experiment (n=3). The red dotted lines represent legal limits given in Austrian legislation. <u>Cl</u>: Indicator value of Austrian drinking water regulation DW_{in} = 200 mg L⁻¹; Threshold value (GW_{th} = 180 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 150 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>F</u>: Threshold value of Austrian drinking water regulation DW_{th} = 1.5 mg L⁻¹; <u>NO₂</u>: Threshold value of Austrian drinking water regulation DW_{th} = 0.1 mg L⁻¹; <u>SO₄²⁻</u>: Threshold values of Austrian General Wastewater Directive (AAEV) for indirect discharge AAEV_{indir} = 200 mg L⁻¹; Indicator value of Austrian drinking water regulation DW_{in} = 250 mg L⁻¹; Threshold value (GW_{th} = 225 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 187.5 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>PO₄³⁻</u>: Threshold value (GW_{th} = 0.3 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 187.5 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>PO₄³⁻</u>: Threshold value (GW_{th} = 0.3 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 187.5 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>PO₄³⁻</u>: Threshold value (GW_{th} = 0.3 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 187.5 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>PO₄³⁻</u>: Threshold value (GW_{th} = 0.3 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.225 mg L⁻¹) of Quality Target Ordinance-Groundwater.

4.3 Soil Column Experiment

To obtain information about the response (buffering, filtering and mobilization processes) of different soils when exposed to the application of wood ash leachate we applied the leachates of GA and FBA, obtained in the Wood Ash Leaching experiment (see 4.2), on the three different experimental soils (S1, S2 and S3). As a control we additionally applied artificial rainwater.

The results of the soil column experiment cannot be directly related to the full-scale field experiment, due to the largely different experimental conditions described in the following:

- The applied ash leachate represents a repeated source of element input. Thus, no decreasing ash effect can be expected.
- The high leachate application rate corresponds to an extreme rainfall event (210 L m⁻² in 3-4 days). This can lead to reducing conditions in the soil columns, altering element mobility.
- The leachates were collected underneath the pure soil and not underneath a soil-ash layer as in the full-scale field experiment.

The soil column experiment can therefore only provide general information of soil responses to wood ash application and cannot directly be used for assessing the risk of groundwater contamination.

4.3.1 Comparison to legal limits

Figure 38, Figure 39 and Figure 40 show the averaged concentrations of the soil column leachates of S1, S2 and S3 in relation to legal limits given in Austrian Legislation. The same legal frameworks as defined in chapter 4.1.1 were applied. For the illustration of the legal limit exceedances the traffic light system, shown in Figure 37, was used.

no threshold existent no exceedance of threshold/indicator value

exceedance of indicator value $(DW_{in})/value$ indicating a trend reversal (GW_{tr})

- < 3 exceedance of DW_{th}/GW_{th}
- > 3 exceedance of $\text{DW}_{\text{th}}/\text{GW}_{\text{th}}$
- < 3 exceedance of threshold values of AAEV or AEVD (dir & indir)
- > 3 exceedance of threshold values of AAEV or AEVD (dir & indir)

Figure 37: Traffic light system for identification of legal limit exceedances in the soil column experiment. DW_{in}/DW_{th} : Indicator value/threshold value of Austrian Drinking Water Regulation; GW_{tr}/GW_{th} : Value indicating a trend reversal/threshold value of Quality Target Ordinance – Groundwater; AAEV/AEVD (dir & indir): Threshold value for direct and indirect discharge of Austrian General Wastewater Directive/Austrian Wastewater Directive on landfill leachates.

The comparison allows a first, rough estimation of the behavior of the different soils and ash leachates. A general decrease of ash impact with increasing soil pH (S1<S2<S3) is observable. Additionally the more pronounced impact of GA, in comparison to FBA, is evident. Especially, the GA treatment on S1, the acidic soil, results in numerous threshold exceedances.



Figure 38: Comparison of the averaged concentrations in the soil column leachates of S1 (n=2) to legal limits given in Austrian Legislation. The identification of the legal limit exceedances is based on the traffic light system shown in Figure 37.



Figure 39: Comparison of the averaged concentrations in the soil column leachates of S2 (n=2) to legal limits given in Austrian Legislation. The identification of the legal limit exceedances is based on the traffic light system shown in Figure 37.



Figure 40: Comparison of the averaged concentrations in the soil column leachates of S3 (n=2) to legal limits given in Austrian Legislation. The identification of the legal limit exceedances is based on the traffic light system shown in Figure 37.

4.3.2 Leachate

Table 11 gives the characteristics of the composite leachate samples, collected in the Wood Ash Leaching experiment and used in the Soil Column experiment.

