Master thesis

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Chemical behavior of tungsten in soils: Solubility, sorption and sequential fractionation

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Abstract: The element tungsten (W) has been receiving increasing interest from researchers in recent years due to rising industrial and military use. Despite this, its behavior in the environment is still poorly understood. The aim of the present work was to establish suitable methods for measuring W in soil samples in our laboratory and to investigate the behavior of W in the soil environment, especially in relation to physico-chemical soil properties.

In a first step, we developed a method for measuring W using inductively coupled plasma mass spectrometry (ICP-MS). In a second step, we tested different methods of acid digestion to determine total W concentrations in soil. To investigate the effect of soil texture and pH on W availability in soil, we spiked one acidic sandy and one acidic clay soil with different concentrations of W and $CaCO_3$ and measured W recovery in soil water extracts. Finally, we adapted a sequential extraction procedure originally developed for arsenic in order to assess the partitioning of W between different mineral soil phases.

Method comparison revealed that the addition of concentrated phosphoric acid to the aqua regia solution resulted in an improved recovery of acid digestible W. Results showed a high dependency of W adsorption on soil pH, with much lower adsorption under alkaline conditions. The sequential extraction further revealed that the majority of W (40-80 % of total extracted W) was held by hydrous oxides of Fe and Al. Other than pH, we found soil texture to be a determining factor for W availability, with more W being held by clay-rich soils. Overall we found that the behavior of W in soil was similar to other anions such as phosphate, molybdate or arsenate.

Zusammenfassung: Wolfram (W) hat in jüngerer Vergangenheit bedingt durch neue Verwendungszwecke im industriellen und militärischen Sektor vermehrte Aufmerksamkeit von Seiten der Wissenschaft erhalten. Bezüglich seines Verhaltens in der Umwelt gibt es allerdings noch viele Wissenslücken. Das Ziel der vorliegenden Arbeit war die Etablierung von Methoden zur Bestimmung von W-Gehalten im Boden, sowie eine Untersuchung des umweltrelevanten Verhaltens von W in diesem. Von besonderem Interesse war für uns der Einfluss physikalisch-chemischer Bodeneigenschaften.

Zu diesem Zweck etablierten wir zunächst eine Methode, um W mittels Massenspektrometrie (ICP-MS) zu messen. Um W-Totalgehalte im Boden zu bestimmen, verglichen wir verschiedene Methoden für Säureaufschlüsse von W-haltigen Bodenproben. Zur genaueren Untersuchung der Einflüsse von Bodentextur und pH auf die Umweltverfügbarkeit von W versetzten wir zwei saure Böden (ein Ton- und ein Sandboden) mit verschiedenen W-Konzentrationen sowie $CaCO_3$. Um die unmittelbare Bioverfügbarkeit im Boden sowie die Partitionierung von W zwischen verschiedenen Bodenphasen zu bestimmen, wurden Wasserextrakte sowie eine adaptierte sequentielle Extraktion (ursprünglich für Arsen entwickelt) durchgeführt.

Unsere Ergebnisse zeigten, dass die Zugabe von konzentrierter Phosphorsäure bei Säureaufschlüssen zu einer stark verbesserten Bestimmung von W-Gesamtgehalten führte. Sowohl Boden-pH als auch die Bodentextur hatten einen großen Einfluss auf die Verfügbarkeit von W. Generell nahm die W-Löslichkeit mit steigendem Tongehalt und sinkendem pH Wert ab. Ergebnisse der sequentiellen Extraktion zeigten auch, dass der Großteil an W an Eisen- und Aluminiumoxide gebunden ist. Zusammenfassend konnten wir zeigen, dass das Verhalten von W in unseren Böden dem anderer Anionen, wie etwa Phosphat, Molybdat oder Arsenat ähnlich ist.

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List of Abbreviations

Abbreviation	Full Name of Item
AAO	Acid ammonium oxalate
CAL	Calcium acetate-lactate extract
CBD	Citrate bicarbonate dithionite
CEC	Cation exchange capacity
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
LOD	Limit of detection
LOI	Loss on ignition
LOQ	Limit of quantification
MWHC	Maximum water holding capacity
n.e.	not extractable
OM	Organic matter
ÖNORM	Norm determined by the Austrian Standards Institute
SE	Standard error
SOC	Soil organic carbon
SSR	Soil to solution ratio
Std Unc	Standard Uncertainty
W	Tungsten
W2	Swiss experimental soil

1. Introduction

1.1 General properties of W

Tungsten (W), also known as wolfram, is a transition metal found in group VI of the periodic table together with elements like chromium and molybdenum. The element, whose atomic number is 74, was discovered in the 18th century and its name derives from the Swedish meaning "heavy stone". W has some remarkable chemical and physical properties, for example the highest melting point of all unalloyed metals at 5660 °C and a high density, which makes it one of the strongest metals at high temperatures. W also has an excellent resistance to attacks from oxygen as well as alkaline and acidic solutions (Dixon and Parsons, 2013).

