

Effects of slags on the chemical soil quality and vegetation in Spanjaards Duin

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Abstract

The soil of nature area Spanjaards Duin is covered with slags originating from the suppletion of sand, and possibly contains contaminants like heavy metals. Leaching of these metals potentially may (1) pollute the soil and (2) may contaminate groundwater. Contamination of the soil might influence the development of the desired moist dune vegetation.

This study aims to assess these potential risks. The assessment includes an investigation of the types of slags and their geochemical reactive/potential metal contents. Subsequently leaching from the two most contaminated slag types was determined by a pH stat test over a pH range of 2-12. To investigate the processes responsible for leaching the results of the test were interpreted using the geochemical model ORCHESTRA, taking into account precipitation/dissolution reactions and adsorption to hydrous ferric oxides (HFO). The model ORCHESTRA including reactive transport was used to assess the development of the soil and water quality in a soil column over time, i.e. 80 and 100 years, respectively. The effect of slags on the development of moist dune vegetation was assessed with a germination experiment with five plant species, typical for a moist dune valley. Plants were grown in sand with and without slags and compared for germination and total biomass.

Heavy metal contents of the slags were very low, only one slag type had a high concentration of reactive zinc. Leaching of metals, originating from slags, to soil and groundwater is also low. The presence of slags had no significant effect on germination, survival and total biomass of the plants tested ($P > 0.34$). Overall, no negative effects of slags on soil and groundwater quality and on the development of moist dune vegetation were observed or predicted for the future. The study reflects a worst case scenario due to the grinding of slags which increases the contaminant availability. Therefore no negative effects are to be expected under natural circumstances.

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1. Introduction

In 2009, a 35 ha large new nature area, Spanjaards Duin, was developed near 's Gravenzande as nature compensation for the growth of the Rotterdam harbour with the extension of "Maasvlakte 2". For the construction of this new nature area beach nourishment was applied. The sea sand that was used for this nourishment appeared to be contaminated with slags. These slags possibly contain contaminants and therefore could have an influence on the chemical soil quality and development of the desired moist dune vegetation in this area. In order to investigate this, we need to assess what type of slags are present, which contaminants they contain and whether these contaminants can possibly leach. From a practical point of view Rijkswaterstaat now wants to know whether the slags pose a threat to the environment and therefore, for example, should be remediated. From a social perspective, Rijkswaterstaat wants to explain citizens whether the presence of these slags in Spanjaards Duin is dangerous or not.

Spanjaards Duin is situated west of 's Gravenzande, and between Hoek van Holland in the south and Monster in the north. About 2/3 of the total 35 ha is situated north of "Slag Vlughtenburg" and about 1/3 south of it. Originally, the dune strip was very narrow at this location and there was a kink in the coast. With the development of Spanjaards Duin, the dune strip has become much broader. In the former 5 years the groundwater level in the area has risen. Also, the valley in the dune area, where the moist dune valley habitat should be realised, was blown out. At the moment the groundwater in the area is still brackish, but the intent is that the water will become fresh, because the fresh water bubble under the area is still growing. In the end, 6.1 ha of moist dune valley habitat should be realised here (van Eerden, 2014-a). The rest of the area will be a grey dune habitat (dune grasslands). Plant species that are characteristic for a moist dune valley are among others *Liparis loeselii* L. (NL: Groenknolorchis) and *Parnassia palustris* L. (NL: Parnassia) (van Eerden, 2014-b).

The development of this new area within the project PMR (Project Mainport Rotterdam) is an agreement between Rotterdam Port Authority, the ministry of Economic affairs, the ministry of Infrastructure and Environment and other public and private stakeholders. In this project, Rijkswaterstaat (RWS) acts as a mediator between these parties. RWS has developed and monitors the area and checks whether the postulated goals will be achieved. If that is not the case, it will be decided whether adjustments are needed in order to achieve the goals.

Because after five years the (abiotic) development phase of the area has greatly been accomplished, Rijkswaterstaat now wants to take stock of the establishment conditions for vegetation. Therefore, it is important to know whether the slags that are present in the soil will be an obstacle for the vegetation, due to leaching of toxic compounds (RWS - Voorstel voor studenten opdracht(en), 2014). This only applies to the moist dune valley, because there the groundwater level is very shallow (van Eerden, 2014-b).

Characteristics of slags and potential effects

Most slags are rest products that originate from the production of metals. Therefore they often contain heavy metals (Shen and Forssberg, 2003). Slags can be divided into three different types; namely ferrous slag, non-ferrous slag and incineration slag. Iron and steel slags belong to the category of ferrous slags. They originate from the production of iron and steel from ore (Piatak et al., 2014). Non-ferrous slags originate from the production of non-ferrous metals, for example Cu, Ni and Pb (Piatak et al., 2014). Incineration slags originate from the burning of household waste (Shen and Forssberg, 2003).

Ferrous slags contain Ca silicates, carbonates and oxides. Therefore these slags often have a very high pH and a high acid buffering capacity (Piatak et al., 2014). Both Piatak et al. (2014) and Shen and Forssberg (2003) indicate that ferrous slags contain less trace elements than non-ferrous slags, and hence are less threatening to the environment. The compounds in ferrous slags that are probably most influencing the environment are As, Co, Cr and Mn. The non-ferrous slags mostly contain heavy metals with a higher solubility than the metals in ferrous slags and therefore pose a larger threat to the environment. Trace elements that are important in non-ferrous slags are As, Ba, Cd, Co, Cu, Cr, Mn, Ni, Pb and Zn (Shen and Forssberg, 2003; Piatak et al., 2014).

If slags end up somewhere in the environment, as happened in Spanjaards Duin, the contaminants in the slags potentially end up in the soil or water. The heavy metals for example can leach or can be taken up by plants. The geochemical availability of the metals in the slags depends on the chemical form in which the metals are present. The release of contaminants is chemically controlled by the reactive content of these contaminants, dissolution and adsorption (van der Sloot and Dijkstra, 2004). In adsorption processes contaminants bind to reactive surfaces. The most important reactive surfaces for adsorption and desorption to slags are metal oxides (Fe, Al and Mn). To make a clear distinction between what is available and what not, a division between total, reactive and available amounts can be made. The actual available fraction consists of trace elements that occur in the soil solution. These elements can directly be taken up by plants or soil organisms (Geochemical soil atlas of the Netherlands, 2012). The reactive fraction is that part of the solid phase that can exchange with the soil solution by processes like adsorption/desorption and dissolution/precipitation. Therefore, this reactive fraction is potentially available for uptake by plants or soil organisms or it can potentially leach. The inert fraction is that part of an element that is not directly available because it is included in minerals that are hardly soluble, like silicates, (hydr)oxides and clay minerals. Only by long lasting, slow processes like weathering the inert metals can be released (Groenenberg et al., 2010). The sum of the available, reactive and inert fraction equals the total amount of a certain element in the soil solid phase (Geochemical soil atlas of the Netherlands, 2012). The pH of a material, the pH of the environment and the buffering capacity of a material are crucial factors that determine adsorption and desorption of contaminants, and hence availability (van der Sloot and Dijkstra, 2004).

In general, slags are alkaline (Piatak et al., 2014). Steel slags for example have pH values ranging between 8 and 10, but it can even be higher than 12. This is especially the case when large amounts of free CaO are present (National Slag Association, 2013).

Since plants occur within a limited range of abiotic conditions (Wamelink et al., 2005), like pH, OM content or groundwater level, these factors are very important for the desired vegetation type. E.g. in an acidic soil, moist dune vegetation will not originate (Ministerie van LNV, 2008).

When slags are present in the environment they are under influence of weathering. They are exposed to CO₂ in the atmosphere and as a consequence of that the pH of the slags will decrease over time (Engström et al., 2014; Huijgen and Comans, 2006). This change in pH can influence the leaching of elements in slags. According to Engström et al. (2014) leachability of aged slags is dramatically lowered. In their investigation on steel slag in Sweden the leaching of among others Cr and Mo decreased during 24 months of weathering.

Another important feature of slags is that some of the present compounds can also be a potential source of plant nutrients. According to Xian and Qing-Sheng (2006), the high levels of Fe in iron slags can fertilize Fe deficient soils. But other compounds in slags, like K, Mn and P can also be useful nutrients for plants. In another experiment it appeared that with the addition of steel slags to corn in an iron poor soil, the corn yield increased significantly for moderate application rates of slag (Xian and Qing-Sheng, 2006).

When investigating the possible harmful effects of contaminants in slags the available and reactive amounts are thus important, rather than the total amount, because these indicate what can really leach. The directly available (or actual available) amount of elements in the slags can be determined by a weak extraction with 0.01 M CaCl₂. With *aqua regia* the pseudo-total amount of an element can be extracted (Groenenberg et al., 2010). In this research, a 0.43 M HNO₃ extraction will be used to determine the reactive fraction (and thus potentially available) of the total amount of an element in the slags (Geochemical soil atlas of the Netherlands, 2012). The leaching behaviour of slags under changing pH conditions will be determined by a pH-stat test (CEN/TS 14997)). In this test the leaching of compounds from slags is determined over a wide pH range, e.g. between 2 and 12. The pH is controlled by the addition of acid and base. To find out which processes control the leaching of the various elements the results of the pH-stat experiments will be interpreted with the help of geochemical modelling. With the geochemical model ORCHESTRA, which includes a mechanistic description of the adsorption and precipitation/dissolution reactions, the concentration in the leachate will be predicted based on pH, reactive metal contents and the amounts of adsorbing phases (Fe- and Al-(hydr)oxides).

With regard to the effect of slags it is thus important to keep in mind that slags can both be a source of contamination, and a source of nutrients for plants. Availability of these compounds in slags is mainly

influenced by pH of the soil and slags and the amounts of adsorbing phases. The objective of this research is to assess whether the slags that are present in Spanjaards Duin have an effect on the chemical soil quality. The soil and the groundwater can be influenced by leaching of harmful elements from the slags; they hence could be contaminated. Furthermore we want to assess the effect of slags on the target vegetation (moist dune valley), at present and in the future. It could be possible that e.g. the growth of the desired vegetation is inhibited by high metal concentrations originating from the slags.

Therefore it will be investigated (1) what type of slags are present, which potential toxic compounds they contain and what the pH of the slags is, (2) which part of these compounds leaches into the environment under changing pH conditions and which processes are responsible for the leaching, (3) how this leaching develops towards the future and (4) how slags influence the development of moist dune vegetation. The research is done for a worst-case scenario in which the slags used for the experiments are ground.

2. Materials and Methods

2.1 Collection of the slags

On 3 September 2014 we (Bert-Jan, Rob and myself) visited Spanjaards Duin, together with Mennobart van Eerden and Charlotte Schmidt from RWS. They guided us through a part of the area, namely the part situated north of "Slag Vlugtenburg". It was clearly visible that most slags were situated in the valley area, but especially on places where the spout head for beach nourishment was situated. During this tour Rob and I collected two plastic bags with, in our opinion, slags. We collected different slags: with different sizes, colours and mass densities. We took the slags with us back to Wageningen and stored them.

2.2 Determination of the various types of slags and their composition

2.2.1 Sorting and grinding of the slags

In Wageningen the collected material was divided in different groups based on visual inspection of mass density, colour, porosity, shape and layering of the slags. Based on their abundance five different types of slag like materials were selected for further research.

Prior to any further investigations the selected types were ground with a grinding machine. Fractions of <1mm, 1-2 mm, 2-4 mm and >4 mm were collected by sieving and stored in plastic bags or flasks. Because we had the impression that one of the types was a steel slag, this type was put in a plastic flask and flushed with nitrogen gas for about ten minutes. This to prevent carbonation as a consequence of contact with atmospheric CO₂ which will decrease the pH of the slag.

2.2.2 Dry weight

The dry weight, and thus the water content of the slags was determined by drying an amount of 5-10 g of slag, in aluminium cups, in an oven at 105°C for 23 hours and 45 minutes. Thereafter the cups were put in an exsiccator for 45 minutes and weighed.

2.2.3 Slag pH determination

The pH of the slag types, fraction 2-4 mm, and two reference samples was determined with a pH electrode in a water extract with L/S 10 (liquid-to-solid ratio). Preparation of this water extract was done according to protocol E0106, version 4.0 (2010). The pH was measured in the settling suspension according to protocol E0103, version 9.0 (2013).

2.2.4 0.43 M HNO₃ extraction

To assess the reactive fraction and hence potentially available elements for leaching and uptake by organisms, the concentration of a broad range of elements was determined in a 0.43 M HNO₃ extract. Therefore, the five slag types, with fraction 1-2 mm, and two reference samples were subjected to a 0.43 M HNO₃ extraction according to protocol E1011, version 2.0 (2011). We did not correct for the lime content in the slags and in the reference samples; instead we measured the pH in the 0.43 M HNO₃ extract. Four gram of slag was weighed in a centrifuge tube and 40 ml 0.43 M HNO₃ was added. Tubes were shaken in an end-over-end shaker for four hours at 30 rpm. All samples were shaken by hand before going into the end-over-end shaker and gas (CO₂) was removed from the tubes, to prevent a pressure build-up in the tubes. Nevertheless type 2, 3 and reference 989 contained such an amount of lime, that the pressure in the tubes was that high, that part of these samples escaped from the tubes. For type 3 the amount of sample lost was substantial, therefore type 3 was extracted again, but now in a 0.5 l bottle. This turned out to work, only 1-2 ml was lost now. Because of the sample loss it is likely that the L/S of the samples changed and that the results are unreliable. However, after analysis of the samples in the lab, it appeared that the concentration measured in reference 989 was still inside the range determined by the CBLB (Chemical Biological Soil Laboratory, Wageningen UR) for this reference sample. Therefore it is assumed that the results of slag type 2 and 3 are also not influenced by the leaking and thus that the results are reliable.

After extraction the suspension was filtered and in 2-3 ml of the filtrate the pH was measured with a pH electrode. This was done because for the determination of the reactive metal content a pH lower than 1 is needed in the extract. This condition was checked because we did not correct for the lime content in

the slags. The pH electrode was calibrated with buffers of pH 4 and 7. It was not possible for this pH electrode to calibrate with buffers with other pH values. However, when the pH of a buffer solution of pH 1 was checked with this same electrode, it turned out to be 0.99. This indicates that the electrode can measure accurately at very low pH values, although it was initially calibrated with pH 4 and 7.

The rest of the filtrate was analysed with ICP-AES/MS by the CBLB laboratory for the amounts of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se and Zn. Samples that were analysed with ICP-MS were diluted 10 times with 0.14 M HNO₃. The concentrations of the elements were compared with background and intervention values in the Circular Soil Remediation (2013). Eventually Ba, Co, Pb, Sb and Se were left out of consideration after the 0.43 M HNO₃ extraction, as these concentrations were very low. Although the concentration of oxy-anions (As and Mo), was even lower than the concentration of Ba and Ca, we still choose to take these compounds into account, as oxy-anions are less extracted by a 0.43 M HNO₃ extraction compared to cat-ions. Also, oxy-anions behave chemically different with respect to processes like adsorption/desorption, compared to cat-ions (Groenenberg, 2014). Therefore it is important to take both cat-ions and oxy-anions into account for further research.

2.2.5 Water extraction

A water extraction batch test with the slag types, fraction <4 mm, was carried out next in order to see which elements leach at native pH of the slags. Protocol prEN 12457-2 was used as a guideline for this extraction. "Using as a guideline" means that it was tried to execute the tests according to this protocol, but if that was not necessary or possible (because of e.g. materials that were not available), the tests were adjusted. For example, other amounts of extraction solutions and other amounts of slags were used (but still in the same L/S ratio), or filters with another mesh size.

Four gram of slag was weighed into a centrifuge tube and 40 ml demi water was added. Samples were agitated in an end-over-end shaker for 24.5 hours at 9 rpm, after which the tubes were centrifuged for 30 minutes at 2000 g and subsequently filtered over a 0.45 µm membrane filter. The pH was measured in 2-3 ml of the filtrate, the rest of the filtrate was analysed for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S and Zn with ICP-AES/MS by the CBLB laboratory. The end concentration of these delivered samples was 0.14 M HNO₃. In another part of the water extract the amount of nutrients, NH₄ and NO₃, was determined by the CBLB laboratory. These samples were acidified with 20 µl 5 M HCl.

Based on the results of the 0.43 M HNO₃ and water extraction it was determined which slag types were further investigated. Therefore it was counted which two types had most often the highest concentration of elements. It appeared that this was the case for slag type 2 and 7, so we decided to do further research with these two types of slags. Due to capacity limitations for the pH-stat leaching test at ECN in Petten, it was not possible to investigate more slag types. All experiments that are described from now on, are thus only executed for slag type 2 and 7.

2.3 Selective chemical extractions

For the geochemical modelling of the pH-stat experiment and the predictive modelling of the soil and water quality, the amounts of Fe-, Al- and Mn-(hydr)oxides of both the slags and soil need to be known. Aluminium (hydr)oxide contents were determined with an oxalate extraction. For the Fe-(hydr)oxides we distinguish between amorphous and crystalline Fe-oxides. The content of amorphous Fe-(hydr)oxides was determined with an ascorbid acid extraction. The total amount of Fe-(hydr)oxides, as well as the content of Mn-(hydr)oxides, was determined with a dithionite extraction (Huijgen and Comans, 2006). The concentration of iron measured in the dithionite extract minus the concentration of iron measured in the ascorbic acid extract is equal to the amount of crystalline Fe-(hydr)oxides in the slags.

2.3.1 Oxalate extraction

For the oxalate extraction protocol E1300, version 3.0 (2012) was used. Preparation of the extraction solution was done by dissolving 8.1 g ammonium oxalate monohydrate ((COONH₄)₂.H₂O) and 5.4 g oxalic acid dihydrate ((COOH₂).2H₂O) under stirring in 500 ml demi water in a 500 ml volumetric flask. The pH and temperature of the solution were measured. For each of the two slag types and reference 989, 1.5 gram sample (fraction <4 mm) was put in a centrifuge tube and 30 ml of the extract was added. Tubes were wrapped with aluminium foil to ensure that the test was executed under dark conditions and they were shaken for 2 hours at 180 shakings/minute. Samples were centrifuged at 3000

g for 10 minutes and the supernatant was decanted in 20 ml tubes and stored in the fridge. The rest of the oxalate extraction liquid was stored in the fridge for later use. After one week the extraction liquid was used for doing the extraction with sand from Spanjaards Duin (composite sample) and reference 949. The samples were delivered to the CBLB laboratory containing 0.65 ml sample and 9.75 ml diluting solution. With ICP-AES the concentration Al was measured, which represents the concentration of amorphous Al-(hydr)oxides.