Characteristic	Unit	GA	FBA	Characteristic	Unit	GA	FBA
рН		12.9	11.9	Mn		0.004	< 0.001
EC	mS cm⁻¹	25688	2866	Мо		0.096	0.045
DOC		10.2	5.14	Na	mg L ⁻¹	343	23
AI		0.515	0.396	Ni		0.001	0.001
As		0.001	0.001	Р		0.10	n.a.
В		1.51	2.56	Pb		0.066	< 0.001
Ba		5.29	0.525	Se		0.118	n.a.
Ca		91.3	164	v		0.003	0.001
Cd	mg L ⁻¹	0.001	< 0.001	Zn		0.283	0.001
Со		0.000	< 0.001	Cl		294	1.45
Cr		1.78	0.001	F		0.498	n.a.
Cu		0.016	0.002	NO ₂ ⁻		2.62	0.207
Fe		0.443	0.664	NO ₃ ⁻		6.76	1.14
к		4488	204	PO ₄ ³⁻		0.05	28.1
Mg		0.014	0.039	SO ₄ ²⁻		1313	132

Table 11: Characteristics of composite leachate samples of GA and FBA for Soil Column Experiment

EC and pH:

The pH of the control treatments (artificial rainwater) reflects the differing pH values of the experimental soils (Table 5). A statistically significant ash effect could only be observed in the leachates of the neutral soil, S2. FBA showed a strongly elevated pH, exceeding the indicator value of Austrian drinking water regulation (DW_{in} = 9.5) in the first sampling step. Thereafter the leachate quickly aligned to a pH of around 8. GA, in contrast, showed a slow increase in the first sampling steps and aligned with FBA during the second half of the experiment. The dissimilar behavior of the two ashes can be attributed to their different concentrations of Ca. K and Mg (Table 4). FBA has a considerable higher concentration of highly soluble K, which is responsible for a fast change in pH. GA, however, has a higher concentration of rather slowly-soluble Ca, responsible for slower but more persistent pH change in soils (Demeyer, et al., 2001). Such pattern of K and Ca was only partly found in the wood ash leaching experiment (Figure 31), however, could be shown in the soil column leachate of S2 (Figure 44).

The acidic soil, S1, has leachates with pH values below the indicator value of Austrian drinking water regulation ($DW_{in} = 6.5$). However, this low pH is caused by the soil itself (pedogenic) and therefore not considered problematic. In the second half of the experiment the leachate of GA showed increased, yet not significantly different, pH values.

Interestingly, the leachates from the alkaline soil showed slightly lower pH values for both ash treatments, however without statistical significance.

Generally, the high pH value of the wood ash leachates was well buffered by all three soils during the soil passage. On S1, however, the elevated pH of the GA leachate may be attributed to the exceedance of the buffer capacity of the soil.



Figure 41: Averaged pH and EC \pm SE in the soil column leachates on S1, S2, and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted lines represent legal limits given in Austrian legislation. <u>pH</u>: Indicator value of Austrian drinking water regulation DW_{in} = 6.5 – 9.5; <u>EC</u>: Indicator value of Austrian drinking water regulation DW_{in} = 2500 μ S cm⁻¹; Threshold value (GW_{th} = 2250 μ S cm⁻¹) and value indicating a trend reversal (GW_{tt} = 1875 μ S cm⁻¹) of Quality Target Ordinance-Groundwater.

The application of GA leachate resulted in significantly increased EC values in the leachates of all three soil columns. The effect was most prominent for S1, followed by S2 and S3. The lower buffering capacity of S1, with respect to EC, can be attributed to its high content of sand in comparison to S2 and S3 (Table 5).

The leachate of S1 after GA application exceeded the legal limits of drinking water and groundwater (DW_{th} = 2500 μ S cm⁻¹, GW_{th} = 2250 μ S cm⁻¹, GW_{tr} = 1875 μ S cm⁻¹) during the last sampling steps.

DOC:

The soil column lechates exceeded the threshold values of Austrian Wastewater Directive (AAEV_{dir} = 25 mg L⁻¹, AEVD_{dir} = 20 mg L⁻¹) throughout the entire test duration for all 3 treatments. The control treatment and FBA treatment did not show statistically different concentrations. The GA treatment, however, resulted in strongly increased DOC concentrations, especially for S1 and S2. The concentration of the applied ash leachates was low and accounted for 10 mg L⁻¹ and 5 mg L⁻¹ for GA and FBA, respectively. Hence, the high DOC concentration originated from the soils and not from the ash input. As described in chapter 4.1.1.2 organic matter is mobilized from the soil layer due to the elevated pH value and related loss of positively charged soil surfaces (Kahl, et al., 1996). The strong pH effect of GA (Figure 41) and the high DOC concentration of S2 (Table 5) are in accordance with the observed results.



Figure 42: Averaged concentration of DOC \pm SE in the soil column leachates on S1, S2, and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted lines represent the threshold values for direct discharge of the Austrian Wastewater Directive on landfill leachates (AEVD_{dir} = 20 mg L⁻¹) and the Austrian General Wastewater Directive (AAEV_{dir} = 25 mg L⁻¹). Mind the different scales.

<u>Fe, Mn, Al:</u>

Iron concentrations marginally exceeded the indicator value of Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$) for the control and the FBA treatment in most sampling steps. Significant differences of FBA to the control were found for S2 and S3, however concentrations remained relatively low. The GA treatment, in contrast, showed strongly increased Fe concentrations, especially for S1. Here, the threshold value of the Austrian Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹) was clearly exceeded. With a concentration of only 0.44 mg L⁻¹ in the input leachate of GA the mobilizing ash effect is evident. A similar effect of GA on the mobilization of Fe has been observed in the full-scale field experiment (Figure 18).

In contrast to the full-scale field experiment big proportions of Fe were not mobilized from S1 due to hydrolysis at high pH but can rather be attributed to cation competition with K and Na, originating from the input leachate. Complexation of Fe with DOC might have additionally contributed to high Fe concentrations in the leachates of S1 and S2, treated with GA (Scheffer, et al., 2010).