1.2 Importance of W

These traits make W the ideal choice for the production of heavy metal alloys and have led to the element being used in a wide range of applications since its discovery, which include for example household necessities but also high-end technology goods. About 60 % of global W consumption is accounted for by production of tungsten carbide (Dixon and Parsons, 2013). Examples for W use include tungsten metal wires, electrodes, tungsten-heavy metal alloys, specialized tools and ammunition (Koutsospyros et al., 2006). The most famous use of W in the past has been in light bulb filaments, although tungsten bulbs have nowadays mostly been replaced with more environmentally friendly ones. Regardless of all these applications, W has historically not been a contaminant of great interest.

With increasing use of W there are however also more anthropogenic pathways for the element to find its way into natural systems. Important sources include waste from industry, W tire stud, soil fertilizer application (Koutsospyros et al., 2006) and especially military activities, since W is frequently used in ammunition (Clausen and Korte, 2009). While in the past W was believed to be relatively insoluble and inert, it is now known that it can be quite soluble under certain conditions (Clausen and Korte, 2009).

It is assumed that human activities account for about 30 % of the total global surficial fluxes or even 60 % if one also includes W transport with human soil erosion and Aeolian dust (Sen and Peucker-Ehrenbrink, 2012).

Due to these new discoveries, the more widespread use of W during the last decades and a cluster of childhood leukemia in the US, which was suspected to be linked to enhanced W concentrations in the environment, the element has received increasing attention in recent years, for example in the studies by Bednar et al. (2008), Koutsospyros et al. (2006) and Clausen and Korte (2009)

Despite this increasing awareness, the environmental and toxicological information on W remains rather limited.

1.3 W in the environment

W is a rather rare element in the earth's crust and its average background concentration is estimated to be about 1.3 mg kg^{-1} (Smith, 1994). There have however been reported W concentrations exceeding this value by a factor of 10 to 2000 in the vicinity of W mines, smelter sites or military firing ranges. (Koutsospyros et al., 2006).

The element has a complex speciation with various oxidation states. Tungsten normally occurs as the oxyanion tungstate WO_4^{2-} in the environment, which can

polymerize with itself and with other ions, resulting in the formation of a number of complexes. In nature W is found in primary minerals like scheelite ($CaWO_4$), hübnerite ($MnWO_4$), ferberite ($FeWO_4$) or wolframite ($[Fe/Mn]WO_4$) (Koutsospyros et al., 2006).

In many ways W behaves similar to molybdenum, which also belongs to the chromium group of the periodic table. Both elements have similar atomic and ionic radii, electronegativity, range of oxidation states and coordination numbers (Koutsospyros et al., 2011). Experimental data also seems to suggest that W behaves similar to other (oxy)anionic compounds in the soil with increased mobility under alkaline conditions (Gustafsson, 2003, Bednar et al. 2008).

1.4 Methods and problems

For the investigation of the behavior of W in soil, the ability to quantify the amount of the metal present in environmental samples is essential. To this purpose our goal was to establish and test suitable methods.

ICP-MS seems to be generally suited for measuring W concentrations in samples and has been used with good results in a number of studies involving W (Bednar et al., 2007; Clausen et al., 2010). Bednar et al. (2007) used ICP-MS to measure samples containing molybdenum and W and found that while there are potential interferences by various oxides (e.g. of holmium, dysprosium, erbium, ytterbium), there would generally be low concentrations of these elements in regular samples. Clausen et al. (2010) also used ICP-MS for measurement of W concentrations in water and soil samples and found the technique to be well-suited for the task with a LOQ of 0.04 $\mu g\ L^{-1}$ for water samples containing W. Both of these studies found no difference in measurability between the different isotopes of W.

Due to the complex chemistry of W there are some obstacles when it comes to quantifying the element. Traditional acid digestion techniques like aqua regia, which would normally be used to determine total soluble concentrations in soil, have been shown to insufficiently extract W because of the precipitation of insoluble tungstates and the polymerization of tungstates onto soil particles (Bednar et al., 2010). Studies done by Bednar et al. (2010) and Griggs et al. (2009) however suggest that the addition of phosphoric acid to standard acid digestion methods greatly increases the recovery of W from soils. The phosphoric acid polymerizes with W and forms acid soluble tungsten species and thus promotes the extraction of W from the soil.

As mentioned before experimental data suggests that W behaves and is sorbed similar to other (oxy)anionic compounds in the soil. Gustafsson (2003) compared the sorption of tungstate and molybdate to ferrihydrate and found similar behavior between the two elements. It is generally known that anions are bound more strongly to the soil at lower levels of pH due to the greater presence of positively charged adsorption surfaces in the soil (Scheffer et al., 2010, p. 144; Zeitz, 2005), which was also the case in the study done by Gustafsson (2003). Despite these findings there are only a few studies about W in natural systems available and the details of its behavior remain unclear.