2.3.2 Ascorbic acid extraction

For the ascorbic acid extraction protocol ISO 12782-1 was used as a guideline. For the preparation of the extraction solution 12.5 g sodium hydrogen carbonate (NaHCO_3) and 12.5 g trisodium citrate dihydrate ($\text{C}_5\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) was dissolved under stirring in ca. 200 ml demi water in a 500 ml erlenmeyer. The solution was deaerated with nitrogen gas for four hours, after which 5.0 gram of L(+) ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) was added little by little under stirring. Eventually demi water was added till 500 ml. This solution was again deaerated with nitrogen gas until pH 8.0. For the two slag types (fraction < 4mm), sand from Spanjaards Duin (composite sample) and reference 949 and 989, 1.5 gram was put in a centrifuge tube and 30 ml of the extract was added. Samples were put in an end-over-end shaker for 24 hours at 9 rpm, after which they were centrifuged for 30 minutes at 3000 g and subsequently filtered over a 0.45 μm membrane filter. To 0.1 ml of the filtrate 9.9 ml 0.14 M HNO_3 was added, this was done to make sure that the salt content was not too high for the ICP machines. These samples were analysed in the CBLB laboratory for Fe by ICP-AES, which represents the amount of amorphous Fe-(hydr)oxides.

2.3.3 Dithionite extraction

For the dithionite extraction protocol ISO 12782-2 was used as a guideline. For preparing the extraction solution 7.2 g sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$) and 15.1 g trisodium citrate dihydrate ($\text{C}_5\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) was dissolved under stirring in 250 ml demi water, after which 12.6 g sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) was added and dissolved. Next 7.1 ml acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) was added to reach pH 4.84. For the two slag types (fraction < 4 mm), sand from Spanjaards Duin (composite sample) and reference 949 and 989, 1.5 gram was put in a centrifuge tube and 30 ml of the extract was added. One and a half hour later the tubes were put in a water bath of 60°C for 3.5 hours (faster was not possible because of a machine failure). Every 20 minutes the tubes were shaken by hand. The samples were allowed to cool down for 30 minutes, after which they were centrifuged at 3000 g for 30 minutes and next filtered over a 0.45 μm membrane filter. To 0.1 ml of the filtrate 9.9 ml 0.14 M HNO_3 was added. These samples were analysed in the CBLB laboratory for Fe and Mn by ICP-AES, which represents the amount of total Fe-(hydr)oxides and the amount of Mn-(hydr)oxides.

2.4 Leaching

A pH stat leaching test was carried out with slag type 2 and 7 to investigate leaching of slags under changing pH conditions.

2.4.1 pH stat leaching test

Protocol NPR-CEN/TS 14997 (2006) was used as a guideline for the pH stat leaching test. In this test, subsamples of the two different slag types were equilibrated for 48 hours and brought to eight different pH values ranging between 2 and 12, including the native pH of the sample. The pH was adjusted by adding HNO_3 or NaOH ; additions were controlled by the pH stat software programme. Fifteen gram slag (<1 mm) was brought into an acid cleaned PTFE vessel, together with 150 ml demi water (L/S 10 l/kg). The suspension was stirred continuously at 20°C and the pH was adjusted. Slag type 2 was brought to target pH values 2, 4, 6, 7.5 (native pH), 8.5, 9.5, 10.5 and 12. Slag type 7 was brought to pH values 2, 4, 6, 7.5, 8.0 (native pH), 9.4, 10.5 and 12. Before and after the experiment the pH electrodes were calibrated using buffers of pH 1, 3, 6, 8, 10 and 13. Also the flow rate of acid and base was determined before and after the experiment. This was done by opening the acid and base valves for one minute and collecting the acid and base. These amounts were weighed and with this information the flow rate (g/min) was calculated. The strength of the used acid and base was in all cases 1 M, except for the acid used to reach pH 2, in that case 5 M HNO_3 was used.

After 48 hours the samples were brought over into centrifuge tubes after which they were centrifuged for 30 minutes at 5000 rpm. The samples were filtered over 0.45 μm (NC45, Whatman™) using a vacuum

filtration device. After filtration the samples were stored for analyses. Samples for ICP analyses were stored in acid-cleaned 50 ml LDPE bottles and were acidified by adding 200 μl 14.4 M HNO_3 . The conductivity was also measured in each sample, to make sure that the salt content was not too high for analyses with ICP. The concentrations Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn (partly) were measured using ICP-AES and As, Ba, Cd, Co, Cr, Mo, Ni, Pb and Zn (partly) concentrations were measured using ICP-MS. The results of P and S can be regarded as PO_4 and SO_4 (Huijgen and Comans, 2006). The rest of the filtrate was stored in 50 ml bottles and not acidified. They were stored in the fridge upon analyses for Cl with FIA (Flow Injection Analysis).

The moisture content of the two slag types was determined at ECN with a halogen lamp (Mettler HR73 Halogen Moisture Analyzer). Within about 90 minutes this device measures the moisture content of a small sample (about 2 g). The moisture content of slag type 2 and 7 was 0.4% and 2.45%, respectively. This means that the L/S ratio during the pH stat test was not exactly 10, but 10.04 for type 2 and 10.28 for type 7. Also the addition of acid or base influences the L/S ratio. However, according to the protocol (NPR-CEN/TS 14997, 2006) the ultimate L/S ratio shall not deviate more than 10% from L/S = 10 l/kg and this was the case for all treatments (data not shown).

2.4.2 Batch leaching test

A two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg was carried out with slag type 2 and 7, using protocol prEN 12457-3 as a guideline. The test was performed on the slags with a grain size <4 mm. First, 6 g slag and 12 ml demi water were put in a centrifuge tube. Samples were shaken in an end-over-end shaker at 9 rpm for 6 hours after which they were centrifuged at 3000 g for 30 minutes. The samples were filtered over 0.45 μm . The filtrate was diluted four times with demi water. To the same centrifuge tubes, containing the slag material of L/S is 2 l/kg, 48 ml demi water was added, reaching a L/S of 8 l/kg. These tubes were agitated in the end-over-end shaker for 18 hours, after which they were centrifuged for 30 minutes at 3000 g and subsequently filtered over 0.45 μm . Part of the filtrate of each sample was acidified to an end concentration of 0.14 M HNO_3 and analysed with ICP for the same elements as in the pH stat test. The other part of the sample was not acidified and analysed for Cl. With the results of L/S 2 and L/S 8 a cumulative release of the constituents at L/S 10 was calculated, according to prEN 12457-3. These values were then compared with the values for non-shaped building materials in the Soil Quality Decree (2007).

2.5 Geochemical modelling

The pH stat leaching test results were modelled with the geochemical model ORCHESTRA in order to assess the processes responsible for the leaching. ORCHESTRA is a multisurface model which takes into account aqueous speciation as well as adsorption to Fe- and Al-(hydr)oxides (Dijkstra et al., 2009). For the aqueous speciation, ORCHESTRA uses thermodynamic data from the MINTEQA database. For simulation of the adsorption to these Fe- and Al-(hydr)oxides, the Generalized Two-Layer Model (GTLM) of Dzombak and Morel (1990) was used, in which it is assumed that the amount of amorphous Fe-(hydr)oxides is represented by HFO. However, Al-(hydr)oxides and crystalline Fe-(hydr)oxides were also modelled as if it was HFO, because the adsorption behaviour of metals to Al-(hydr)oxides and crystalline Fe-(hydr)oxides is comparable to the adsorption behaviour of metals to HFO (Dijkstra et al., 2004). See appendix I for a schematic overview of the processes that can be taken into account by ORCHESTRA.

Modelling with ORCHESTRA was done by predicting the concentrations in the liquid phase on the basis of the total reactive heavy metal concentrations (0.43 M HNO_3 extraction results). The model simulates the soil system in terms of adsorption of heavy metals to Fe- and Al-(hydr)oxides and precipitation/dissolution of minerals. An overview of all the minerals that were taken into account in the model, is depicted in appendix II. Input that was used for the model was (1) the reactive heavy metal concentrations of the 0.43 M HNO_3 extraction, (2) the dissolved concentrations of Al, Ca, Cl, Fe, K, Mg, Mn, Na and P measured in the pH stat extractions, (3) the amount of hydrous ferric oxides (HFO) (kg/kg) in the slags, (4) a fixed value for the CO_2 concentration ($\text{pCO}_2 = -2.52$) and (5) a moderately oxidizing environment ($\text{pe} + \text{pH} = 11$) was assumed (Groenenberg, 2015-a). The dissolved concentrations measured in the pH stat extractions should have the unit mol/l, so with the molar weight of the elements and the fact that L/S is 10 l/kg, this was calculated. The different specific surface areas of amorphous iron and aluminium (hydr)oxides, 600 m^2/g , and crystalline iron (hydr)oxides, 100 m^2/g were taken into account (Dijkstra et al., 2004). Together with the molar mass of HFO, 89 g/mol, the amount of HFO was

recalculated to kg/kg. At the end of preparing the input file a balance between cations and anions was made by adding the amount of missing anions, in this case NO_3^- . With a certain script in ORCHESTRA it was modelled for the different pH values that were reached with the pH stat test, what the metal concentrations in the liquid phase were and which fraction was adsorbed to HFO or precipitated. Subsequently graphs of pH versus dissolved metal concentrations modelled by ORCHESTRA were compared with graphs of pH versus dissolved metal concentrations measured from the pH stat test.

2.6 Predictive modelling of the chemical soil and water quality

The development of the chemical soil and water quality in time due to leaching of metals from the slags is assessed by predictive modelling using the geochemical model ORCHESTRA. The modelling was done for a soil column of in total 2 meter depth, of which the groundwater is situated at 1 to 2 m depth. In addition to the model as described in section 2.5, now also sorption to organic matter (OM) and clay was taken into account. Sorption to organic matter and clay was modelled with the NICA-Donnan model and Donnan model, respectively. We assumed that clay was not present in the sand, and hence a small value (2×10^{-10} mol/kg) for the clay content was used. A constant water flux and constant moisture content of the soil was assumed. Modelling was done with soil containing slag type 2 or slag type 7. The soil column of 1 meter depth was divided in layers of 10 cm depth each. In the field it was observed that slags were present only in the upper 10 cm. In this layer the amounts of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn thus originate from the dune sand as well as from the slags. The amount present in the dune sand was determined with a 0.43 M HNO_3 extraction of the sand (composite sample). From the collection of slags from a square meter in Spanjaards Duin that contained most slags, it was determined that there was 0.25 litre slag of type 2 on 1 m^2 in the upper 10 cm and 0.6 litre of slag type 7 (see also section 2.7.1). These fractions were multiplied with the results of the 0.43 M HNO_3 extraction of the slags and added to the amount of metals present in the dune sand. For the other layers only the metal content in the sand was taken. The amount of HFO in the upper 10 cm was calculated in the same way. For the other layers the amount of HFO of the sand only, determined with the selective chemical extractions, was used. The pH of the composite sample, measured in a water extract, was 9.61. Furthermore, the amount of dissolved organic carbon (DOC) in the sand was determined in a CaCl_2 extract, in which the amount of total carbon and inorganic carbon was determined by segmented flow analysis (SFA). The difference between these two numbers is equal to the amount of DOC, in this case 1.3 mg/l. The pCO_2 was set at -6 and $\text{pe} + \text{pH}$ was 11. With this input ORCHESTRA calculated for 80 years the metal concentrations in the upper meter of soil for each layer of 10 cm depth. It also provided for each element an average groundwater concentration in the layer of 1 to 2 meter depth, up to 100 years.

2.7 Influence on vegetation

2.7.1 Soil sampling Spanjaards Duin

Soil samples for analysis and for the pot experiment were taken in Spanjaards Duin on 17 November 2014. A composite gouge sample was taken in the valley area, around 250-300 meter north of "Slag Vlugtenburg". A composite gouge sample consists of 10 gouge samples taken in a 2x2 m square, 10 cm deep and without litter layer. Although a litter layer was hardly present in the area, the upper 1 cm of each gouge sample was removed to be sure that no litter was taken into account. Within the square the samples were taken in the pattern as shown in figure 1.

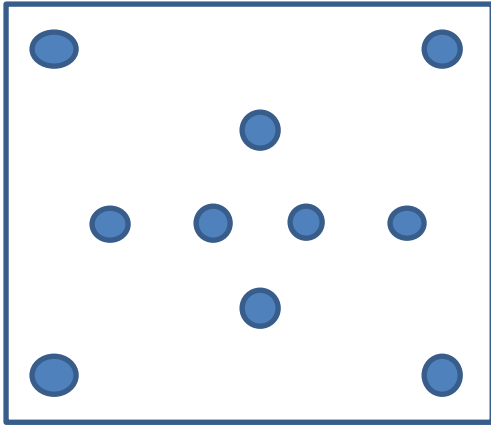


Figure 1: Pattern at which the soil samples were taken in Spanjaards Duin. The square is 2x2 m.

See figure 2 for pictures of the location where the composite sample was taken. This composite sample was dried at 40°C and sieved over 4 mm before using it for analyses. The organic matter content of the soil was determined by loss-on-ignition, in duplo (protocol E0100, version 6.0, 2014).

In order to determine the slag density in Spanjaards Duin, and hence the amount of slags needed for the pot experiment, in the valley on 1 m² all slags that were present in the upper 5 cm were collected. But actually almost all slags were on top of the soil. This 1 m² was the place in the valley that contained, according to my visual observations, most slags. Figure 3 and figure 4 show the location where slag sampling took place. The slags were divided into two groups: slags of type 7 and other slags. The amount of type 7 collected in this 50 litre soil (1m² * 0.05m) was a measure for the amount that was used in the pot experiment and for the modelling. In total 491.95 g slag of type 7 (after drying at 40°C), which equals about 0.6 litre, was collected in this area.



Figure 2: Location where the composite sample was taken (between the four sticks).



Figure 3: This was the area in the valley in which on 1 m² slags were collected.



Figure 4: The square after collection of the slags.

Against the old dune three buckets of sand from the upper 15 cm were collected for the pot experiment. This soil was free of slags and contained hardly any shells. In figure 5 and figure 6 the location is shown where the sand was collected.



Figure 5: Location of soil sampling in Spanjaards Duin.



Figure 6: Location of soil sampling in Spanjaards Duin.

2.7.2 Pot experiment

To assess the influence of the slags on the germination and development of moist dune vegetation, a greenhouse pot experiment was conducted. The soil used for the pot experiment was brought to 60% water holding capacity (WHC) with tap water prior to the start of the experiment. The amount of water needed to reach 60% WHC was determined by means of determining the liquid limit. For that purpose, each time 2 kg soil was put in a bucket and a certain amount of water was added and mixed with a small scoop. Then the bucket was bumped on the table a few times and when the water in the sand started to flow, the liquid limit was reached. The amount of water needed to reach the liquid limit for this 2 kg soil was between 250 g and 300 g. This procedure was repeated for the rest of the soil. Eventually to 46.3 kg soil 6.1 kg tap water was added. To in total 10 litre soil 98.39 g slag of type 7 with size < 4 mm was added, which is a representative amount for the area. Type 7 was chosen because this type was most omnipresent in Spanjaards Duin.

Small black plastic pots, with dimensions 7x7x8 cm, were used for the experiments. They were filled up to 1 cm under edge. A plastic gauze was put on the bottom of the pots, to prevent the loss of sand via the gaps in the bottom (see figure 7). Thirty-six pots were filled with only sand and 36 pots were filled with the mixture of sand and slag. With a plastic gauze the topsoil was flattened. Each pot was put in a petri dish to prevent water loss and roots growing into other pots. Pots were left in the greenhouse for 29 days (figure 8). During this time equilibrium between the soil and slags could establish. Each one or two days the pots were watered with tap water using a plant sprayer, so that the soil stayed moist.



Figure 7: A plastic gauze was put on the bottom of the pots. The pots were filled with sand till 1 cm under the edge.



Figure 8: Pots were left in the greenhouse so that an equilibrium situation could establish.

On 6 January 2015 the plant seeds were sown. In total five plant species were used, namely Buck's-horn plantain (*Plantago coronopus* L.), Wild carrot (*Daucus carota* L.), Purple loosestrife (*Lythrum salicaria* L.), Marsh helleborine (*Epipactis palustris* L.), and Marsh Grass-of-Parnassus (*Parnassia palustris* L.). Seeds were ordered at Cruydt-Hoeck (Nijeberkoop). In each pot, five seeds of one plant species were sown. *E. palustris* and *P. palustris* are target vegetation types for a moist dune valley habitat. The other species are more general species, but all species belong to vegetation types that are typical for moist dune areas (Ministerie van LNV, 2008; Schaminée et al., 2010). There were seven replicates. Sowing was done by taking a seed with a forceps or a needle and dropping the seed on top of the soil; one seed towards each corner and one in the middle. After sowing the pots were watered, to make sure that the seeds stayed in contact with the soil. Table 1 gives an overview of the treatments in each pot. The pots were put in a completely randomized block design (table 2). This means that the sequence in which the pots are situated in the greenhouse, is determined randomly. This is done to make sure that possible differences that occur between plants are caused by the availability of slags and not by other variables, like the amount of light and shadow a pot receives.

Day time in the greenhouse lasted for 16 hours. Lamps were switched on if the sunlight intensity was below 150 W/m^2 and were switched off when the sunlight intensity was above 250 W/m^2 .