Manganese was leached out of the acidic (S1) and neutral (S2) soil to a large extent, independent of the treatment. However, for FBA a strong increase of Mn leaching from S2 was found towards the end of the experiment. The indicator value of Austrian drinking water regulation ($DW_{in} = 0.05 \text{ mg L}^{-1}$) was exceeded in most leachates of S1 and S2. The alkaline soil (S3) showed low Mn concentrations in the control leachates. During the last sampling steps the Mn concentration of the GA leachate was quickly increasing, also confirmed by statistical significance.

Al concentrations decreased markedly in the order S1>S2>S3 for all three treatments. The leachates of S1 had mean concentrations of around 1.5 mg L⁻¹ (exceedance of the indicator value of Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$)) for the control and the FBA treatment. The GA treatment resulted in the mobilization of vast amounts of Al from the soil, yielding in concentrations up to 80 mg L⁻¹. In comparison, the threshold value of the Austrian Wastewater Directive AAEV_{dir} is 2 mg L⁻¹. On S2 the FBA leachate showed increased concentrations only in the first two steps, thereafter Al concentrations were near the indicator value of Austrian drinking water regulation ($DW_{in} = 0.2 \text{ mg L}^{-1}$) for all three treatments. The leachate concentrations of S3 remained below 0.2 mg L⁻¹ during all sampling steps.

Similar to Fe, high leachate concentrations of Al from S1, treated with GA, are mainly due to cation competition with K and Na, originating from the input leachate. DOC complexation might have also played a role in the solubilization of Al from S1 (Scheffer, et al., 2010).

Generally it can be stated that the solubility of Fe, Mn and Al decreases, with increasing soil pH, in the order, S1>S2>S3 (acidic>neutral>alkaline) (Figure 41 and Figure 43). Additionally, S3 has a considerably higher CEC than S1 and S3. Furthermore, S1 has by far the highest sand and lowest clay concentration of the three experimental soils (SI-Table 1).



Application steps

Figure 43: Averaged concentration of Fe, Mn and AI \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted lines represent legal limits given in Austrian legislation. <u>Fe:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.2 mg L⁻¹; Threshold values for direct discharge of the Austrian General Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹); <u>Mn:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.05 mg L⁻¹; <u>Al:</u> Indicator value of Austrian General Wastewater Directive (AAEV_{dir} = 2 mg L⁻¹); <u>Mn:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.2 mg L⁻¹. Mind the different scales.

<u>Ca, K, Mg, Na:</u>

The Ca concentrations of the control treatments represent the pH values of the soils by showing an increase in the order S1<S2<S3. In S1 most of the Ca input was retained in the soil. S2 and S3 showed significantly elevated Ca concentrations for GA and FBA.

The high K concentrations caused by the GA treatment on S1 is very evident, here big proportions of the K input (concentration of composite leachate sample was 4488 mg L^{-1}) were leached through the soil. Significantly elevated K concentrations were also found in the GA and FBA leachates of S2 and S3, however, at considerably lower concentrations.

Magnesium did not show significant differences in the leachates of S1. In S2 and S3 the application of pure GA and FBA leachates resulted in significantly increased Mg concentrations, especially pronounced for GA on S2.

Sodium concentrations were significantly increased in the leachates of S1 and S3. On the acidic soil the GA treatment resulted in a strong increase of Na leaching with the exceedance of the indicator value of Austrian drinking water regulation ($DW_{in} = 200 \text{ mg L}^{-1}$) during the last sampling steps. A similar effect of GA was present in the leachates of S3, however, delayed in time and with lower Na concentrations. The FBA treatment resulted in constantly elevated concentrations of around 50 mg L⁻¹ throughout the experiment.

The four elements showed a similar pattern as the EC of the leachates of the three soils and acted as the main factors for pH changes.

Generally, grate ash showed a higher effect on the leachate concentrations of Ca, K, Mg, and Na than FBA (Figure 44).



Figure 44: Averaged concentration of Ca, K, Mg and Na \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted line in the graph, showing Na, represent the indicator value of Austrian drinking water regulation DW_{in} = 200 mg L⁻¹. Mind the different x-axis scales for K.

Trace elements: As, B and Ni:

These three trace elements have been identified as potentially critical characteristics in the fullscale field experiment (Figure 15) and are therefore here discussed in further detail.

Arsenic showed statistically increased leachate concentrations solely on the neutral soil (S2) for both ash treatments. However, the effect of GA was well observable on S1, as well. The GA treatment resulted in rising leachate concentrations, exceeding the legal limits (DW_{th} = 0.01 mg L⁻¹, GW_{th} = 0.009 mg L⁻¹, GW_{tr} = 0.0075 mg L⁻¹) after the first few application steps on S1 and S2. Despite statistical significance the FBA treatment on S2 only exceeded the legal limits in the first sampling step and thereafter aligned with the control treatment. The leaching pattern of GA on S1 can be attributed to high concentrations of DOC, which is known to strongly compete with As for sorption sites. Concomitant leaching of As, sorbed to Al and Fe oxides, was an additional effect and was confirmed by the similarity of the leaching curves (Figure 43). The high leaching rate of As, induced by GA on S2, however, is mainly affected by high leachate concentrations of PO₃⁴⁻ (Figure 47) and associated As-anion competition for positively charged exchange sites (Adriano, 2001; Alloway, 2012). The observed higher leaching of As in response to GA is in contrast to the results of the full-scale experiment, where higher leachate concentrations were found for the FBA treatment.

The applied wood ash leachates represented a relatively high B input with a concentration of 1.51 mg L⁻¹ and 2.56 mg L⁻¹ for GA and FBA, respectively. The control treatment resulted in low leachate concentrations during the entire test duration. The GA and FBA treatments showed significantly increased concentrations on S1 and S2, with higher values for FBA. Here, the legal water quality limits (DW_{th} = 1 mg L⁻¹, GW_{th} = 0.9 mg L⁻¹, GW_{tr} = 0.75 mg L⁻¹) were exceeded in many sampling steps. The B input was best buffered by S3, where leachate concentrations comply with legal limits and did not significantly differ from the control. The bigger effect of FBA on B concentrations is in accordance with the findings of the full-scale field experiment (Figure 21).

The Ni concentrations of the leachates of the control and FBA treatment did not significantly differ and remained below the legal water quality limits. Solely on S2 the FBA treatment resulted in Ni concentrations exceeding the legal water quality limits in the last two sampling steps. The GA treatment, in contrast, resulted in significantly increased Ni leaching on S1 and S3. Here, the legal water quality limits (DW_{th} = 0.02 mg L⁻¹, GW_{th} = 0.018 mg L⁻¹, GW_{tr} = 0.015 mg L⁻¹) were exceeded during the last two thirds of the experiment. The low Ni input (GA = 0.0011 mg L⁻¹; FBA = 0.0007 mg L⁻¹) shows the strong mobilizing effect on soil-borne Ni of the wood ash leachates.

The high Ni concentrations in the leachate of S1, treated with GA, may be mainly attributed to the co-dissolution of Ni associated with Mn oxides (Scheffer, et al., 2010), whereas complexation with DOC appears to be of little importance.

High Ni leaching on S3 might have been enhanced by the high Ni concentration of the soil (SI-Table 1) and its replacement with Ca (additionally: K, Na and Mg) by cation competition.



Application steps

Figure 45: Averaged concentration of As, B and Ni \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted lines represent legal limits given in Austrian legislation. <u>As:</u> Indicator value of Austrian drinking water regulation DW_{in} = 0.01 mg L⁻¹; Threshold value (GW_{th} = 0.009 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.0075 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>B:</u> Indicator value of Austrian drinking water regulation DW_{in} = 1 mg L⁻¹; Threshold value (GW_{th} = 0.9 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.75 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>Ni:</u> Threshold value of Austrian drinking water regulation DW_{th} = 0.02 mg L⁻¹; Threshold value (GW_{th} = 0.018 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.015 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>Ni:</u> Threshold value (GW_{th} = 0.018 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.015 mg L⁻¹) of Quality Target Ordinance-Groundwater; <u>Ni:</u> Threshold value (GW_{th} = 0.018 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.015 mg L⁻¹) of Quality Target Ordinance-Groundwater.

Other trace elements:

The GA treatment resulted in highly increased concentrations of Ba, Cd, Co, Cr, Pb, V, W, and Zn in the leachates of the acidic soil (S1). Barium, Cd, Pb, and Zn exceeded the corresponding legal water quality limits (SI-Figure 48, SI-Figure 49, SI-Figure 51). For all other soils and treatments the concentrations of these elements remained low.

One possible explanation for this pattern is the low buffering and filtering capacity of S1, based on its low clay content and low cation exchange capacity (Table 5). The GA treatment represented a high input of Ba, Cr, and Zn (Table 11) which could not be buffered effectively by the soil.

Cadmium, Co, Pb, V, W, and Zn were mobilized from the soil. Possible mechanism of their mobilization include complex formation of cations (Cd, Co, Pb, and Zn) with SO_4^{2-} and DOC, cation exchange with ash-derived Ca, and anion competition between anions from the ash leachates (+ DOC anion competition) and the oxyanions of V and W. (Adriano, 2001; Scheffer, et al., 2010).

<u>Anions:</u>

Chloride concentrations remained well below the indicator value of Austrian drinking water regulation ($DW_{in} = 200 \text{ mg L}^{-1}$) for all treatments and soils. Elevated chloride concentrations of GA, as shown in SI-Figure 52, were also found in the wood ash leaching experiment (Figure 36).

Similar to the full-scale field experiment, a relevant ash effect on the fluoride concentrations of the leachates was not found (SI-Figure 52).

Nitrite concentrations were significantly increased only on S2. Here the control treatment complied with the threshold value of Austrian drinking water regulation ($DW_{th} = 0.1 \text{ mg L}^{-1}$) and the threshold value of the Austrian Wastewater Directive ($AAEV_{dir} = 1 \text{ mg L}^{-1}$) for all sampling steps. Whereas the FBA treatment showed strongly increased nitrite concentrations almost throughout the entire test duration, the GA treatment resulted in elevated nitrite concentrations solely during the application steps 4 - 7. On S1 and S3 the leachate concentrations of nitrite of all three treatments clearly exceed the legal limits. High nitrite concentrations could be owed to partly reducing conditions in the soil columns.