Table 1: Overview of the treatments per pot.

pot number	plant species	slag yes/no
1-7	<i>Plantago coronopus</i>	no
8-14	<i>Daucus carota</i>	no
15-21	<i>Epipactis palustris</i>	no
22-28	<i>Lythrum salicaria</i>	no
29-35	<i>Parnassia palustris</i>	no
36-42	<i>Plantago coronopus</i>	yes
43-49	<i>Daucus carota</i>	yes
50-56	<i>Epipactis palustris</i>	yes
57-63	<i>Lythrum salicaria</i>	yes
64-70	<i>Parnassia palustris</i>	yes

Table 2: The setup of the completely randomized block design. Numbers are the pot numbers.

block 1		block 2		block 3		block 4		block 5		block 6		block 7	
35	40	44	10	31	5	28	55	52	9	45	60	48	2
67	54	18	30	12	27	61	32	49	42	64	8	56	69
47	23	62	36	19	46	11	7	70	22	50	34	63	33
21	14	25	66	57	68	39	43	58	29	6	15	13	41
3	59	53	1	37	51	20	65	16	4	26	38	17	24

Plants were watered each one or two days by spraying with tap water. Each day (except for the weekends) it was checked and noted down which seeds were already germinated or died, and in which part of the pot this happened.

In the same week as the seeds were sown, also the pH and the amounts of Ca, K, Mg, N (NH₄ and NO₃) and P (PO₄) were determined. This was done with sand from one of the extra pots that had the same treatment as the other 70 pots in the greenhouse. First the soil sample was dried at 40°C. Then 4 g of the sample was weighed into a centrifuge tube and 40 ml demi water was added. This was done in duplo. Both tubes were put in an end-over-end shaker for 24 hours at 9 rpm, after which they were centrifuged for 30 minutes at 2000 g and subsequently filtered over a 0.45 µm membrane filter. The pH in this water extract was measured in both samples with a pH electrode. The elements Ca, K and Mg were determined with ICP-AES by the CBLB. For that, this sample was acidified to an end concentration of 0.14 M HNO₃. The nutrients were analysed with SFA by the CBLB. For that, 10 ml of this filtrate was acidified with 20 µl 5 M HCl.

On 3 March 2015, 57 days after sowing, the total biomass was harvested and sand was removed from the plants roots. Removing the sand was relatively easy as the soil received no water 4 days before harvesting. The biomass was dried in a stove for 24 hours at 70°C. After cooling down the biomass was weighed. With a t-test ($\alpha=0.05$) in Excel it was checked whether there was a significant difference between biomass of plants growing in sand containing slag and biomass of plants growing in sand without slag. This was done for all plant species together and for each species separately. The same test was done for determination whether there was a difference in germination between plants growing in soil with and without slag.

2.8 Quality control

In some experiments also two reference samples were taken into account, the two reference samples are a sandy soil from Droevendaal (Wageningen), named 'reference 949' and a clayey soil from a floodplain, named 'reference 989'. The CBLB has exactly determined the composition and the characteristics of these two soils for all kind of experiments (e.g. a 0.43 M HNO₃ extraction). The reference samples are subjected to the same experiments as the slag and/or composite soil sample. The results of the reference samples are then compared with the results of the references in the database of the CBLB laboratory. If the results deviate from a certain range, this could indicate that something went wrong during the experiment or during analysis in the lab. The reference samples thus are a control treatment. In this research reference samples were used for the pH determination of the slags, the 0.43 M HNO₃ extraction, OM determination, and the oxalate, ascorbic acid and dithionite extractions.

3. Results

3.1 Slag types and their composition

Based on mass density, colour, porosity, shape and layering a division was made with the naked eye between different sort of slags. A broad range of different materials was found. In figures 9 - 13 the slag types are shown which were selected for further investigation (slag type 2, 3, 7, 10 and 12), together with a short description. These five types were selected because of the large amount of these slags in the area and because we were quite sure that these were no cokes or lime or other waste materials. The 2 euro coin in some pictures was put there to get an idea of the size of the slags. The other slags types, those that were not selected for further research, are depicted in appendix III.



Figure 9: Type 2. These slags have different colours: brown, orange, grey. They all contain a lot of shells. One part contains some rope.



Figure 10: Type 3. This piece looks like the slags in type 2, but this one is larger and it does not contain shells.



Figure 11: Type 7. This type was most present in the area. There are large and small pieces and there are a lot of different colours: black, white, grey, orange, purple/blue. They are quite heavy and they have a very rough surface.



Figure 12: Type 10 is very heavy, especially the large chunk. The small slag is much more smooth than the large one, but the colour is almost the same. Most likely this is steel slag.



Figure 13: Type 12 is partly layered. There are black, grey, brown and orange spots. I am not sure whether these are all the same.

The largest amount was collected of type 7 (9.16 kg). See table 3 for an overview of the collected amounts of the five slag types. Table 3 also shows that the water content of the slags was for all types < 3%.

Table 3: Weight (g), dry matter content (%) and water content (%) of the collected slags in Spanjaards Duin.

Sample description	mass (g)	dry matter content DR (%)	% water
type 2	717	98.02	1.98
type 3	374	97.22	2.78
type 7	9158	99.75	0.25
type 10	1790	99.69	0.32
type 12	782	99.32	0.68

The slags were all alkaline, especially the steel slag (type 10) had a high to very high pH (see table 4). These pH values were measured in a settling suspension.

Table 4: pH values of the slags in a water extract at L/S is 10 l/kg, measured in a settling suspension

Sample description	pH_H ₂ O slag
type 2	8.00
type 3	8.45
type 7	9.31
type 10	11.68
type 12	9.57
reference 949	5.97
reference 989	7.89

The results of the 0.43 M HNO₃ extraction give a first impression of which elements are present in the slags, because this extraction is a measure for the reactive amount present in the slags. In this extract slag type 3 and 10 show a pH of 2.63 and 5.09 respectively, the other slag types all have pH values below 1 (table 5).

The compounds As, Ba, Cd, Co, Cr, Mo, Ni, Pb, Sb and Se were measured with ICP-MS, as the concentration was lower than the detection limit of the ICP-AES. See table 6 (ICP-AES) and table 7 (ICP-MS) for an overview of the results.

Table 5: pH of the slags in 0.43 M HNO₃ extract

Sample description	pH_HNO ₃ slag
type 2	0.69
type 3	2.63
type 7	0.51
type 10	5.09
type 12	0.49
reference 949	0.47
reference 989	0.75
blank 1	0.45
blank 2	0.45

The results of the water extraction are shown in table 8 (ICP-AES) and table 9 (ICP-MS). Keep in mind that the units are mg/kg and $\mu\text{g}/\text{kg}$, respectively. The asterisk (*) for values in table 8 means that the concentration for that specific slag type and compound is measured with ICP-MS instead of ICP-AES. The measured concentrations in the water extract are much lower than the concentrations in the 0.43 M HNO_3 extract.

Table 6: Results 0.43 M HNO₃ extraction (kg/mg). Measured with ICP-AES.

Sample description	Al [mg/kg]	Ca [mg/kg]	Cu [mg/kg]	Fe [mg/kg]	K [mg/kg]	Mg [mg/kg]	Mn [mg/kg]	Na [mg/kg]	P [mg/kg]	S [mg/kg]	Zn [mg/kg]
detection limit	0.3	12	0.1	0.9	4	1.5	0.1	3	1	2	0.2
type 2	164	24900	58.6	16970	49	1660	440	207	310	980	944
type 3	17.8	40080	0.14	61690	38	440	360	350	1	4.4	4.36
type 7	1120	7470	13.8	2430	197	500	86.6	140	157	59.1	3.44
type 10	214	73670	< 0.1	11660	53	1830	5200	287	22.5	190	1.79
type 12	513	5060	6.09	2140	219	269	38.1	168	43	24.1	3.67
blanc 1	0.5	< 12	< 0.1	2.1	< 4	< 1.5	< 0.1	6	< 1	< 2	< 0.2
blanc 2	< 0.3	< 12	< 0.1	< 0.9	< 4	< 1.5	< 0.1	< 3	< 1	2	< 0.2
reference 949	850	867	3.96	1310	131	57.4	108	21	527	36.1	6.74
reference 989	2240	34150	107	5570	254	3110	813	178	1440	117	625

Table 7: Results 0.43 M HNO₃ extraction (mg/kg). Measured with ICP-MS.

Sample description	As [mg/kg]	Ba [mg/kg]	Cd [mg/kg]	Co [mg/kg]	Cr [mg/kg]	Mo [mg/kg]	Ni [mg/kg]	Pb [mg/kg]	Sb [mg/kg]	Se [mg/kg]
detection limit	0.0002	0.0003	0.00005	0.00005	0.0002	0.0018	0.0003	0.0004	0.016	0.001
type 2	1.41	8.99	0.669	8.34	29.6	0.068	28.8	25.1	0.08	0.033
type 3	0.0333	70.4	0.0139	1.45	0.324	0.03	3.08	0.016	< 0.016	0.82
type 7	0.82	20.9	0.0109	4.44	4.78	0.208	11.5	1.34	0.02	0.034
type 10	0.0506	9.52	< 0.00005	0.169	3.34	0.302	0.536	0.014	< 0.016	< 0.001
type 12	0.501	14.5	0.0101	1.09	1.23	0.135	3.83	1.37	< 0.016	0.181
blanc 1	0.0029	0.051	< 0.00005	< 0.00005	0.0051	< 0.0018	0.034	0.007	< 0.016	0.008
blanc 2	0.0085	0.021	< 0.00005	0.002	0.002	< 0.0018	0.049	0.005	< 0.016	0.374
reference 949	1.1	6.67	0.168	0.203	3.99	0.043	0.618	10.1	0.04	0.045
reference 989	15	317.7	8.08	8.81	59.1	0.071	15	224.4	0.18	0.022

Table 8: Results water extraction (mg/kg). Measured with ICP-AES, except for values with an asterisk (*); these are measured with ICP-MS.

Sample description	Al [mg/kg]	Ca [mg/kg]	Fe [mg/kg]	K [mg/kg]	Mg [mg/kg]	Na [mg/kg]	S [mg/kg]
detection limit	0.3/0.009*	12	0.9/0.006*	4	1.5	3	2
type 2	0.013 *	2700	0.033 *	12	127	61	2080
type 3	0.009 *	639	0.349 *	6	5.5	42	53
type 7	4.3	99	8.2	10	9.2	22	31.9
type 10	6.5	1320	0.029 *	< 4	< 1.5	47	37.4
type 12	5.5	80	5.9	11	8.4	33	8.5
blanc	0.018 *	< 12	0.020 *	< 4	< 1.5	< 3	< 2

Table 9: Results water extraction (µg/kg). Measured with ICP-MS.

Sample description	As [µg/kg]	Cd [µg/kg]	Cr [µg/kg]	Cu [µg/kg]	Mn [µg/kg]	Mo [µg/kg]	Ni [µg/kg]	P [µg/kg]	Zn [µg/kg]
detection limit	0.2	0.05	0.2	0.3	0.9	1.8	0.3	4	18
type 2	30.5	0.06	0.42	15.2	674	4.7	24	172	70
type 3	4.38	< 0.05	< 0.2	1.78	8.4	< 1.8	1	33	20
type 7	39.8	0.24	25.9	94.2	134	43.4	85	1026	52
type 10	1.42	0.04	19.6	17.2	6.9	18.8	0.5	107	24
type 12	40.3	0.1	15.2	17.1	75	10.4	17.8	771	47
blanc	< 0.2	< 0.05	0.41	2.07	2.5	< 1.8	0.3	13	31

In the water extract also the nutrients NO₃ and NH₄ that are present in the slags were measured with ICP-AES (table 10). The concentration NH₄ is less than 1 mg/kg for all slag types. The concentration NO₃ is ranging between 0.6 mg/kg and 5.4 mg/kg.

Table 10: Concentration NH₄ and NO₃ (mg/kg) in the slags, measured in a water extract.

Sample description	N (NH ₄) [mg/kg]	N (NO ₃) [mg/kg]
detection limit	0.4	0.3
type 2	< DL	1.5
type 3	0.6	2.3
type 7	0.5	0.6
type 10	0.5	5.4
type 12	0.5	3.7
blank	< DL	< DL

3.2 Selective chemical extractions

The results of the oxalate, ascorbic acid and dithionite extraction, needed for the modelling, are shown in table 11, 12 and 13, respectively. The two slag types as well as the composite soil sample are included.

Table 11: Concentration amorphous Al-(hydr)oxides (mg/kg) determined with an oxalic acid extract.

Sample description	Amorphous Al-(hydr)oxides [mg/kg]
type 2	50
type 7	300
composite sample	36
reference 949	862
reference 989	1474
blank	0

Table 12: Concentration amorphous Fe-(hydr)oxides (mg/kg), measured with an ascorbic acid extraction.

Sample description	Amorphous Fe-(hydr)oxides [mg/kg]
type 2	5020
type 7	460
composite sample	100
blank	0

Table 13: Concentration total Fe-(hydr)oxides and Mn-(hydr)oxides (mg/kg), measured with a dithionite extraction.

Sample description	total Fe-(hydr)oxides [mg/kg]	Mn-(hydr)oxides [mg/kg]
type 2	94200	828
type 7	3720	42
composite sample	1220	50
blank	0	0

The amount of crystalline Fe-(hydr)oxides was calculated as the result of the dithionite minus the result of the ascorbic acid extraction. See table 14 for the results.

Table 14: Concentration crystalline Fe-(hydr)oxides (mg/kg).

Sample description	Crystalline Fe-(hydr)oxides [mg/kg]
type 2	89180
type 7	3260
composite sample	1120

The organic matter (OM) content of the composite soil sample, measured in duplo, was below 0.5%. See table 15 for the results.

Table 15: Organic matter content of the composite soil sample.

Sample description	Organic matter content (%)
composite sample	0.43
composite sample	0.44
reference 949	2.85
reference 989	12.4

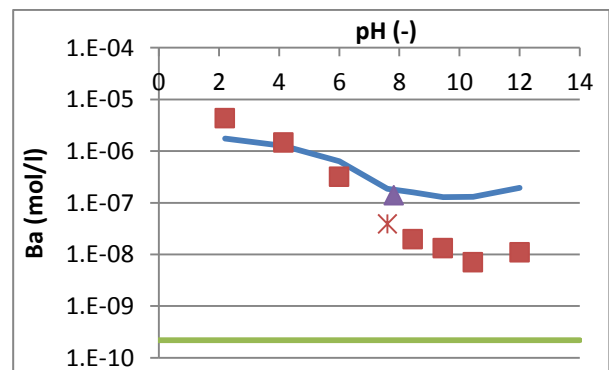
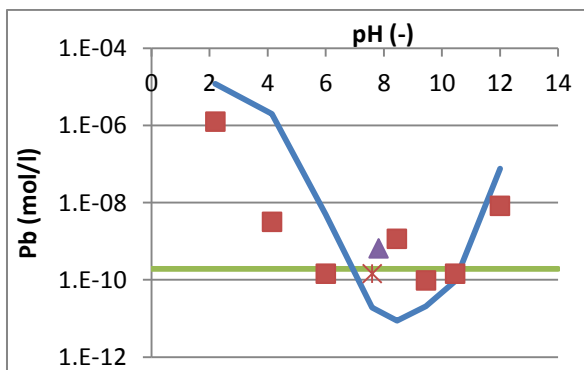
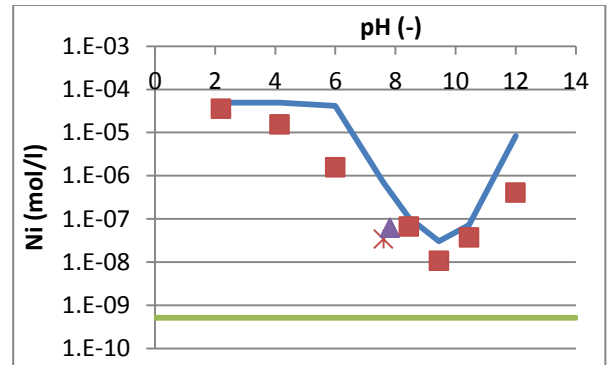
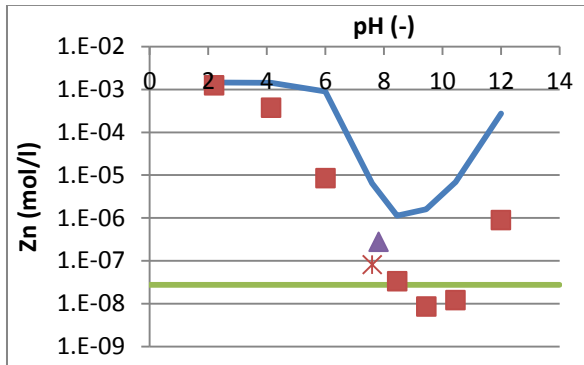
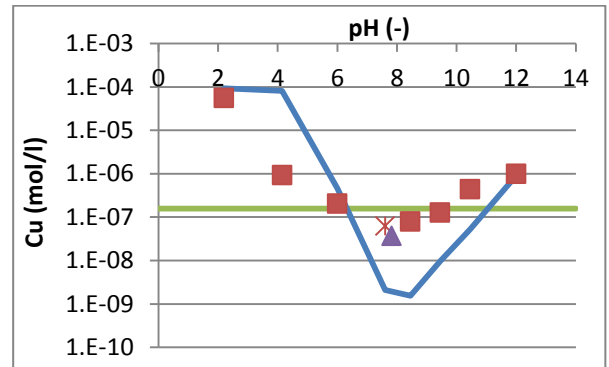
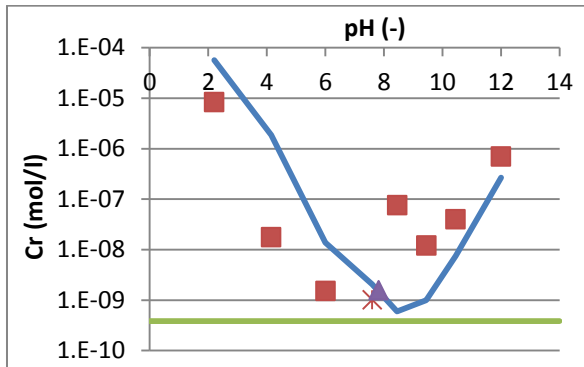
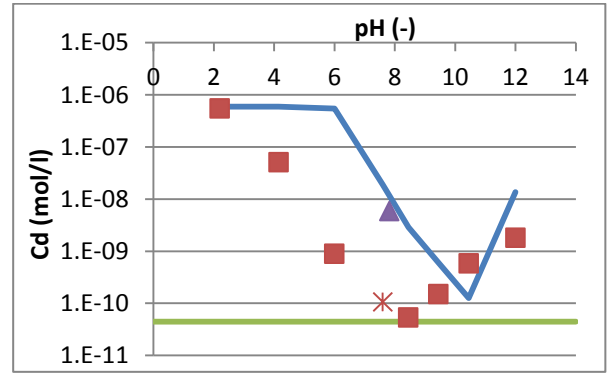
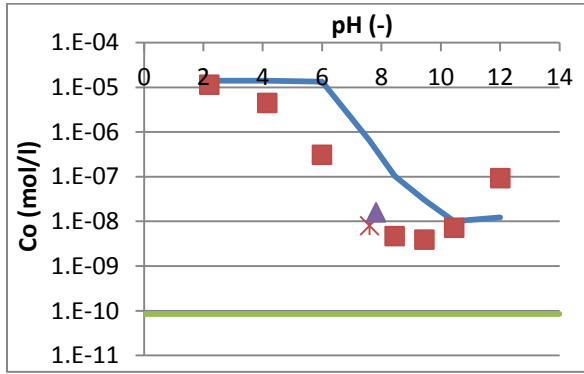
3.3 Leaching