Nitrate concentrations were significantly increased by the GA treatment only on S3, where the threshold value of Austrian drinking water regulation ($DW_{th} = 50 \text{ mg L}^{-1}$) was exceeded in the first half of the experiment. Based on the high water-extractable nitrate concentration of S1 (SI-Table 1) the high leachate concentrations for all treatments were as expected.

The increase of nitrite and nitrate can be attributed to the pH rising effect of the ash and the induced enhanced nitrification processes (Pitman, et al., 2006).



Figure 46: Averaged concentration of NO₂⁻ and NO₃⁻ ± SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted lines represent indicator or threshold values of Austrian legislation. <u>NO₂⁻</u>: Threshold value of Austrian drinking water regulation DW_{th} = 0.1 mg L⁻¹; Threshold value for direct discharge of the Austrian Wastewater Directive (AAEV_{dir} = 1 mg L⁻¹); <u>NO₃⁻</u>: Threshold value of Austrian drinking water regulation DW_{th} = 50 mg L⁻¹. Mind the different scales.

The GA treatment resulted in significantly elevated phosphate concentrations on S1 and S2. On S3 an increase was also found, however without statistical significance. The legal limits for groundwater given in Austrian legislation ($GW_{th} = 0.3 \text{ mg L}^{-1}$, $GW_{tr} = 0.225 \text{ mg L}^{-1}$) were strongly exceeded. The FBA treatment only resulted in concentrations slightly above the legal thresholds on S2. High phosphate loads of S2 can be attributed to its high water-extractable concentrations (SI-Table 1). Phosphate was likely mobilized from the soil via anion competition with DOC (Figure 49) (Guppy, et al., 2005).

Sulfate concentrations were slightly increased by GA and strongly increased by FBA. Statistical significance is given for both treatments on all soils. On S1 and S3 the FBA treatment resulted in steadily rising concentrations, which finally approached given threshold values. On S2 sulfate concentrations exceeded the threshold value of the Austrian Wastewater Directive (AAEV_{indir} = 200 mg L⁻¹), yet remained below the threshold value of Austrian drinking water regulation (DW_{th} = 250 mg L⁻¹) for the entire test duration. Increased sulfate concentrations were also found in the leachates of the road sections constructed with FBA.



Figure 47: Averaged concentration of PO_4^{3-} and $SO_4^{2-} \pm SE$ in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). The red dotted lines represent legal limits given in Austrian legislation. $\underline{PO_4^{3-}}$: Threshold value (GW_{th} = 0.3 mg L⁻¹) and value indicating a trend reversal (GW_{tr} = 0.225 mg L⁻¹) of Quality Target Ordinance-Groundwater; $\underline{SO_4^{2-}}$: Threshold values of Austrian General Wastewater Directive (AAEV) for indirect discharge AAEV_{indir} = 200 mg L⁻¹; Indicator value of Austrian drinking water regulation DW_{in} = 250 mg L⁻¹. Mind the different scales.
4.3.3 Water-extractable concentrations of the soil columns

Similarly to the soil sampling of the full-scale field experiment we tested the dismantled soil columns for their water-extractable concentrations. Analysis was done in two sampling depths. We compared the water-extractable concentrations to the legal thresholds for excavated soil given in Austrian legislation (Deponieverordnung, 2008).

The soil columns exceeded the legal limits of pH, EC, DOC, Ba and PO₄³⁻. The ash influence was found to generally decrease with increasing soil depth. GA had a stronger influence on the water-extractable element concentrations in the soil columns and was responsible for almost all threshold value exceedances.

All other characteristics are shown in SI-Figure 54 to SI-Figure 62.

EC and pH:

As expected, the GA treatment resulted in increased pH and EC values in the soil columns of all three soils. On the alkaline soil the pH exceeded the legal limit with a value of 11.3 in the upper part of the soil column (0-10 cm soil depth). In the lower part (10-20 cm), however, the pH effect of the ash was already well buffered and did not show a significant difference to the control. The EC exceeded the legal limit of 150 μ S cm⁻¹ in the upper part of all three soil columns and in the lower part of S2 and S3. Especially high values were found in the alkaline soil. The relatively low EC value of the corresponding leachate (Figure 41) confirms the high buffering capacity of this soil. The FBA treatment did not show a relevant increase of pH or EC in the soil columns.



Figure 48: Averaged pH and EC \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).

DOC:

The GA treatment resulted in increased DOC concentrations in the soil columns of all three soils. The legal limit for excavated soil of 200 mg kg⁻¹ was exceeded in both soil depths of the three columns. DOC concentrations were especially high in the columns of S2, maybe due to the high leaching potential, based on the high DOC concentration of the soil (Table 5). The columns of the FBA treatment did not show relevant increases of DOC. Here, solely the upper part (0-10 cm) of the column of S3 showed an increased concentration and slight exceedance of the threshold. The results are in accordance with the soil column leachates, where increased concentrations were solely found for the GA treatment.



Figure 49: Averaged DOC concentration \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).

Barium:

The water-extractable Ba concentration was significantly increased by the GA treatment. The columns of S1 and S3 exceeded the threshold value for excavated soil (10 mg kg⁻¹) in both sampling depths. On S2 only the upper part of the column (0-10 cm) exceeded the legal limit. Statistical significance was only given for the upper part of S1 and the lower part of S3. The FBA treatment did not significantly affect Ba extractability. Based on the different Ba concentrations of the ashes (Table 4) and input leachates (Table 11) this result could be expected.



Figure 50: Averaged water-extractable concentration of Ba \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).

Phosphate:

The GA treatment resulted in significantly increased water-extractable phosphate concentrations in the columns of S2, where they strongly exceeded the legal limit (5 mg kg⁻¹) in both sampling depths. Additionally, phosphate concentrations in the columns of the acidic soil, treated with GA leachate, exceeded the legal limit in the upper (0-10 cm) column layer. Increased PO₄³⁻ concentrations might be attributed to DOC-phosphate competition for positively charged sorption sites. High DOC extractability in the corresponding soil columns confirms this assumption (Figure 49) (Guppy, et al., 2005).

An effect of FBA on the extractability of phosphate was not observed. High water-extractable PO_4^{3-} concentrations of the pure grate ash (Table 4) and S2 (Table 5) agree with the high phosphate concentrations in the corresponding soil columns. Similar results were also found for the soil column leachates. However, the findings are in contrast to the wood ash leaching experiment, where more phosphate was leached from the FBA.



Figure 51: Averaged water-extractable concentration of $PO_4^{3-} \pm SE$ in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).

4.4 Comparison of the Experiments

The ashes of the full-scale field experiment and the laboratory experiments (wood ash leaching experiment and soil column experiment) differ in their chemical composition. The grate ash, used in the full-scale field experiment (GA-W) had a considerable higher content of Ca and B than the grate ash, used in the laboratory experiments (GA). The higher content of Ca is also reflected in its higher pH. GA, in return, had higher contents of AI, As and Ba.

FBA-W had a considerable lower pH and Cr concentration, than FBA. The lower pH of the ash, used in the full-scale field experiment, can be mainly attributed to its high water-extractable concentration of sulfate (Table 4).

Based on the differences of the used ashes and the differing experimental conditions (see 4.3) the findings of the experiments cannot be directly related.

The surface runoff of the full-scale field experiment was proven not to be affected by the ash treatments and can therefore be evaluated as ecologically safe.

A general decrease of harmful elements over time was found in the leachates of the full-scale field experiment. Three years after the implementation of the experiment solely pH, DOC, AI and Ni were found to be present in relevantly increased concentrations in the leachates of the road sections constructed with grate ash. The leachates of the road sections, constructed with fluidized-bed ash, only showed potentially critical element concentrations during the first year of the experiment. Unexpectedly, the FBA-W 15% treatment resulted in higher leachate concentrations for most relevant elements, than the FBA-W 30% treatment. The road sections, constructed with grate ash, however, showed higher leachate concentrations with higher ash application rates (GA-W 30%).

Total and water-extractable element concentrations of the undisturbed soil layer underneath the Weyregg forest road complied with the legal thresholds for excavated soil given in Austrian legislation. A direct ash effect on the undisturbed soil layer could not be identified. Most statistically significant differences could be attributed to natural variability. It is concluded that the ash treatments of the full-scale field experiment did not pose a risk for the contamination of the sub-road soil layer.

The wood ash leaching experiment revealed a general decreasing trend in leachate concentrations for most elements over time. After the water application, corresponding to 1000 mm of rainfall, most characteristics complied with the legal water-quality limits, given in Austrian legislation. The GA had a higher pH and EC and, additionally, higher leachate concentrations of the Ba, Cr, Ni, Pb and Zn, than FBA. The leachate of FBA had high concentrations of B, which exceeded the legal limits throughout the entire test duration. At the end of the experiment the GA leachate exceeded relevant legal thresholds of pH, EC, Ba, Fe, Pb, Se and Zn. The FBA leachate only showed exceedances of pH, Al and B.

The soil column experiment revealed a general decrease of ash impact with increasing soil pH (S1<S2<S3) and increasing content of fine soil particles and CEC. Various harmful elements were mobilized from the soil columns, especially the acidic soil (S1), treated with GA leachate, showed high leachate concentrations for numerous elements. However, it has to be considered that the applied leachate represented a repeated source of element input, which would not occur in full-scale field implementations.

The analysis of the soil columns showed elevated pH & EC values for all three soils after the application of GA leachate. Additionally, the concentrations of DOC, Ba and PO_3^{4-} were increased by the GA leachate. The FBA leachate only marginally affected water-extractable concentrations in the soil columns. It was found that with increasing soil depth the ash effect was attenuated due to soil buffer processes.

5. Conclusion

The experiments, conducted in the course of this Master Thesis, highlight the difficulties present in the prediction of wood ash behavior in the environment. Based on the heterogeneous character of wood ash, the complex interactions within the soil matrix and the big influence of environmental site-conditions generalizations about the behavior of wood ash, used in forest road construction, have to be made with caution and require specific safety requirements.

The leachates of the full-scale field experiment reflected the highest possible ash impact, since they were collected directly underneath the soil-ash layer. In the environment the leachate would undergo filtration, buffering and dilution processes during the soil passage before reaching the groundwater body. However, additional mobilization of harmful substances from the soil layer, underneath the forest road, might present an environmental risk under specific circumstances.

The reducing conditions of the soil column experiment led to the mobilization of various elements (As, Ni, and DOC) from the soil. Such conditions, however, are not expected to that extent in the natural environment.