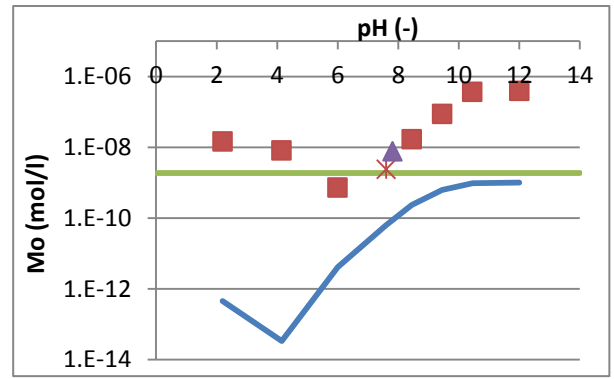
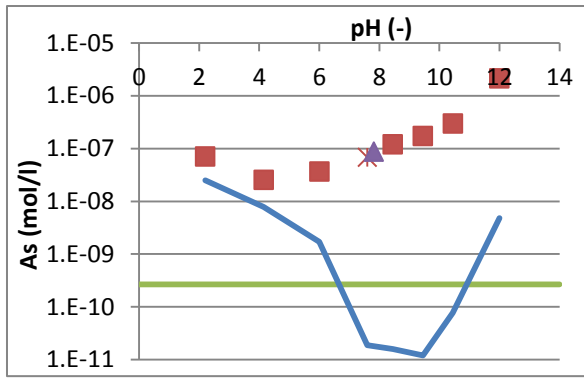
3.3.1 pH stat leaching test and geochemical modelling

During the pH stat test different target pH values between 2 and 12 were set. Eventually these target pH values were not exactly reached, because we had to set a range around the target value. The pH values for type 2 were ranging between 2.2 and 12 and the pH values for type 7 were ranging between 2 and 11.95. The results of the pH stat tests are visualised in figure 14 (slag type 2) and figure 15 (slag type 7). The concentrations of all elements are listed in table II and III in appendix IV.

The red star in each plot in figure 14 and figure 15 is the concentration measured at the native pH of the slag. The metal cat-ions Co, Cd, Cr, Cu, Zn, Ni and Pb show a "V-shaped" curve, having the lowest concentrations at intermediate pH values. This pattern is more pronounced for slag type 2 compared to slag type 7. The anions As and Mo have increasing concentrations towards higher pH values.

In figure 14 and figure 15 also the modelled concentrations of the pH stat tests are depicted. The metal cat-ions Cd, Cr, Cu, Zn, Ni and Pb again show a "V-shaped" curve. Arsenic shows very low concentrations between pH 6 and 10. Molybdenum shows a minimum concentration at pH 4.

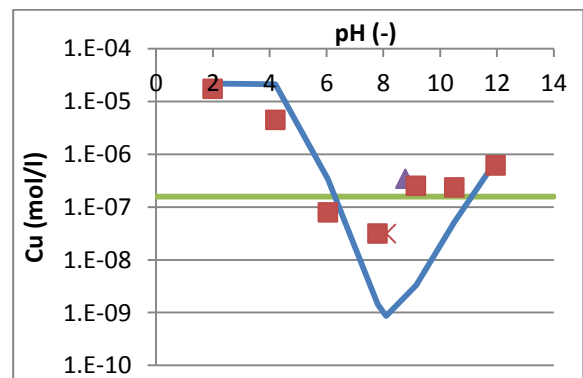
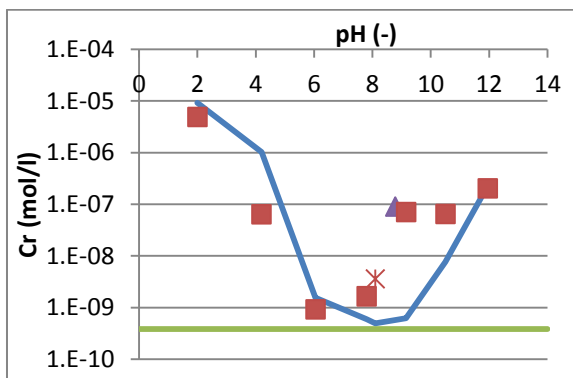
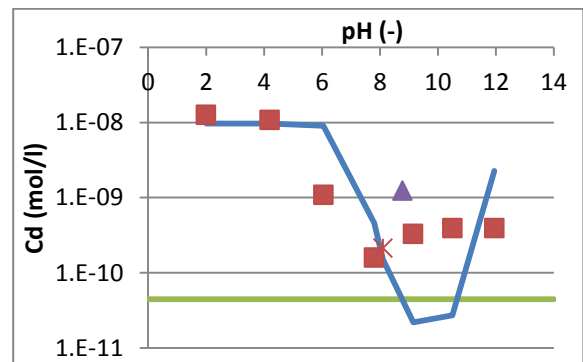
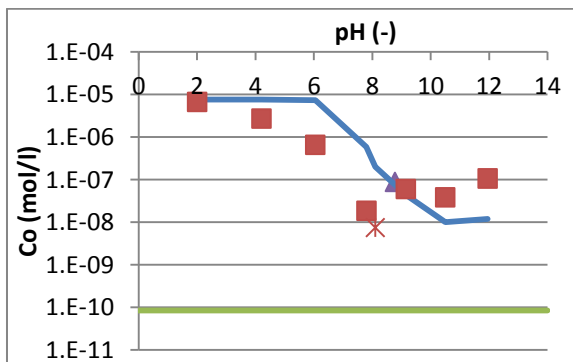


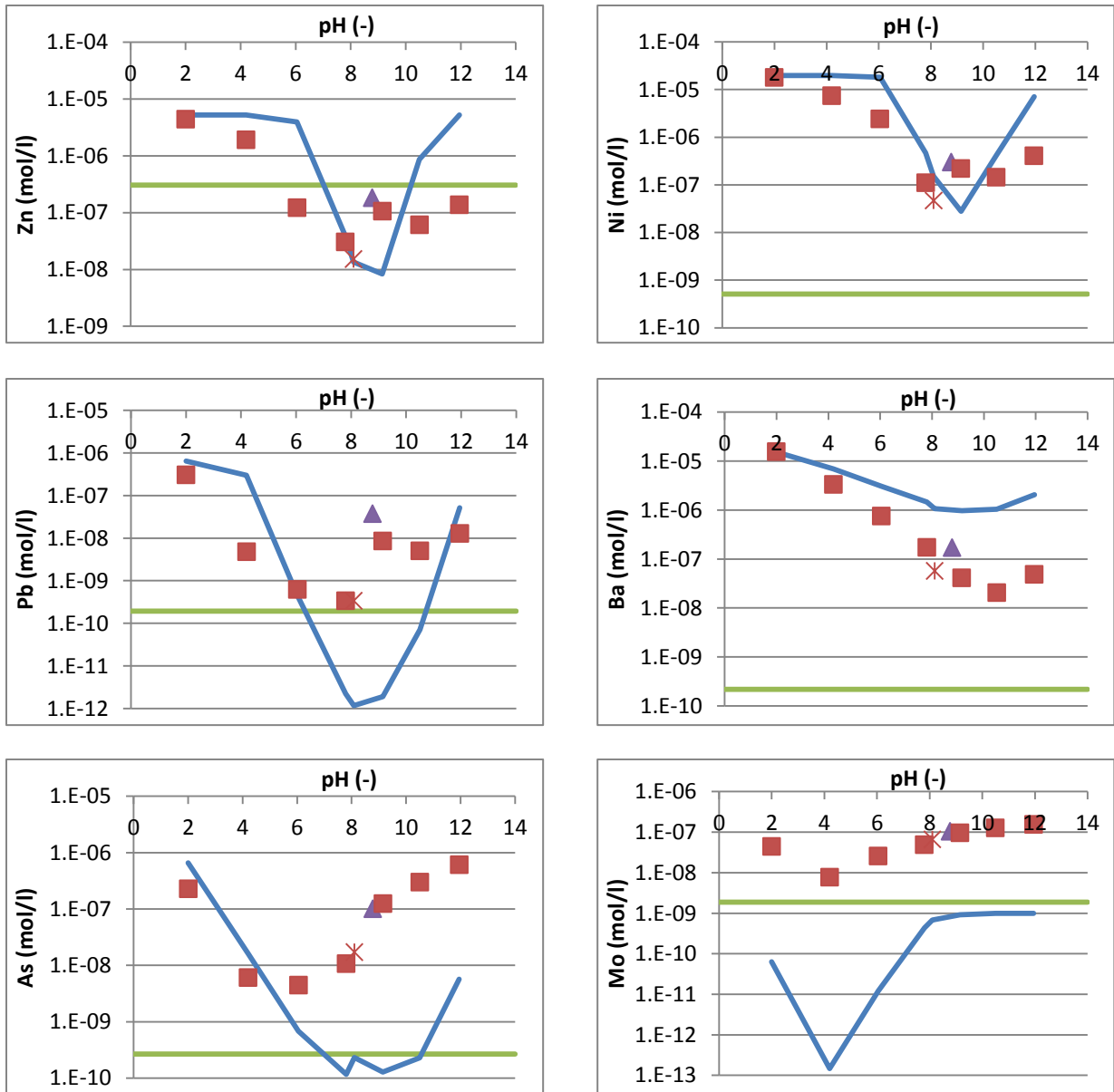


Legend:

- model
- measurement pH stat
- ▲ batch leaching test L/S 10
- detection limit

Figure 14: pH stat leaching curves and model predictions as a function of pH for Co, Cu, Cr, Zn, Ni, Cd, Pb, Ba, Mo and As for slag type 2. The red star is the measurement at native pH (7.6).





Legend:

- model
- measurement pH stat
- ▲ batch leaching test L/S 10
- detection limit

Figure 15: pH stat leaching curves and model predictions as a function of pH for Co, Cu, Cr, Zn, Ni, Cd, Pb, Ba, Mo and As for slag type 7. The red star is the measurement at native pH (8.1).

3.3.2 Batch leaching test

Table 16 shows the leached concentrations at L/S 10, determined from the batch tests at L/S 2 and L/S 8. A complete overview of all element concentrations measured from the batch leaching test at L/S 2 and 8 can be found in appendix V. The concentrations at L/S 10 are also depicted in the graphs in figure 14 and figure 15.

Table 16: Leached concentrations at L/S 10, determined from batch tests at L/S 2 and L/S 8.

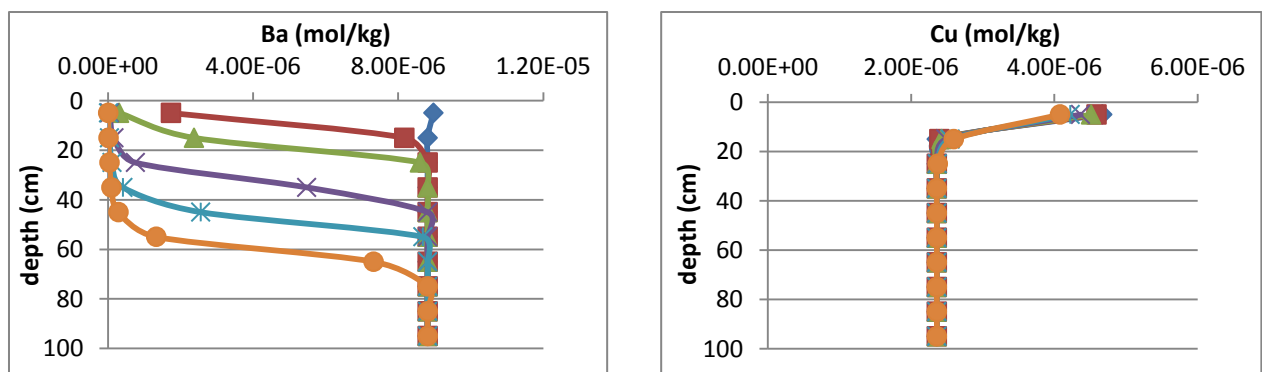
sample description	As [mg/kg]	Ba [mg/kg]	Cd [mg/kg]	Co [mg/kg]	Cr [mg/kg]
type 2	0.0309	0.0493	0.0021	0.0056	0.0006
type 7	0.0356	0.0603	0.0004	0.0311	0.0318

	Cu [mg/kg]	Mo [mg/kg]	Ni [mg/kg]	Pb [mg/kg]	Zn [mg/kg]
type 2	0.0131	0.0027	0.0217	0.0002	0.0964
type 7	0.1214	0.0369	0.1070	0.0134	0.0649

3.4 Predictive modelling of the chemical soil and water quality

Figure 16 shows for slag type 2 for each layer of 10 cm depth in the upper meter of soil the solid phase concentration of Ba, Cu and Mo up to 80 years, simulated by ORCHESTRA. For Ba we see that the concentration peak is going down with depth. For Cu we see that the concentration in the upper 10 cm is decreasing a little bit over time, between 10 and 20 cm the concentration is increasing a little bit over time. In the layers below 20 cm the concentration of Cu is constant. Molybdenum (Mo) shows a sharp decrease in the concentration over the whole soil layer within 10 years: from about $3.44 \cdot 10^{-7}$ mol/kg to about $1.48 \cdot 10^{-16}$ mol/kg (not visible in the graph). The graphs of the other metal concentrations in the soil, both for slag type 2 and 7 are shown in figure XIII (type 2) and XIV (type 7) in appendix VI, because they have more or less the same shape as one of the three graphs in figure 16. The elements Co and Ni have the same shape as Ba. Arsenic (As), Cd, Cr and Pb have the same shape as Cu, and Zn the same shape as Mo.

For slag type 7 only Ba has the same shape as Ba in type 2. Arsenic (As), Cd, Co, Cr, Cu, Ni, Pb and Zn have the same shape as Cu in type 2 and Mo has the same shape as Mo in type 2. All elements have in common that they leach over time and that the concentration in each layer is very low.



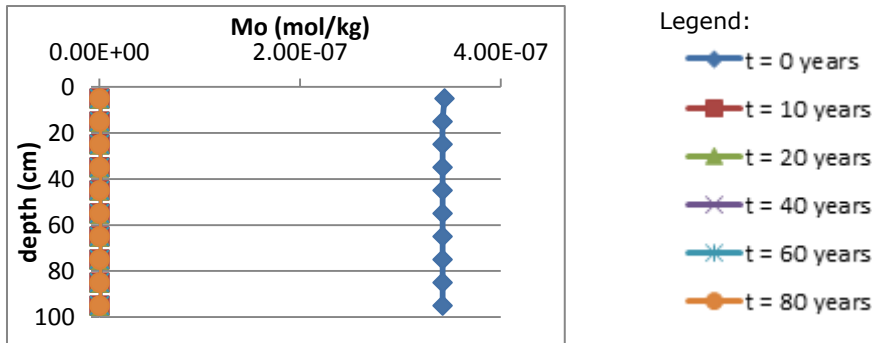


Figure 16: The modelled concentrations of Ba, Cu and Mo (mol/kg) over time for slag type 2, for each layer of 10 cm depth in the upper meter of soil.

Figure 17 shows for slag type 2 the average concentration of Ba, Cu and Mo in the 1 m groundwater layer up to 100 years. For all three compounds the concentration increases sharply in the first two years. After that the concentration of Ba and Cu is constant over time. For Mo there is a sharp decrease after two years. The decrease is still going on after 10 years, although this is not visible in the graphs, because of the low concentrations. The graphs of the other metal concentrations in the groundwater, both for slag type 2 and 7, are shown figure XV and XVI in appendix VI. The elements Co, Cr, Ni and Zn have the same shape as Ba and Cu. Arsenic (As), Cd and Pb start with a higher concentration, which decreases during the first two years, after which the concentration stays constant.

For slag type 7 the elements Co, Cr, Ni and Zn have the same shape as Ba and Cu in type 2. Molybdenum (Mo) has the same shape as Mo in type 2. Arsenic (As), Cd and Pb start again with a higher concentration, which decreases during the first two years, after which the concentration stays constant.