Based on the findings of the experiments, the use of uncontaminated wood ash in forest road construction can be evaluated as an appropriate way of wood ash recycling. However, some prerequisites have to be met to reduce potential environmental risks.

Fluidized-bed ash seemed to be more suitable for the reuse in forest roads than grate ash, however, special attention should be paid on its B content. If grate ash is utilized, it preferably should be used at low ash:soil ratios (15:85) to reduce the ash impact on soils.

Low carbon levels of the used ashes, assured with effective combustion techniques, can minimize the risk associated with the complexation of hazardous elements with dissolved organic carbon. Forest soils with high contents of As, B and Ni require special attention.

In general, wood ash application should be restricted on sensitive forest areas. Sensitive areas might be characterized by highly acidic soils with sandy soil texture and low cation- and anion exchange capacity. Additionally, areas with a high groundwater table and/or high portion of waterlogged soils can only be partly characterized as suitable for ash-recycling via forest roads. A subsoil layer with a depth > 2 m underneath the soil-ash layer of the forest road should be ensured to minimize the risk of groundwater pollution.

Since the full-scale field experiment only examined the ash effects on an alkaline soil and the soil column experiment revealed higher impacts on the acidic soil, the implementation of an additional experiment in a forest area with acidic soils would be needed to fully assess associated environmental risks.

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9. Annex

Character- istics	Unit		w		S1		S2		S3
pH (H₂O)	-	7.7		5.6		7.8		8.1	
EC	µS cm⁻¹	58		55.3		160		134	
DOC	' ma ka⁻¹	160		219		725		206	
SOM	a ka ⁻¹	63.3		61.2		23		A1 2	
050	g kg	05.5		100				41.5	
CEC	ninoic kg	313		713		/5.2		275	
Sanu	g kg	625		233		430		230 296	
Clay	g kg	203		53 /		88 /		268	
Ciay	g kg		Water-		Water-	Water-		Water-	
		Total	extractable	Total	extractable	Total	extractable	Total	extractable
AI		34100	4.70	29200	7.1	14500	10	16300	1.8
As		7.1	0.009	1.9	0.006	6.6	0.06	10	0.028
В		62	< LOQ	17	0.2	25	0.69	51	0.19
Ва		80	0.13	225	1	79	0.24	125	0.07
Ca		8420	87	2950	36	7110	108	72100	191
Cd		0.36	0.001	0.16	0.002	0.16	0.001	0.3	0.001
Co		12	0.002	10	0.018	8.2	0.012	9.80	0.003
Cr		49	0.009	31	0.005	17	0.016	59	0.006
Cu		22	0.08	12	0.018	12	0.095	22	0.074
Fe	mg kg⁻¹	30600	9.30	45200	2.9	16800	7.5	22500	1.9
К		6050	8.60	12100	38	4140	277	6210	65
Mg		6320	4.20	9650	7.10	4290	36	10300	26
Mn		825	0.056	691	4.7	782	0.51	568	0.068
Мо		0.6	0.007	0.22	< LOQ	0.57	0.034	0.37	0.02
Na		252	1.80	354	1.5	225	3.8	n.a	1
Ni		22	0.025	< LOQ	0.018	11	0.04	52	0.032
Р		307	0.94	1280	2	1440	56	886	1.4
Pb		23	0.005	15	0.016	15	0.005	16	0.002
Se		0.50	0.004	0.35	0.005	0.21	0.006	0.32	0.012
V		63	0.015	45	0.01	22	0.062	42	0.065
Zn		78	0.48	111	0.59	63	0.26	91	0.28
Cl			3.6		1.6		2.7		6.6
F ⁻			1		1.3		1.4		9.4
NO ₂ ⁻	mg kg⁻¹		0.93		< LOQ		2.2		2.1
NO ₃ ⁻			2.4		143		37		53
PO4 ³⁻			0.32		0.43		150		1.3
SO4 ²⁻			3.20		12		20		17

SI-Table 1: Analysis of	experimental	soils (Total	element	concentrations	and	water-extractable
concentrations) $(n = 2)$.						



Weyregg Forest Road (Full-scale Field Experiment): Surface Runoff

SI-Figure 1: Averaged period values of pH, EC and DOC \pm SD insurface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 2: Averaged period concentrations of AI, As and B \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 3: Averaged period concentrations of Ba, Cd and Co \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 4: Averaged period concentrations of Cr, Cu and Fe \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 5: Averaged period concentrations of Mn, Mo and Ni \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



x....no data available

SI-Figure 6: Averaged period concentrations of P, Pb and Se \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



x....no data available

SI-Figure 7: Averaged period concentrations of V, W and Zn \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



x....no data available

SI-Figure 8: Averaged period concentrations of Ca, K and Mg \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 9: Averaged period concentrations of Na \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 10: Averaged period concentrations of CI⁻ and F⁻ ± SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 11: Averaged period concentrations of NO₂, NO₃ and PO₄³⁻ \pm SD in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 12: Averaged period concentrations of $SO_4^{2^-} \pm SD$ in surface runoff from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



Weyregg Forest Road (Full-scale Field Experiment): Leachate

SI-Figure 13: Averaged period values of pH, EC and DOC \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 14: Averaged period concentrations of AI, As and B \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 15: Averaged period concentrations of Ba, Cd and Co \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 16: Averaged period concentrations of Cr, Cu and Fe \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 17: Averaged period concentrations of Mn, Mo and Ni \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



x...no data available

SI-Figure 18: Averaged period concentrations of P, Pb and Se \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



x...no data available

SI-Figure 19: Averaged period concentrations of V, W and Zn \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



x....no data available

SI-Figure 20: Averaged period concentrations of Ca, K and Mg \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).


SI-Figure 21: Averaged period concentrations of Na \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 22: Averaged period concentrations of Cl⁻ and F⁻ \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 23: Averaged period concentrations of NO₂⁻, NO₃⁻ and PO₄³⁻ \pm SD in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



SI-Figure 24: Averaged period concentrations of $SO_4^{2-} \pm SD$ in leachate from Weyregg forest road. Different letters indicate significant differences between the ash treatments for each sampling period (p < 0.05).



Weyregg Forest Road (Full-scale Field Experiment): Soil Sampling - Total element concentrations

SI-Figure 25: Averaged total concentration of AI, As, and B \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 26: Averaged total concentration of Ba, Cd, and Co \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 27: Averaged total concentration of Cr, Cu, and Fe \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 28: Averaged total concentration of Mn, Mo, and Ni \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 29: Averaged total concentration of P, Pb, and Se \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 30: Averaged total concentration of V, W, and Zn \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).

Weyregg Forest Road (Full-scale Field Experiment): Soil Sampling – Water-extractable element concentrations



SI-Figure 31: Averaged values of pH, EC, and DOC \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 32: Averaged water-extractable concentrations of Al, As, and B \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 33: Averaged water-extractable concentrations of Ba, Ca, and Cd \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 34: Averaged water-extractable concentrations of Co, Cr, and Cu \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 35: Averaged water-extractable concentrations of F, K, and Mg \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 36: Averaged water-extractable concentrations of Mn, Mo, and Na \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 37: Averaged water-extractable concentrations of Ni, P, and Pb \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



*below LOQ

SI-Figure 38: Averaged water-extractable concentrations of Se, V, and W \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 39: Averaged water-extractable concentrations of Zn \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).

Soil Depth 20 - 40 cm



*below LOQ

Soil Depth 0 - 20 cm

SI-Figure 40: Averaged water-extractable concentrations of Cl⁻ and F⁻ \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



*below LOQ

SI-Figure 41: Averaged water-extractable concentrations of NO₂, NO₃, and PO₄³⁻ \pm SD in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).



SI-Figure 42: Averaged water-extractable concentrations of $SO_4^{2^-} \pm SD$ in the soil samples from Weyregg forest road (n = 3). The two control sites were combined to one mean value (n = 6). Different letters indicate significant differences between the ash treatments within each soil depth (p < 0.05).





SI-Figure 43: Averaged pH and EC and concentration of DOC, AI, As, B, Ba and Ca \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3).



SI-Figure 44: Averaged concentration of Cd, Co, Cr, Cu, Fe, K, Mg and Mn \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3).



SI-Figure 45: Averaged concentration of Mo, Na, Ni, P, Pb, Se, V and Zn and $PO_4^{3-} \pm SE$ in GA and FBA leachates from wood ash leaching experiment (n=3).



SI-Figure 46: Averaged concentration of Cl⁻, F⁻, NO₃⁻, NO₂⁻, SO₄²⁻ and PO₄³⁻ \pm SE in GA and FBA leachates from wood ash leaching experiment (n=3).





SI-Figure 47: Averaged pH and EC and concentrations of DOC, AI and As \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). Mind the different scales.



SI-Figure 48: Averaged concentrations of B, Ba, Ca, Cd and Co \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05).



SI-Figure 49: Averaged concentrations of Cr, Cu, Fe, K and Mg \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). Mind the different scales.



SI-Figure 50: Averaged concentrations of Mn, Mo, Na, Ni and P \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). Mind the different scales.



SI-Figure 51: Averaged concentrations of Pb, Se, V, W and Zn \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05).



SI-Figure 52: Averaged concentrations of Cl⁻, F⁻, NO₂⁻ and NO₃⁻ \pm SE in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). Mind the different scales.



SI-Figure 53: Averaged concentrations of PO_4^{3-} and $SO_4^{2-} \pm SE$ in the soil column leachates on S1, S2 and S3 (n=2). Different letters indicate significant differences between the leachates within each individual soil (p < 0.05). Mind the different scales.



Soil Column Experiment: Water-extractable element concentrations

SI-Figure 54: Averaged pH and EC and concentrations of DOC and Al \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 55: Averaged concentrations of As B, Ba and Ca \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 56: Averaged concentrations of Cd, Co, Cr and Cu \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 57: Averaged concentrations of Fe, K, Mg and Mn \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).


SI-Figure 58: Averaged concentrations of Mo, Na, Ni and P \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 59: Averaged concentrations of Pb, Se, V and W \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 60: Averaged concentrations of Zn \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 61: Averaged concentrations of Cl⁻, F- and NO₂⁻ \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).



SI-Figure 62: Averaged concentrations of NO₃⁻, PO₄³⁻ and SO₄²⁻ \pm SE in the soil columns (n = 2). Different letters indicate significant differences between the ash treatments within each individual soil (p < 0.05).