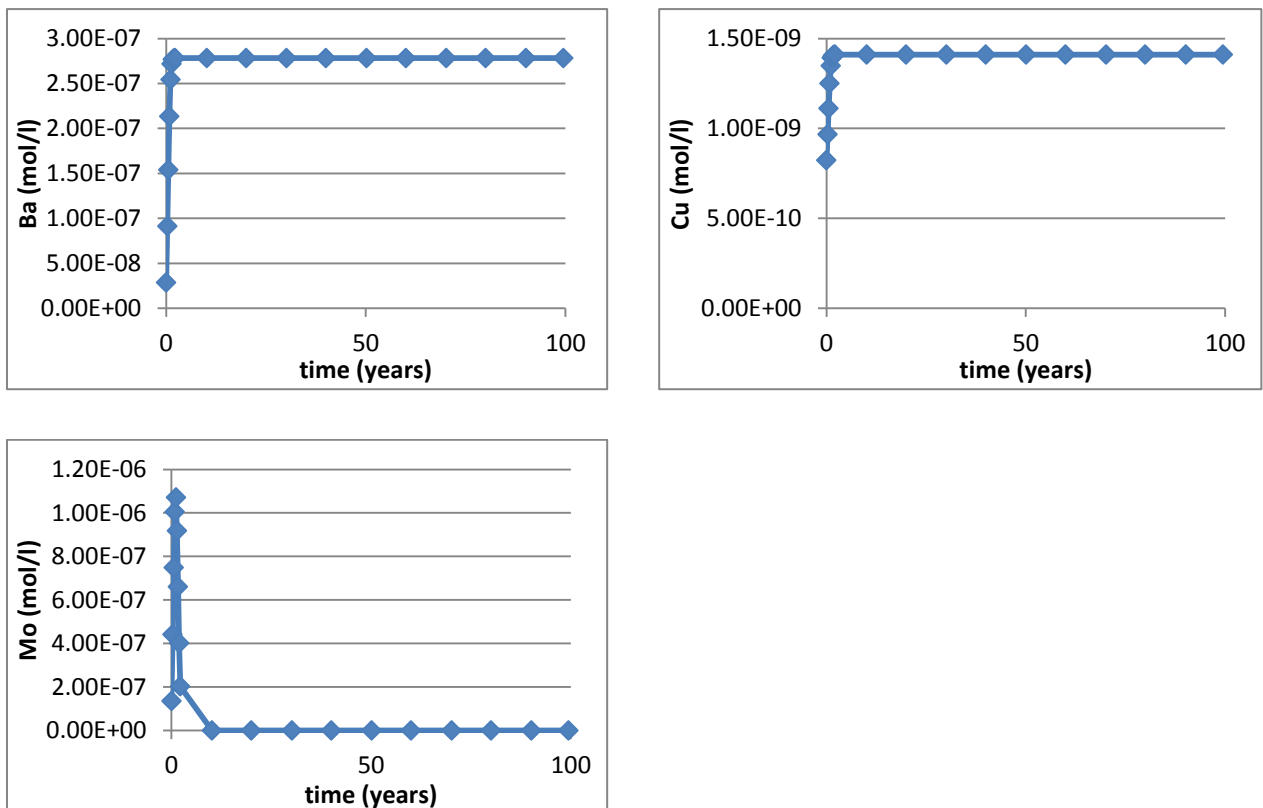


Figure 17: The modelled average concentrations of Ba, Cu and Mo (mol/l) for slag type 2, in the upper meter of groundwater, over time.

3.5 Influence on vegetation

Table 17 shows that the concentration of N (NH₄ and NO₃) and P (PO₄) in the soil of the pot experiment, is less than 1 mg/kg. Table 18 shows the concentration of Ca, K and Mg in the soil of the pot experiment, also after equilibration time. The pH of the soil after equilibration time, measured in a water extract, was measured in a duplo sample: 9.50 and 9.64.

Table 17: Concentration NH₄, NO₃ and PO₄ (mg/kg) in the soil of the pot experiment after equilibration time, measured in a water extract.

Sample description	NH ₄ [mg/kg]	NO ₃ [mg/kg]	PO ₄ [mg/kg]
soil pot experiment	0.01	0.4	0.5
blank	0.01	-0.1	-0.06

Table 18: Concentration Ca, K and Mg (mg/kg) in the soil of the pot experiment after equilibration time, measured in a water extract.

Sample description	Ca [mg/kg]	K [mg/kg]	Mg [mg/kg]
soil pot experiment	67	6	4.8
blank	1	0	0

At the end of the experiment 93 seeds (27% of total) were germinated and no plants had died during the experiment. The species *E. palustris* and *P. palustris* did not germinate at all. From the other species in total 46 seeds germinated in 16 pots that contained slag and 47 seeds germinated in 17 pots that contained no slag. Most of the plants had purple/brown leaves at the end of the experiment, irrespective of treatment (see photo's in appendix VII).

Table 19 shows that most plants that germinated were from the species *P. coronopus*. Least germinations were from *L. salicaria*. Between brackets the number of pots in which plants germinated is indicated. A complete overview of the amount of plants per pot can be found in table V in appendix VIII. A t-test (including the pots without germination) for comparison of the number of germinations between pots containing sand with and sand without slag yielded a P-value of 0.95. When this t-test was done for the germination of each species separately, the P-values were 0.88, 0.34 and 0.78 for *P. coronopus*, *D. carota* and *L. salicaria*, respectively.

Table 19: The number of plants that germinated for each species growing in sand with or without slag. The number between brackets indicates the number of different pots these plants were growing in.

	<i>P. coronopus</i>	<i>D. carota</i>	<i>L. salicaria</i>
slag	32 (7)	7 (5)	7 (4)
no slag	31 (7)	10 (6)	6 (4)

The highest biomass was obtained in pot 41 (82.6 mg) and the lowest biomass in pot 45 (0.7 mg). Table VI in appendix VIII gives an overview of the biomass in each pot. A t-test (including the pots without biomass) for comparison of the amount of total biomass between plants growing in sand with and without slag yielded a P-value of 0.73. When this t-test was done for each plant species separately, the P-values were 0.42, 0.76 and 0.68 for *P. coronopus*, *D. carota* and *L. salicaria*, respectively.

4. Discussion

4.1 Determination of the various types of slags and their composition

The stocktaking of the slags shows that a lot of different types and materials are present in the area. Possibly there are even more than the sixteen types I distinguished, as these were collected in only a part of the area. However, it is likely that not all the material we collected were slags. Some material was probably cokes, lime or just rusted iron. Therefore these materials were excluded for further research.

The pH of the slags is higher than 8 for all slag types, except for type 2. It is not known for how long the slags were situated on the sea bottom, and whether they were already weathered because of exposure to atmospheric CO₂. In the research of Engström et al. (2014), the leaching and pH development of different types of steel slag was investigated before weathering and after 24 months of weathering in an environment open for seasonable weather conditions. The pH decreased in two years with one unit, from about 11 to 10. Because at the moment the pH of our steel slag (type 10) is still 11.68, it is likely that this slag was not exposed to weathering for a long time, and hence situated on the sea bottom, where no contact with atmospheric CO₂ is possible. As it can be assumed that all slags were deposited in Spanjaards Duin at the same time, we can conclude that also the other slags are not influenced by weathering. However, the slags were deposited in the dune area already in 2008/2009. Based on the drop in pH of 11 to 10 in two years, shown by Engström et al. (2014), we would expect a pH lower than 11.68 for our steel slag, because of the longer weathering time (six years). Maybe the difference is caused by the fact that Engström et al. (2014) used in their experiment fresh steel slag samples, while the slags in Spanjaards Duin are not fresh at all.

The pH measured in the slag types 3 and 10 was significantly above pH 1. Likely these slags contain a substantial amount of lime for which we did not correct by adding extra acid according to the protocol. As a consequence the reactive metal content is therefore likely somewhat underestimated for these two slag types.

According to the Circular Soil Remediation (2013), the concentration of Zn in slag type 2, measured in the 0.43 M HNO₃ extract, exceeds the intervention value. For the same slag type the concentration of Cd and Cu exceed the background value. All other measured elements in other slag types are very low. Slag type 2 thus can possibly cause a serious contamination regarding Zn. The other four slag types are not heavily polluted and therefore this first investigation of the slags indicates that the threat of these four slag types to the environment is most likely low.

Comparison of the reactive amounts determined with the 0.43 M HNO₃ extraction with the reactive amounts present in the top layer of sandy soils in the Netherlands (Geochemical soil atlas of the Netherlands, 2012), shows that the concentrations Cr and Ni in both slag types and Cu and Zn in type 2 are somewhat higher than the maximum values given in the atlas. This indicates that the slags have a higher metal content than an average sandy soil in the Netherlands, but not that high that there is a potential risk for contamination, except for slag type 2 regarding Zn.

The concentrations in the water extract are low, indicating that the elements do not dissolve easily. What is striking is that the concentration Zn in type 2 in the water extract is not much higher than in the other slag types, while this was the case for the 0.43 M HNO₃ extract. The same can be observed when we compare the measured Zn concentration of the pH stat test at native pH for both slag types. This shows also no large difference between the two slag types ($8.15 \cdot 10^{-8}$ mol/l for type 2 and $1.53 \cdot 10^{-8}$ for type 7). This indicates that the Zn does not dissolve easily in water, but is only released at very low pH.

4.2 Leaching and modelling

4.2.1 pH stat leaching test

The results of the pH stat test can be interpreted as an indication of what compounds will leach from the slags into the soil and groundwater at a certain pH of the slag or soil. It did not matter whether P and S are inserted as dissolved (results of pH stat test) or total concentrations (results of the 0.43 M HNO₃ extraction) in the input. The model gives almost the same results for these situations.

The results show that the metal cat-ions Co, Cd, Cr, Cu, Zn, Ni and Pb have a "V-shaped" curve. The concentrations thus increase with decreasing pH to the left of the minimum and with increasing pH to the right of the minimum. The increase at lower pH values is because cat-ions are more soluble at lower pH values, because the reactive surfaces (oxides) to which the metal cat-ions bind, are less negatively charged at low pH. At intermediate pH (7-10) the reactive surfaces are negatively charged. The cat-ions then bind to the oxide surfaces resulting in the minimum. At very high pH (>10) the solubility of the cat-ions increases again due to the formation of metal hydroxide complexes (e.g. ZnOH⁺). The oxy-anions As and Mo show the highest concentrations at high pH values, because then there is less binding to oxide surfaces due to their negative charge. At low pH the oxy-anions bind to the positively charged oxide surfaces, causing a lower concentration. We see that leaching from the slags at native pH (7.6 and 8.1 for slag type 2 and 7, respectively) is around the minimum and thus very low. In case of a small future increase or decrease in pH of the slags, leaching from slags will still be limited.

4.2.2 Geochemical modelling

The modelled concentrations of the pH stat test show for the cat-ions Cd, Co, Cr, Cu, Zn, Ni and Pb a "V-shaped" curve for both slag types. Barium (Ba) shows a minimum concentration at high pH. For both slag types the concentration As and Mo shows, to a lesser extent, a "V-shaped" curve. Arsenic has a minimum concentration between pH 6 and 10, while Mo shows a minimum at pH 4.

Comparison of the results of the pH stat test with the model (figure 14 and figure 15), shows that the cat-ion concentrations in type 7 are quite well calculated at low pH values. In type 2 the cat-ion concentrations at lower pH are somewhat more overestimated by the model compared to type 7. At pH 2 the cat-ions and As concentrations are predicted almost perfectly by the model. For Co, Cd, Zn and Ni the model predicts for slag type 2 as well as type 7 that in the pH range 2-6 the concentrations do not change. The modelled Cu concentration shows the same, but only for the pH range 2-4. The measurements however, show that the concentrations are decreasing in these pH ranges. Dzombak and Morel (1990), who designed the Generalized Two-Layer Model with HFO, found that between pH 4 and 6 the adsorption of metal cat-ions also increases with pH. It is thus strange that this is not observed for our model. It seems that or the model does not represent adsorption to oxides in a proper way, or the model lacks some processes that are needed for a correct simulation.

The metals are not all in solution or adsorbed to Fe- and Al-(hydr)oxides (HFO), but can also be present in minerals. The model calculates for slag type 2 that Cr minerals form above pH 8.45, Co minerals above pH 9.45, Cu and Zn minerals above pH 10.45 and Ni and Pb minerals above pH 12. Barium (Ba) minerals are present at all pH values. Slag type 7 starts to form Cr minerals above pH 9.15, Co and Cu minerals above pH 10.5 and Ni and Pb minerals above pH 11.95. Barium minerals are formed at all pH values except at pH 2. Adsorption and desorption, and hence leaching, of metals thus plays a larger role at lower pH values: below 8.45 for type 2 and below 9.15 for type 7. At high pH mineral formation plays a role. There is a chance that not all minerals that play a role in the high pH range are taken into account, which causes then a deviation between the model and the measurements.

The concentration Zn in slag type 2 is strongly overestimated by the model, except at low pH. On the contrary, the Zn concentration in slag type 7 is quite well estimated, only at a pH higher than 10 it is overestimated. According to Marzouk et al. (2013), there are indications that a 0.43 M HNO₃ extraction overestimates the concentration of Zn, Cd and Pb in calcareous soils with high concentrations of Pb/Zn. When the results of such a HNO₃ extraction are then used for prediction of the solution concentrations, these are automatically also overestimated (Groenenberg and Lofts, 2014). That could be the reason

why the Zn concentrations in type 2 and to a less extent in type 7 are overestimated at higher pH. However, Cd and Pb are not overestimated at higher pH values. Another explanation for overestimations in the model could be the fact that only adsorption to Fe- and Al-(hydr)oxides (HFO) is taken into account in the model, and not adsorption to Mn-(hydr)oxides. However, the amount of Mn-(hydr)oxides is 0.15 mol/l and $7.6 \cdot 10^{-3}$ mol/l for slag type 2 and 7, respectively. This is very low compared with 3.58 mol/l HFO for type 2 and 0.29 mol/l HFO for type 7, so that is not a satisfying explanation. Another cause for the discrepancy between the measurement and the model could be that there are processes going on at high pH that are not taken into account in the model. Perhaps one of these processes is adsorption to OM. Dijkstra et al. (2008; 2009) took OM into account in their modelling, while in our research we assumed there was no OM present in the slags. The absence of OM is maybe the reason for the fact that the concentration of metal cat-ions in our model shows quite some deviations from the pH stat results, while this was not the case for Dijkstra et al. (2008; 2009). The oxy-anions are not influenced by the presence of OM, because at low pH the OM is charged neutrally and it is charged negatively at higher pH values. So the absence of OM cannot be an explanation for the large difference between measurement and model for As and Mo.

The concentration dissolved As is underestimated at pH values above 6 and the concentration Mo is underestimated over the whole pH range, but especially between pH 2 and 6. A 0.43 M HNO₃ extract however, on which the input of the model is based, is less efficient in extracting oxy-anions (Groenenberg, 2014). In Dijkstra et al. (2009) it was found that a 0.43 M HNO₃ extract underestimated the Mo concentration, and because of that it is also underestimated in the model. That could be an explanation for the fact that the modelled concentrations of As and Mo are much lower than measured in the pH stat tests.

For some constituents, especially Cr, Ni and Pb in type 2 the fifth point (pH 8.45) in the measurements seems to be an outlier compared with the other measured values. The same is the case for Co, Pb and Zn in type 7, but then for the sixth point (pH 9.15). We do not know why that is. There are no indications that something went wrong during the execution of the pH stat test.

Because we wanted to know whether the overestimation of some cat-ions by the model is due to overestimated or underestimated concentrations of metals in the HNO₃ extract, which were used as input, the model was also run using the concentrations of the pH stat test at pH 4.15 (slag type 2) and pH 4.2 (slag type 7) as input. The measured metal concentrations in the pH stat extract at these pH values are lower than the concentrations in the 0.43 M HNO₃ extract. Therefore, also the modelling results give lower metal concentrations. The concentrations Co, Ni and Zn, which were initially overestimated (figure 14 and figure 15), are in the new situation better predicted (graphs not shown). Those concentrations that were initially quite well estimated, like Cr and Pb, are in the new situation substantially underestimated. The concentrations As and Mo, which were initially underestimated, are even more underestimated when the concentrations at pH 4.15 and 4.2 are used as input. This confirms the idea that some cat-ions (e.g. Zn) are overestimated by a 0.43 M HNO₃ extraction and that some oxy-anions (As and Mo) are underestimated by a 0.43 M HNO₃ extraction. The deviations between model and measurements are thus partially caused by the input that is used and partially by the model itself, e.g. a lack of processes.

4.2.3 Predictive modelling of the chemical soil and water quality

With regard to the predictive modelling of the soil and groundwater quality, the graphs in figure 16 show that Cu is not a mobile element in slag type 2; the concentration in the soil below 20 cm stays constant. There is also no Cu leaching from the upper meter of soil to the groundwater (figure 17). Barium (Ba) and Mo on the contrary, are more mobile elements, because the concentration in the soil is going down over time and with depth. The fact that in the groundwater the concentrations are sharply increasing for the first two years (figure 17), is only caused by the fact that the initial concentrations below the upper meter of soil were set at very low values ($2 \cdot 10^{-10}$ mol/kg) for all elements. Other more mobile elements in both slag types are Co and Ni, as the concentration in the soil lowers over time and with depth. There is thus some leaching of these compounds. None of the elements in the layer with groundwater shows increasing concentrations due to leaching from the upper soil layer.

The concentrations in the upper meter of soil and in the meter of groundwater are for all elements very low. None of them exceed the intervention value of soil and groundwater. However, initially this modelling was done with a $p\text{CO}_2$ -value of -2.52 instead of -6 and with metal concentrations in the sand taken from the 5% percentile reactive amounts in the top layer of sandy soils from the Geochemical soil atlas of the Netherlands (2012). We used these values because we assumed that the metal concentrations in the sand would be very low. The amount of OM in the soil, to which metals can bind, is namely also low (0.435%). The result then was that the concentration Ni and Pb in the groundwater was for both slag types exceeding the intervention values of 75 $\mu\text{g/l}$. See table VII in appendix IX for the peak concentrations and the duration time of exceedance. These high concentrations were not what we expected, because the metal concentrations in the slags were low and we assumed that they were also low for the sand. A possibility was that this last assumption was not right. To be sure that the high concentrations in the groundwater did not originate from high metal concentrations in the sand, a 0.43 M HNO_3 extraction and a 0.01 M CaCl_2 extraction (protocol E2408, 2013) were carried out with the composite soil sample. This indicated that the metal concentrations in the sand are indeed far below background values (see appendix X and XI). The high metal concentrations in the groundwater are thus not caused by high concentrations in the slags or the sand. The pH of the sample in the 0.01 M CaCl_2 extract was 8.3 and the DOC content measured in this CaCl_2 extract was 1.3 mg/l .

The only cause for the very high Ni and Pb concentrations is then that the model is not able to correctly estimate the metal concentrations. After investigation of the different parameters and input in the model, it appeared that the combination of the pH and $p\text{CO}_2$ caused the high Ni and Pb concentrations. The pH in a soil which contains calcium carbonate (CaCO_3) is among others dependent on the CO_2 concentration in the atmosphere, which is at the moment about 0.0035%. Precipitation of CaCO_3 limits the rise in soil pH, because the solubility of CaCO_3 is limited. When the CO_2 in the soil solution and the atmosphere is in equilibrium, the pH of the soil cannot rise above 8.4 (Brady and Weil, 2008). Therefore, the pH of 9.61 of the sand, used as input for predictive modelling of soil and groundwater quality, might seem strange. However, in Arens et al. (2013) it is shown that a pH higher than 9 can occur in suppleted embryonic dunes in the rhodunal (calcareous) district of the coast, in which Spanjaards Duin is also situated. In the 'Annual Management Report Spanjaards Duin 2013' (Stichting het Zuid-Hollands Landschap, 2014), it is described that the vegetation composition in Spanjaards Duin indicates that the current habitat type is the 'embryonic dune', so this high pH value is not impossible. A possible cause for pH values higher than 8.4 could be the presence of sodium (bi)carbonates in the soil. Sodium (bi)carbonate is more water soluble than CaCO_3 , therefore more hydroxyl ions are produced and hence a pH of higher than 10 can be reached (Brady and Weil, 2008).

However, the pH of the soil is also dependent on the amount of CO_2 in the soil. Initially we used a $p\text{CO}_2$ -value of -2.52, which is a value that is often used for soils. This CO_2 concentration is ten times higher than in the atmosphere, where the $p\text{CO}_2$ is -3.5. The CO_2 concentration in the soil is assumed to be higher than in the air because of biological activity in the soil. But the soil in the valley is still bare; there are almost no plants growing there. The very high pH of the soil is only possible in combination with a lower CO_2 concentration, because if the CO_2 concentration in the air and in the soil is in equilibrium, the soil pH cannot become higher than 8.4. The CO_2 that diffuses from the air into the soil, will be used for dissolution of CaCO_3 . Therefore the $p\text{CO}_2$ will at least be lower than in the air. Because there is a lot of CaCO_3 present in the soil, the CO_2 consumption will be very high. Next to this, the fact that the soil in the valley is quite wet hinders the diffusion of CO_2 from air to soil (Groenenberg, 2015-b). It was found that in a soil with pH 10.06 the $p\text{CO}_2$ -value is -6.4 (Appelo and Postma, 2005). Because the pH in our soil is 9.61, we estimated the $p\text{CO}_2$ -value at -6. When this value is used in the model, together with the metal concentrations in the sand determined with the 0.43 M HNO_3 extraction and a DOC-value of 1.3 mg/l , none of the metals shows high concentrations in the groundwater.

When in the future plants will grow in the valley area, the CO_2 concentration in the soil will increase due to biological activity. Together with the increase in CO_2 the pH of the soil will go down, because the plants can also excrete acids. In case the modelling is done with the standard $p\text{CO}_2$ -value for soils (-2.52) and a soil pH of 7.0, representing a possible future situation, the metal concentrations in the soil and groundwater are still all very low.

Eventually it was checked whether ORCHESTRA predicts the metal concentrations accurately. To this end the measured metal concentrations determined in the 0.01 M CaCl_2 soil suspension were compared with an ORCHESTRA prediction for the concentration in the groundwater. As input the metal concentrations in

the sand determined by the 0.43 M HNO₃ extraction were used, a pH of 8.3 (which was the pH of the CaCl₂ extract) and a pCO₂-value of -3.5. This last value was chosen because the pCO₂ of air is -3.5 and because the CaCl₂ suspension was shaken in contact with the air. Therefore we assumed that there is equilibrium between the amount of CO₂ in the CaCl₂ soil suspension and in the air. The results of this comparison are shown in appendix XII. A comparison for Cd, Cu, Pb and Zn is not available, because in the CaCl₂ extract these concentrations were below the detection limit of the ICP-AES/MS. The Ba, Co, Mo and Ni concentrations calculated by ORCHESTRA are higher compared to these measured in the CaCl₂ extract. The concentration Ba and Mo are considerably overestimated. Chromium (Cr) concentrations are almost the same. The As concentration is a factor 10 times higher in the CaCl₂ compared to the model. However, the model predicts no too high concentrations. This check indicates that the model deviates from the measurements, but still simulates quite well.

4.2.4 Batch leaching test

The results of the batch leaching test at L/S 2 and L/S 8 were used to calculate the metal concentrations at L/S 10. For slag type 7, the concentrations As, Co, Cr, Cu, Ni and Pb were higher at L/S 8 compared to L/S 2. This is not what I expected, as it can be presumed that most of the elements are already leached in the treatment at L/S 2. A possible explanation for this is the difference in pH. The pH increased from 7.89 at L/S 2 to 8.78 at L/S 8. The only reason for this increase in pH we can think of is that more carbonates dissolve during the longer agitation time (16 h) for the treatment with L/S 8 in comparison with the treatment with L/S 2. Such a difference in pH can cause a change in the solubility of the different elements (van Zomeren, 2015). When the results of the batch leaching test (L/S 10) are plotted in the figure with the results of the pH stat test (figure 15), this shows that in the area of pH 7.89-8.78 the concentration of the elements As, Co, Cr, Cu, Ni and Pb is rising. This indicates that indeed the change in pH causes the higher concentration at L/S 8 compared to L/S 2.

Comparison of the concentrations of the batch leaching test at L/S 10 and the measured concentrations of the pH stat at own pH, shows that the concentrations are almost the same for slag type 2, except for Cd. For slag type 7, the L/S 10 value is higher than the result of the pH stat. This difference is maybe caused by the rise in pH during the batch leaching test, because the result at L/S 10 is more in line with the result of the pH stat measurement at pH 9.15 instead of the native pH (8.1).

When the metal concentrations of the batch leaching test at L/S 10 (table 16) are compared to the maximum allowed concentrations for non-shaped building material in the Soil Quality Decree (2007), it appears that none of the concentrations in the slags exceeds the maximum value. In the field, especially in the valley area, the soil will be dry in summer. In winter, the soil will be wet or even inundated. However, I think that a L/S of 2 is more realistic, even in wet times. Because the L/S will be lower in the field than in the batch leaching test, we can conclude that leaching of the slags is very low and hence will not cause problems with regard to the soil and water quality.

4.3 Influence on vegetation

In the pot experiment there were apparently some pots that contained more than five seeds, as there were four pots in which 6 or 7 seeds germinated. Two of these pots contained slag, the other two pots did not contain slag (see table V in appendix VIII). This was caused by the fact that the seeds of some species were that small, that they were almost invisible by the naked eye. However, these extra germinated seeds were not removed. Otherwise, also the non-germinated seeds that were sown too much should be removed, and that is not possible.

With a t-test ($\alpha = 0.05$) it was determined that there is no significant difference in germination between plants growing in sand with and sand without slag ($P = 0.95$). Also germination in soil with and without slag, but then compared for each plant species separately, does not show a significant difference: $P = 0.88, 0.34$ and 0.78 for *P. coronopus*, *D. carota* and *L. salicaria*, respectively. Determination of the total biomass yielded also no significant differences by doing a t-test: not between plants growing in sand with and without slag ($P = 0.73$), and not when compared for each plant species separately ($P = 0.42, 0.76$ and 0.68 for *P. coronopus*, *D. carota* and *L. salicaria*, respectively). There are thus no significant differences between plants growing in sand with slag and plants growing in soil without slag: not in germination, nor in survival and total biomass.

The nutrient content in the slags is very low, so a fertilizing effect of slags on vegetation is not present. Xian and Qing-Sheng (2006) showed that the concentrations of e.g. Mn, K and P in a steel slag, determined in a water extract at L/S is 2.5, were in the order of g/kg, while in our water extract these concentrations are in the order of mg/kg or even µg/kg (table 8 and table 9). Also the amount of N and P in the soil of the pot experiment is almost nil. The organic matter content of the sand in the valley area is <0.5%. The sand is almost pure dune sand with some shell parts through it, so no fertilising effect of OM can be expected. The low nutrient status of the soil and slags is confirmed during the experiment, as most of the plants had yellow and purple/brown leaves (Appendix VII), which is most likely an indication of nutrient shortage.

The fact that three species germinated and that there were no differences in germination and biomass between plants growing in soils with and without slags, indicates that there will be no negative influence of the presence of slags in the area on these plant species. These plant species thus can develop in Spanjaards Duin. Unfortunately, none of the two target species *P. palustris* and *E. palustris* germinated. When these seeds were ordered at Cruydhoeck, they already told us that there was a small chance on germination. *E. palustris* is an orchid species with very tiny seeds. These seeds contain no reserve food that can be used for germination. For germination of orchids some fungi types need to be present in the soil. The fungi then penetrate with a mycelium thread into the orchid seed and the orchid uses this thread to take up nutrients (Andeweg, 2011). The orchid species thus needs very specific soil circumstances for germination, which makes it very difficult for the species to germinate. Just like *E. palustris*, also *P. palustris* is a species that does not germinate easily. This species is also on the 'Red List' with threatened plant species. The pot experiment was done with only a small amount of soil that was taken from one place in Spanjaards Duin. Possibly in other parts of the area there are other circumstances, e.g. the presence of fungi, which make that *E. palustris* and *P. palustris* can grow nevertheless.

With regard to the influence of the slags on the germination and development of moist dune vegetation, we can conclude that the slags have no significant effect on the development of the moist dune vegetation. The conditions for the growth of these plants in Spanjaards Duin are rather determined by other (a)biotic variables.

4.4 Implications

The measurements and modelling indicate that, even in a worst-case scenario, no problems are to be expected under natural circumstances. The reactive Zn content in one slag type causes a potential risk, but from the pH stat leaching test it turns out that the expected leaching is very low under field circumstances. For this reason, there is no effect of leaching on the soil and groundwater quality. Not at present and also not within 80 or 100 years from now. The pH of the soil, which is at the moment 9.61, will gradually decrease over time. Grey dune in the rhenodunal district has a pH value of about 7.5 (Arens et al., 2013), so the pH in the area will develop towards this value. The leaching of metals from the slags at this pH value is however still around the minimum. The vegetation shows, regarding germination and biomass, no effect in the presence of slags, so this can also be expected in the field.

Acknowledgements

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Appendices

Appendix I

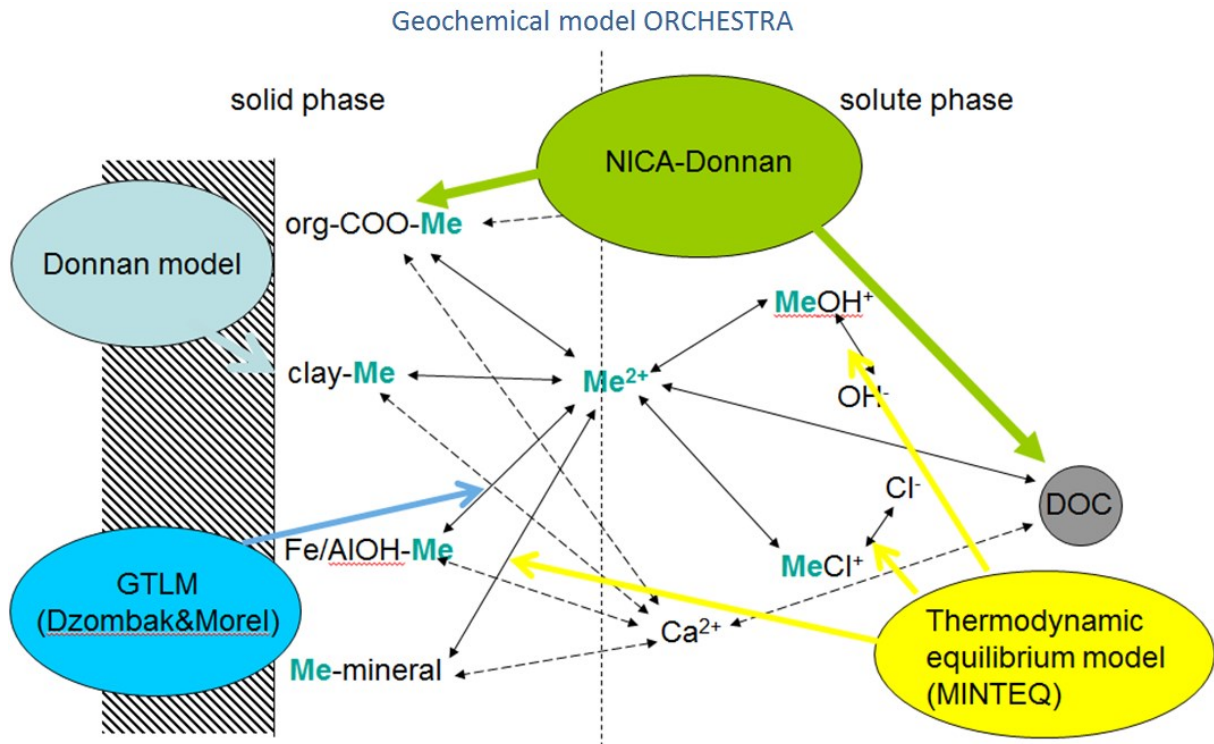


Figure I: An overview of the processes that can be taken into account by the multi surface model ORCHESTRA. Different processes are adsorption of metals to Fe- and Al-(hydr)oxides, adsorption of metals to clay and organic matter and the speciation of metals in solution.

Appendix II

Table I: Overview of minerals that were taken into account by ORCHESTRA for modelling the results of the pH stat test.

Minerals	
BaSO ₄ (s)	Cu(OH) ₂ (s)
Cd(OH) ₂ (s)	Ni(OH) ₂ (s)
Co ₃ O ₄ (s)	Pb(OH) ₂ (s)
Cr ₂ O ₃ (s)	Zn(OH) ₂ (s)

Appendix III

Overview of slag types that were not used for further research.



Figure II: Type 1. One side is yellow/brownish (large stone right), the other side is dark brown/orange (small stone left). This slag is not colourfast.



Figure III: Type 4. These slags are very layered, pitch-black and have a very low mass density. They do not peel off. Looks like charcoal and you can draw with it on paper. Possibly this are cokes.



Figure IV: Type 5. These slags are somewhat more grey than type 4 and the mass density is much higher. They are also layered, but they do peel off heavily.



Figure V: Type 6. These slags have a very low mass density, even lower than type 4 and they contain tiny pores.



Figure VI: Type 8. Heavy material, (looks like) rusted iron.



Figure VII: Type 9. I am not sure whether these slags are all the same. Some parts are layered and some parts contain some small pores. There are black, grey and orange spots.



Figure VIII: Type 11 looks like the small slag in type 10, but this one is more dark.



Figure IX: Type 13. Very low mass density, very large pores. It has white and black spots and looks like lime.



Figure X: Type 14. Black slags that look like type 6, but these contain larger pores than type 6. Low mass density.



Figure XI: Type 15. These slags have black, grey, brown and orange spots. It looks like they are less layered than type 12. But maybe they are the same type.



Figure XII: Type 16. These were some left-overs. I did not know to which group they belong.

Appendix IV

Table II: Results pH stat test (mg/kg). Measured with ICP-AES, except for values with an asterisk (*); these are measured with ICP-MS.

Sample description	pH	Al [mg/kg]	Ca [mg/kg]	Cu [mg/kg]	Fe [mg/kg]	K [mg/kg]	Mg [mg/kg]	Mn [mg/kg]	Na [mg/kg]	P [mg/kg]	S [mg/kg]	Zn [mg/kg]
detection limit		0.3	12	0.1	0.9	4	1.5	0.1	3	1	2	0.2/0.018*
type 2	12	4.6	15	0.63	25.2	31	< 1.5	0.2	7900	51.6	4070	0.58
type 2	10.45	< 0.3	92	0.28	< 0.9	50	< 1.5	< 0.1	4330	17	2840	< 0.018
type 2	9.45	< 0.3	587	< 0.1	< 0.9	75	7.6	< 0.1	3170	5.6	2650	< 0.018
type 2	8.45	< 0.3	1690	< 0.1	< 0.9	70	65.8	< 0.1	2530	1.4	3040	0.02141 *
type 2	7.6	< 0.3	3250	< 0.1	< 0.9	70	183	0.76	85	< 1	2690	0.05329 *
type 2	6	< 0.3	15140	0.13	< 0.9	76	760	48	139	< 1	2230	5.49
type 2	4.15	3.6	24170	0.59	145	86	1160	266	198	1.1	1630	243
type 2	2.2	96.8	31290	35	4480	103	1940	459	266	4.9	642	806.9
type 7	11.95	80.7	15	0.39	19.8	42	2.6	0.24	3040	11.3	199	< 0.2
type 7	10.5	12.9	22	0.15	7.7	60	1.7	0.11	537	5.5	97.3	< 0.2
type 7	9.15	6.7	79	0.16	19	74	8.6	0.2	224	2.2	96.7	< 0.2
type 7	8.1	0.4	265	< 0.1	< 0.9	72	23.9	0.58	37	< 1	97.8	< 0.2
type 7	7.8	0.3	744	< 0.1	< 0.9	82	36.9	1.6	71	< 1	105	< 0.2
type 7	6.05	< 0.3	2780	< 0.1	< 0.9	79	81.3	17.4	101	< 1	77	< 0.2
type 7	4.2	56.8	6300	2.83	197	112	234	42.3	75	< 1	45.9	1.25
type 7	2	1290	8150	10.9	1310	271	428	75.8	142	63.1	50.4	2.89

Table III: Results pH stat test (mg/kg). Measured with ICP-MS. The concentration Cl (mg/kg) is measured with FIA.

Sample description	pH	As [mg/kg]	Ba [mg/kg]	Cd [mg/kg]	Co [mg/kg]	Cr [mg/kg]	Mo [mg/kg]	Ni [mg/kg]	Pb [mg/kg]	Cl [mg/kg]
detection limit		0.0002	0.0003	0.00005	0.00005	0.0002	0.0018	0.0003	0.0004	6
type 2	12	1.6	0.015	0.00203	0.0544	0.362	0.377	0.237	0.0172	821
type 2	10.45	0.223	0.0096	0.00066	0.00423	0.0205	0.352	0.0217	< 0.0004	284
type 2	9.45	0.129	0.018	0.00017	0.00229	0.00623	0.0836	0.0062	< 0.0004	237
type 2	8.45	0.09	0.0271	0.00006	0.00278	0.0395	0.0161	0.0386	0.0024	161
type 2	7.6	0.0509	0.0535	0.00012	0.0047	0.00053	0.0023	0.02	< 0.0004	154
type 2	6	0.0276	0.435	0.00101	0.182	0.00079	< 0.0018	0.919	< 0.0004	135
type 2	4.15	0.0192	2.01	0.0571	2.62	0.00916	0.0079	8.95	0.0066	159
type 2	2.2	0.053	5.92	0.614	6.74	4.3	0.0139	20.62	2.61	197
type 7	11.95	0.455	0.0664	0.00044	0.0628	0.105	0.15	0.239	0.0266	180
type 7	10.5	0.224	0.0282	0.00044	0.0227	0.0336	0.122	0.0845	0.0105	166
type 7	9.15	0.0933	0.0564	0.00037	0.0357	0.0365	0.0918	0.129	0.0179	150
type 7	8.1	0.0129	0.0786	0.00024	0.00442	0.00188	0.064	0.0274	0.0007	146
type 7	7.8	0.00798	0.237	0.00018	0.0109	0.00086	0.0468	0.0652	0.0007	159
type 7	6.05	0.00335	1.03	0.00123	0.386	0.00048	0.0248	1.43	0.0013	126
type 7	4.2	0.00453	4.6	0.0122	1.6	0.0331	0.0074	4.39	0.01	115
type 7	2	0.17	21.23	0.0142	3.9	2.53	0.0429	10.54	0.633	117

Table II and III show for both slag types and all pH values reached during the pH stat test the concentrations (mg/kg) of all elements measured by ICP-AES and ICP-MS. pH 7.6 is the native pH of slag type 2 and pH 8.1 is the native pH of slag type 7. The asterisk (*) for some Zn values in table II means that these concentrations are measured with ICP-MS. The concentration Cl (mg/kg) (needed to construct an ion balance) was measured with FIA. In general, almost all elements have increasing concentrations towards lower pH values. Exceptions are As, Mo, Na and S for both slag types, and P for slag type 2. The Zn concentration in slag type 7 is again very high (806.9 mg/kg), which is in accordance with the very high Zn concentration found in the 0.43 M HNO₃ extract.

Appendix V

Table IV: Concentrations (mg/kg) of compounds in slag type 2 and 7, determined from the batch leaching test at L/S 2 and 8. Cl is determined by FIA. Ca, Fe, K, Mg, Na and S are determined by ICP-AES, the rest of the compounds by ICP-MS.

sample description	Al [mg/kg]	As [mg/kg]	Ba [mg/kg]	Ca [mg/kg]	Cd [mg/kg]	Cl [mg/kg]	Co [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Fe [mg/kg]
type 2, L/S 2	0.0144	0.0124	0.01016	1192	0.000544	23.2	0.003808	0.000112	0.00736	0.08
type 7, L/S 2	0.0952	0.002672	0.01368	61.6	0.000152	9.2	0.001448	0.000464	0.0152	0.08
type 2, L/S 8	0.0184	0.02056	0.03928	1712	0.001568	23.2	0.002664	0.00044	0.00728	0
type 7, L/S 8	6.032	0.03136	0.04736	75.2	0.000312	26.4	0.02792	0.02928	0.1032	11.44

sample description	K [mg/kg]	Mg [mg/kg]	Mn [mg/kg]	Mo [mg/kg]	Na [mg/kg]	Ni [mg/kg]	P [mg/kg]	Pb [mg/kg]	S [mg/kg]	Zn [mg/kg]
type 2, L/S 2	8	79.44	0.4136	0.0008	56	0.0168	0.032	0.00008	1032	0.0696
type 7, L/S 2	6.4	7.6	0.0856	0.01304	19.2	0.0092	0.0688	0.0004	32	0.0144
type 2, L/S 8	7.2	72.16	0.38	0.002	22.4	0.00896	0.1232	0.00016	1304	0.0432
type 7, L/S 8	5.6	6	0.1568	0.02608	7.2	0.0936	0.7992	0.01216	20.72	0.0512

Appendix VI

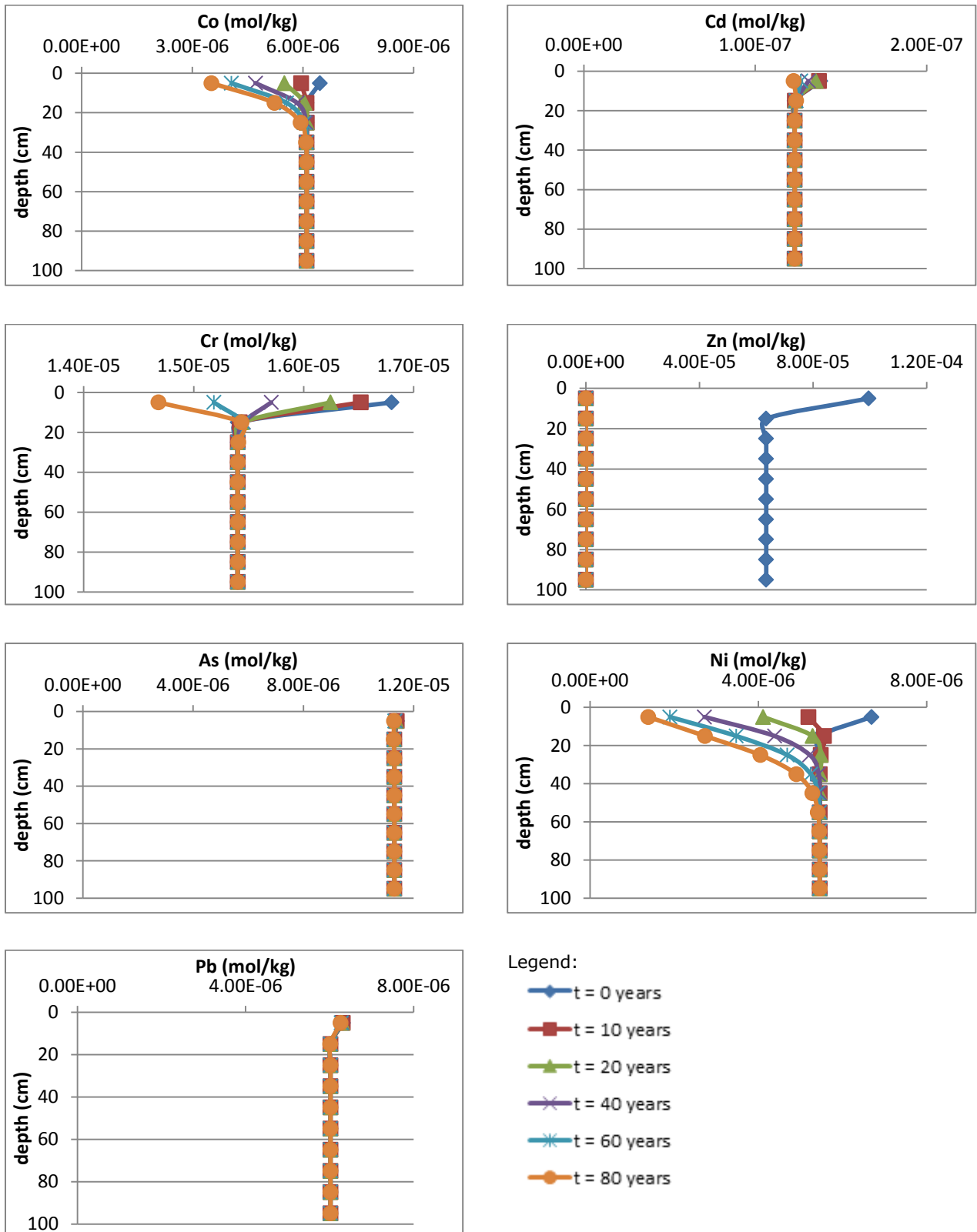
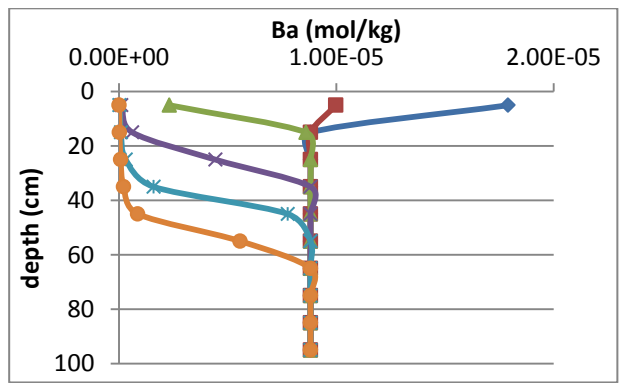
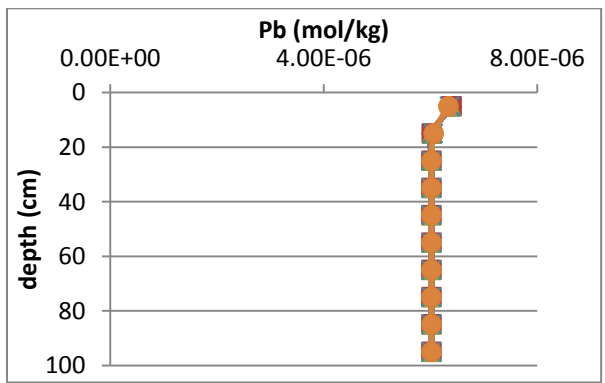
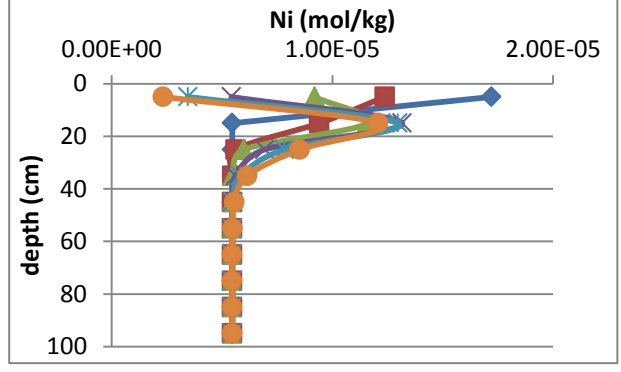
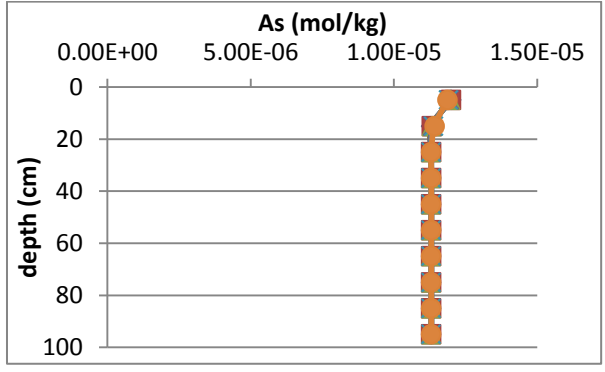
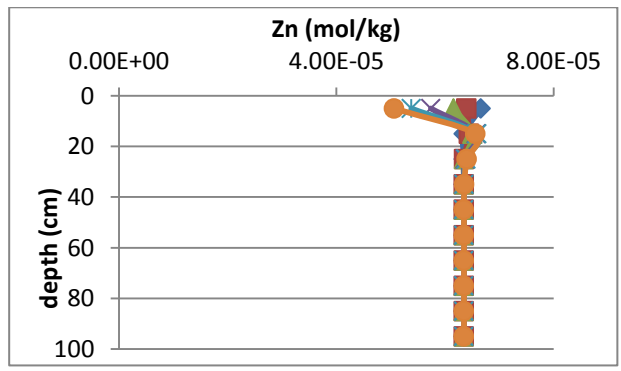
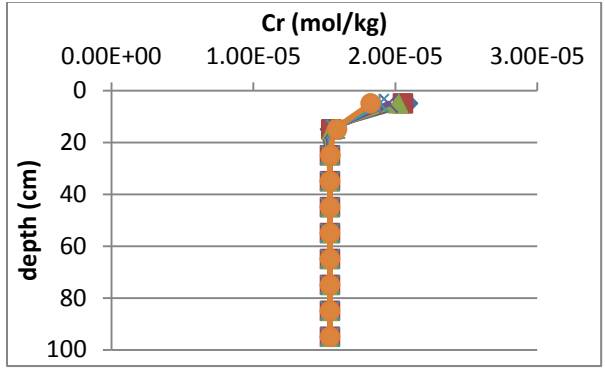
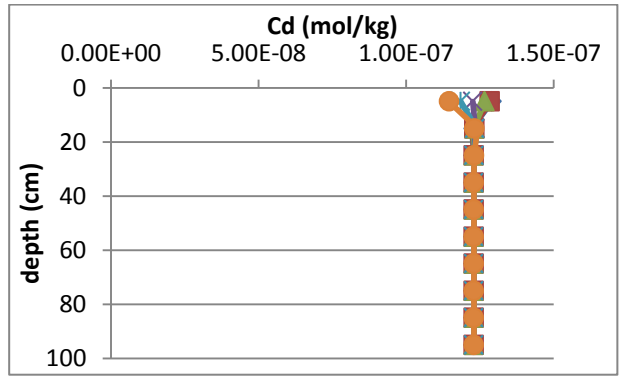
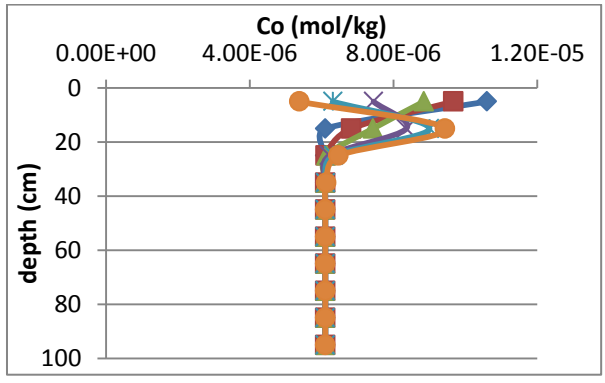
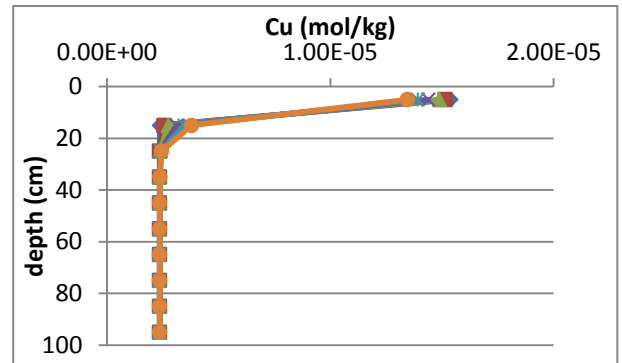
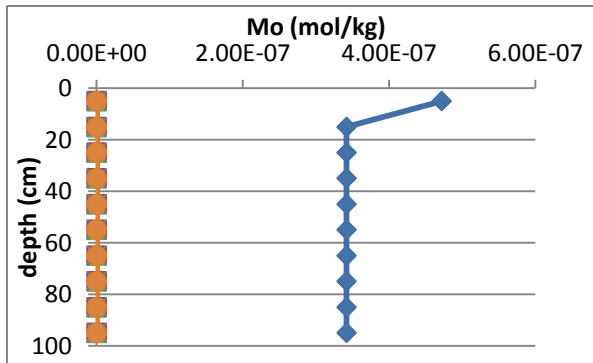


Figure XIII: The modelled concentrations of Co, Cd, Cr, Zn, As, Ni and Pb (mol/kg) over time for slag type 2, for each layer of 10 cm depth in the upper meter of soil.





Legend:

- ◆ t = 0 years
- t = 10 years
- ▲ t = 20 years
- ✕ t = 40 years
- ✱ t = 60 years
- t = 80 years

Figure XIV: The modelled concentrations of Co, Cd, Cr, Zn, Ba, As, Mo, Cu, Ni and Pb (mol/kg) over time for slag type 7, for each layer of 10 cm depth in the upper meter of soil.

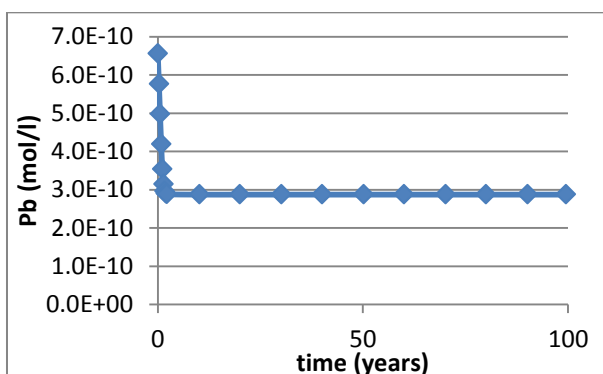
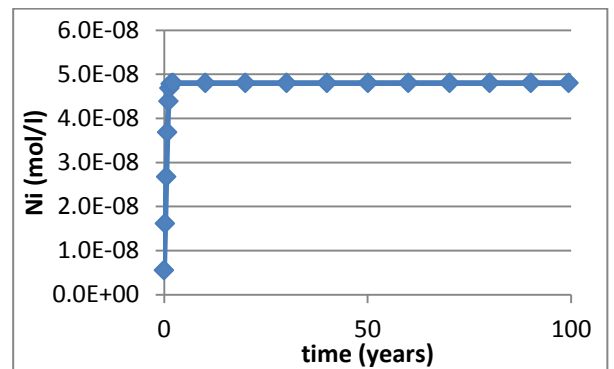
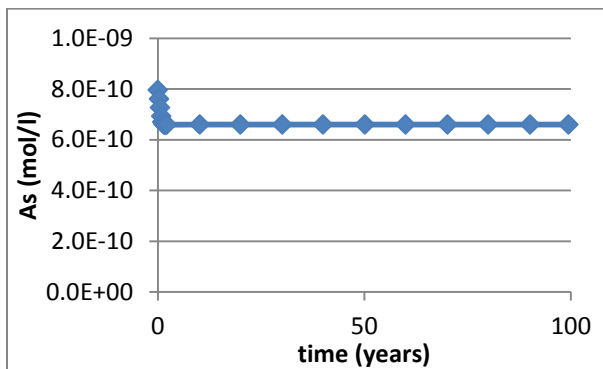
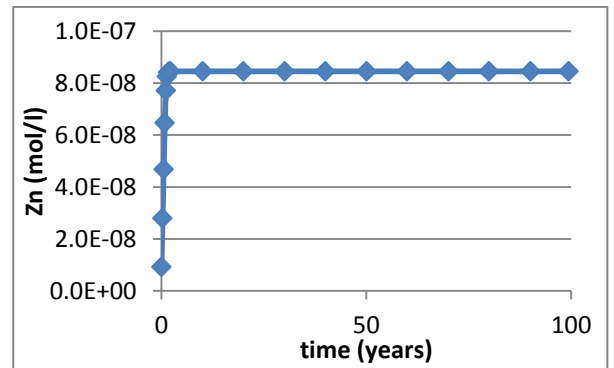
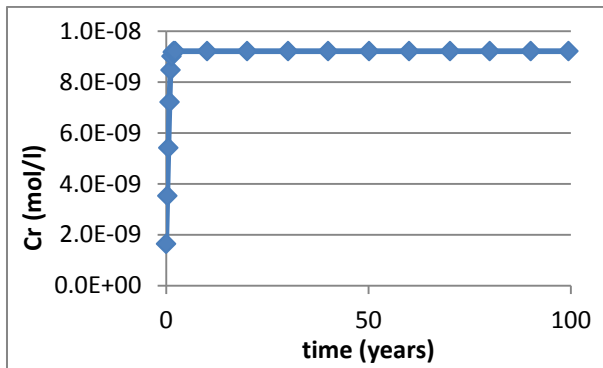
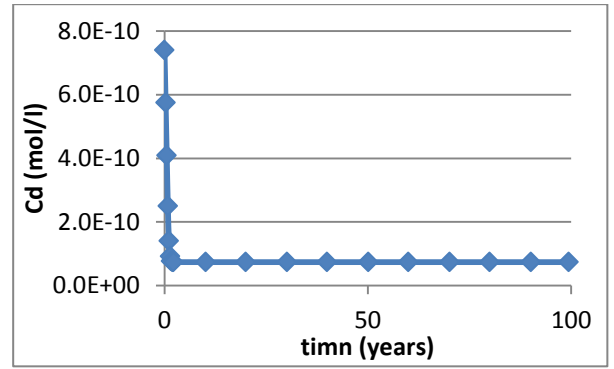
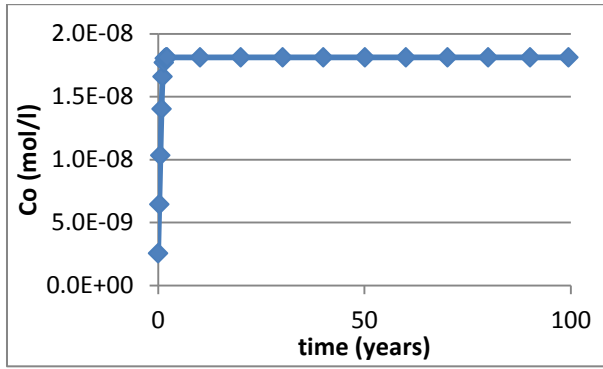
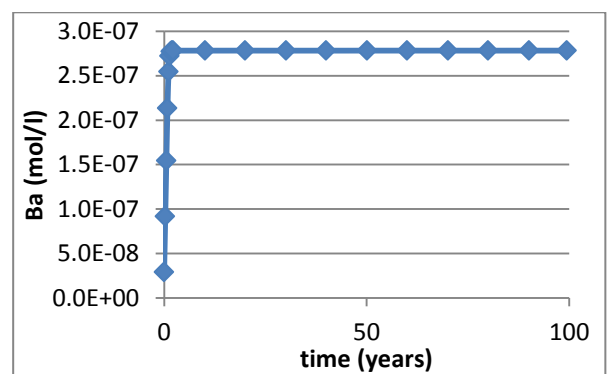
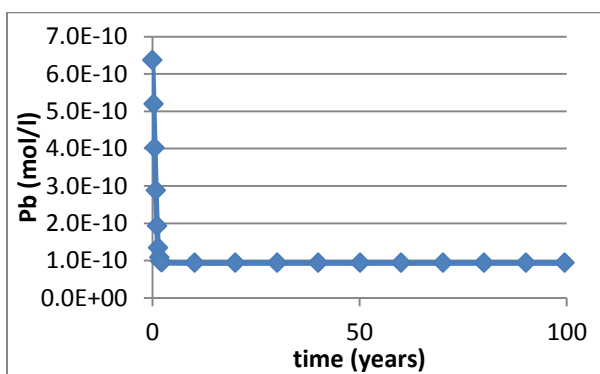
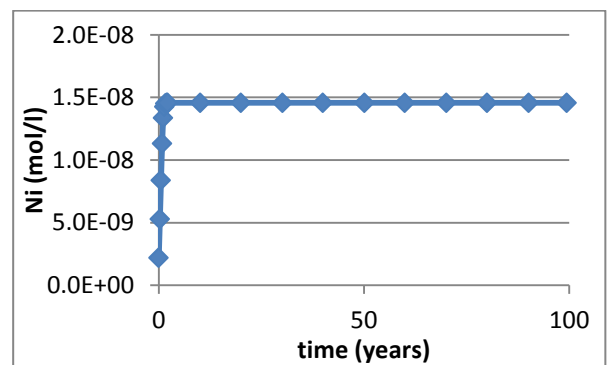
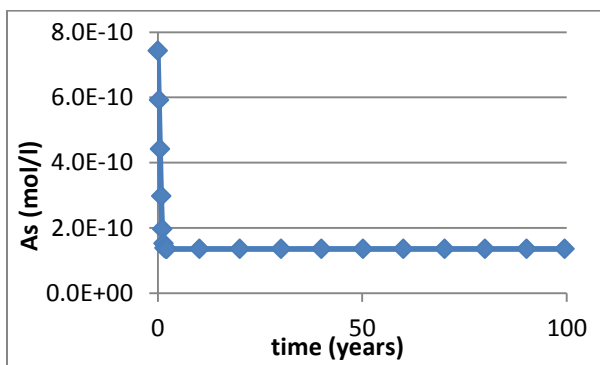
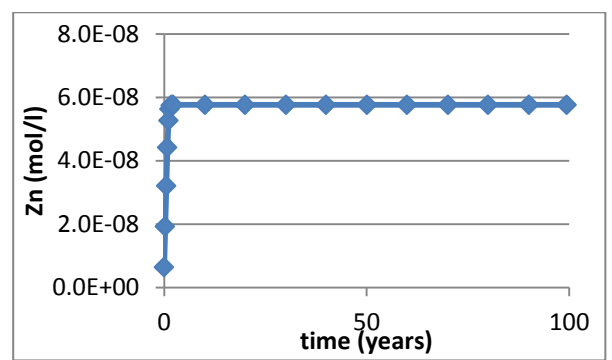
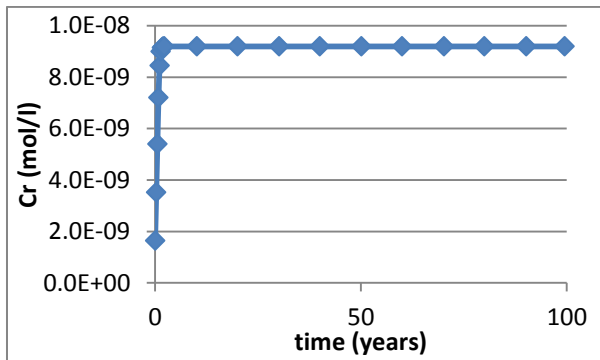
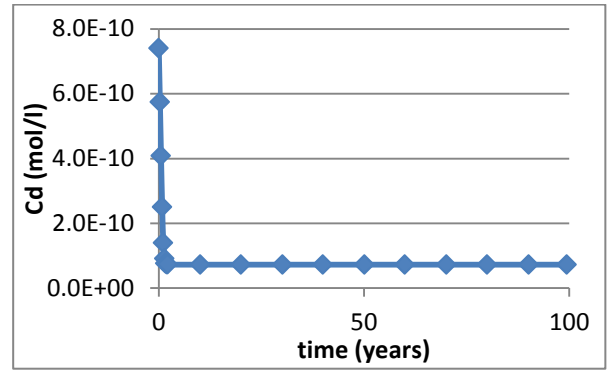
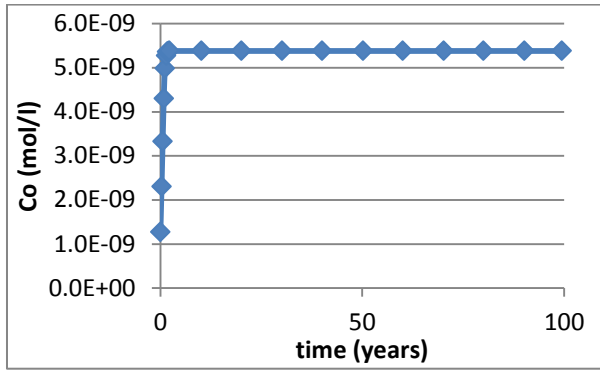


Figure XV: The modelled average concentrations of Co, Cd, Cr, Zn, As, Ni and Pb (mol/l) for slag type 2, in the upper meter of groundwater, over time.



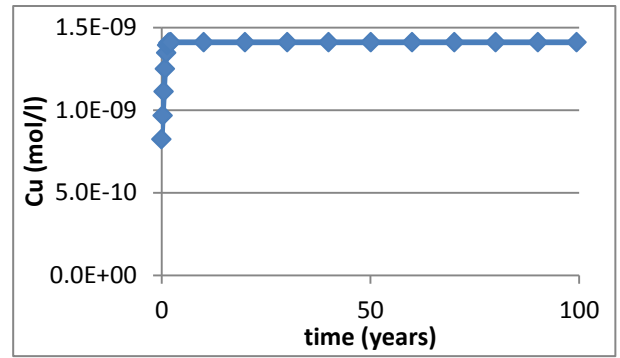
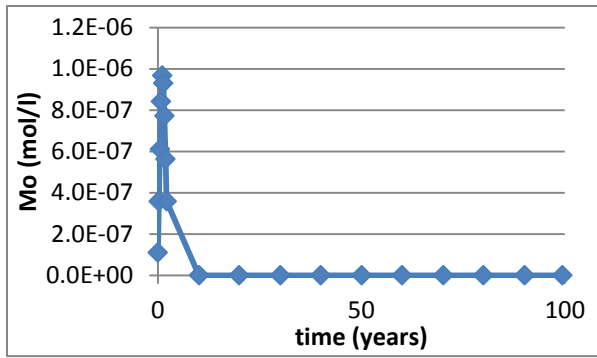


Figure XVI: The modelled average concentrations of Co, Cd, Cr, Zn, Ba, As, Mo, Cu, Ni and Pb (mol/l) for slag type 7, in the upper meter of groundwater, over time.

Appendix VII



Figure XVII: The plants in the pot experiment have purple/brown leaves.

Appendix VIII

Table V: Number of germinated and survived plants. The numbers in e.g. 1PC- stand for pot nr. 1. PC refers to plants species *P. coronopus*.

without slag	# plants	with slag	# plants
1PC-	5	36PC+	4
2PC-	5	37PC+	4
3PC-	7	38PC+	4
4PC-	1	39PC+	5
5PC-	2	40PC+	3
6PC-	5	41PC+	6
7PC-	6	42PC+	6
8DC-	2	43DC+	2
9DC-	2	44DC+	0
10DC-	2	45DC+	1
11DC-	1	46DC+	1
12DC-	0	47DC+	2
13DC-	1	48DC+	1
14DC-	2	49DC+	0
15EP-	0	50EP+	0
16EP-	0	51EP+	0
17EP-	0	52EP+	0
18EP-	0	53EP+	0
19EP-	0	54EP+	0
20EP-	0	55EP+	0
21EP-	0	56EP+	0
22LS-	1	57LS+	2
23LS-	1	58LS+	0
24LS-	2	59LS+	2
25LS-	0	60LS+	0
26LS-	0	61LS+	1
27LS-	0	62LS+	2
28LS-	2	63LS+	0
29PP-	0	64PP+	0
30PP-	0	65PP+	0
31PP-	0	66PP+	0
32PP-	0	67PP+	0
33PP-	0	68PP+	0
34PP-	0	69PP+	0
35PP-	0	70PP+	0

Table VI: Total biomass of the plants after drying. The numbers in e.g. 1PC- stand for pot nr. 1. PC refers to plants species *P. coronopus*.

without slag	weight (g)	with slag	weight (g)
1PC-	0.0679	36PC+	0.0317
2PC-	0.0503	37PC+	0.0391
3PC-	0.0556	38PC+	0.0351
4PC-	0.0330	39PC+	0.0786
5PC-	0.0319	40PC+	0.0293
6PC-	0.0276	41PC+	0.0826
7PC-	0.0314	42PC+	0.0623
8DC-	0.0225	43DC+	0.0335
9DC-	0.0151	44DC+	0.0000
10DC-	0.0289	45DC+	0.0007
11DC-	0.0040	46DC+	0.0158
12DC-	0.0000	47DC+	0.0106
13DC-	0.0134	48DC+	0.0270
14DC-	0.0176	49DC+	0.0000
15EP-	0.0000	50EP+	0.0000
16EP-	0.0000	51EP+	0.0000
17EP-	0.0000	52EP+	0.0000
18EP-	0.0000	53EP+	0.0000
19EP-	0.0000	54EP+	0.0000
20EP-	0.0000	55EP+	0.0000
21EP-	0.0000	56EP+	0.0000
22LS-	0.0132	57LS+	0.0265
23LS-	0.0055	58LS+	0.0000
24LS-	0.0030	59LS+	0.0029
25LS-	0.0000	60LS+	0.0000
26LS-	0.0000	61LS+	0.0017
27LS-	0.0000	62LS+	0.0046
28LS-	0.0020	63LS+	0.0000
29PP-	0.0000	64PP+	0.0000
30PP-	0.0000	65PP+	0.0000
31PP-	0.0000	66PP+	0.0000
32PP-	0.0000	67PP+	0.0000
33PP-	0.0000	68PP+	0.0000
34PP-	0.0000	69PP+	0.0000
35PP-	0.0000	70PP+	0.0000

Appendix IX

Table VII: Peak concentrations in the groundwater for the elements Ni and Pb, and the duration of exceeding the intervention value (75 µg/l).

Sample description	Element	Peak concentration (µg/l)	Duration of exceedance (years)
type 2	Ni	283	2
	Pb	364	60
type 7	Ni	279	10
	Pb	84	100

Appendix X

Table VIII: Results 0.43 M HNO₃ extraction (mg/kg) of the composite soil sample, measured with ICP-AES.

Sample description	Al [mg/kg]	Ca [mg/kg]	Cu [mg/kg]	Fe [mg/kg]	K [mg/kg]	Mg [mg/kg]	Mn [mg/kg]	Na [mg/kg]	P [mg/kg]	S [mg/kg]	Zn [mg/kg]
detection limit	0.3	12	0.1	0.9	4	1.5	0.1	3	1	2	0.2
composite soil sample	77	26080	0.15	548	44	554	45.8	115	119	76.8	4.15
reference 949	880	882	5.04	1290	134	58.5	110	24	541	38	6.8
reference 989	2510	33650	115	6700	276	3030	842	199	1680	196	655
blank 1	1.2	21	< DL	3.5	< DL	1.7	0.42	7	1.1	< DL	0.36
blank 2	< DL	< DL	< DL	< DL	< DL	< DL	< DL	6	< DL	< DL	< DL

Table IX: Results 0.43 M HNO₃ extraction (mg/kg) of the composite soil sample, measured with ICP-MS.

Sample description	As [mg/kg]	Ba [mg/kg]	Cd [mg/kg]	Co [mg/kg]	Cr [mg/kg]	Mo [mg/kg]	Ni [mg/kg]	Pb [mg/kg]
detection limit	0.0002	0.0003	0.00005	0.00005	0.002	0.0018	0.0003	0.0004
composite soil sample	0.847	1.21	0.0139	0.36	0.799	0.0328	0.32	1.25
reference 949	1.1	6.93	0.148	0.2	4.5	0.0745	0.594	10.27
reference 989	19.1	344.21	7.38	8.93	81.45	0.0946	18.64	228.63
blank 1	0.00097	0.0408	< DL	0.00192	0.107	0.0041	0.004	0.008
blank 2	0.00193	0.0318	0.00099	0.0125	0.111	0.003	0.004	0.005

Appendix XI

Table X: Results 0.01 M CaCl₂ extraction (mg/kg) of the composite soil sample, measured with ICP-AES.

Sample description	Al [mg/kg]	Cu [mg/kg]	Fe [mg/kg]	K [mg/kg]	Mg [mg/kg]	Mn [mg/kg]	Na [mg/kg]	P [mg/kg]	S [mg/kg]	Zn [mg/kg]
detection limit	0.3	0.1	0.9	4	1.5	0.1	3	1	2	0.2
composite soil sample	0.3	< DL	1	12	20.1	< DL	4	< DL	< DL	< DL
reference 949	2.5	< DL	3.5	71	41.3	23.7	12	4.3	16.2	0.8
reference 989	1.2	0.6	< DL	57	170	2.3	44	4.8	34	0.6
blank 1	0.3	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
blank 2	0.4	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL

Table XI: Results 0.01 M CaCl₂ extraction (mg/kg) of the composite soil sample, measured with ICP-MS.

Sample description	As [µg/kg]	Ba [µg/kg]	Cd [µg/kg]	Co [µg/kg]	Cr [µg/kg]	Mo [µg/kg]	Ni [µg/kg]	Pb [µg/kg]
detection limit	0.2	0.3	0.05	0.05	0.2	1.8	0.3	0.4
composite soil sample	6.75	13.2	< DL	0.2	4.99	3.5	7.6	< DL
reference 949	10.2	72.2	24.7	16.9	7.53	5.9	44.6	1.9
reference 989	75.3	3850	50.3	4.23	18.3	43.8	82.9	1.7
blank 1	< DL	8.5	< DL	0.1	4.54	< DL	6.6	< DL
blank 2	< DL	8.2	0.06	0.13	5.02	< DL	7.5	< DL

Appendix XII

Table XII: Comparison of metal concentrations between the 0.01 M CaCl₂ soil suspension and the concentration in the groundwater modelled with ORCHESTRA.

	As [µg/l]	Ba [µg/l]	Co [µg/l]	Cr [µg/l]	Mo [µg/l]	Ni [µg/l]
CaCl₂ extract	0.675	1.315	0.020	0.499	0.354	0.756
ORCHESTRA	0.058	38.376	0.608	0.478	48.096	4.354