Sequential extractions are a useful tool for estimating the partitioning of metals among different operationally defined geochemical phases (Ianni et al., 2001). By adapting a sequential extraction procedure for the use on W we should be able to assess sorption of W and later on through follow up experiments the changes over time. To do this a sequential extraction procedure (SEP) originally developed by Wenzel et al. (2001) for the use with arsenate will be adapted. The SEP was based on a method developed by Zeien and Brümmer (1989) and

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modified to take into account the anionic nature of As. Since W is thought to behave similar to other (oxy)anions we expect to be able to adapt the method for the use on W.

2. Hypothesis

The work described in this thesis was part of a larger project investigating the biogeochemistry of W in the plant-soil environment (FWF # P25942). The main purpose of this study was to characterize solubility, sorption behavior and chemical fractionation of W in soils.

The overall research question addressed in our study was:

"Does W behave like other similar anions (eg. molybdate, phosphate, arsenate) in soil and which geochemical properties mainly govern W solubility in soil?"

The main objectives of the study included:

(1) to determine the feasibility of using ICP-MS for measuring W in soil water extracts as well as finding a suitable acidification procedure for measuring W to avoid polymerization and precipitation in acidified samples;

(2) to modify an ÖNORM method for the purpose of determination of total W concentrations in soils using acid digestion;

(3) to evaluate the adsorption of W to soils as affected by soil pH and texture;

(4) to test and – if required - modify a sequential extraction procedure initially developed by Wenzel et al. (2001) for arsenic for its suitability to fractionate W and testing out additional steps, which might be necessary to include in the final sequential extraction.

To this end we started with a series of experiments on the methodical aspects of measuring W (objectives 1 and 2). First of all soil water extracts were spiked with W at different concentrations and W recovery was measured using ICP-MS. In a

similar way we tested different acidification treatments for water extracts and compared two acid digestion methods.

Furthermore to achieve objective 3 we added different concentrations of $CaCO_3$ and Na_2WO_4 to our experimental soils and measured W recovery after an incubation period of four weeks to determine adsorption to the soils with differing texture and level of pH.

To address objective 4 we used soils spiked with Na_2WO_4 as well as soils spiked with metallic W powder. The soils were incubated for four weeks and two months respectively and afterwards we carried out the sequential extraction procedure as well as two pre-experimental extraction steps.

3. Materials and Methods

3.1 Soil selection and treatment preparation

Experimental soils were collected from Siebenlinden (N 48° 40.513, E 14°59.933') and Litschau (N48° 57.37167 E 15° 3.95167) in the Waldviertel area in Lower Austria. The soil from Siebenlinden is an acidic, sandy soil and the soil from Litschau is an acidic clay soil. Soils were air dried at ambient temperature and passed through a 2-mm sieve. The soils will from here on be referred to as "sandy soil" and "clay soil", according to their texture.

Half of the soil material was then mixed with 25 g kg^{-1} CaCO$_3$ (Calcium carbonate precipitated puriss., Sigma-Aldrich) to achieve a higher pH for further experiments. For the adsorption test of our experiment smaller subsamples of the soils were spiked with five different concentrations of CaCO$_3$ (0%, 0.1%, 0.5%, 2.5%, 5%).

Aliquots of the acidic and limed soils were spiked with either metallic W (Tungsten powder, 99.95+, Inframat Advanced Materials) or sodium-tungstate salt (Sodium tungstate purum. ≥ 99 %, Sigma-Aldrich). The soils spiked with metallic powder were incubated at 60 % maximum water holding capacity (MWHC) for 2 months, while the soils spiked with sodium tungstate were incubated for 4 weeks at 20 °C. The concentrations of W applied were 50, 500 and 5000 mg kg^{-1} for the soils spiked with metallic powder and 500 and 5000 mg kg^{-1} for the soils spiked with sodium tungstate.

For some of the preliminary experiments we used a clay soil from Moosbierbaum in Lower Austria which serves as an internal reference material in our laboratory. We did this because at the time the soil characterization was not finished and we wished to use a soil with known properties in the experiment

We also used contaminated soils from a military firing range in Wicheln in Switzerland with known concentrations of W, which were determined by a Swiss laboratory. We used these soils as internal control material for some of the experiments, as having soils with known W concentrations was advantageous.

3.2 Soil characterization

The particle size distribution (sand 2000 – 63 µm, silt 63 – 2 µm, clay < 2 µm) of the experimental soils was analyzed using a combined sieve and pipette technique as described in ÖNORM L 1061-2.

The pH of the soils was measured in water suspension as well as in a 0.01 M $CaCl_2$ suspension using a soil to solution ratio (SSR) of 1:2.5 (mass:volume) according to ÖNORM method L 1083-89. After preparing the soil suspension, samples were shaken for 10 minutes and then left to settle for 2 hours. The pH was then measured using a Thermo Scientific ORION 3 Star pH meter.

The plant-available phosphate and potassium was determined by a calcium acetate-lactate extract according to ÖNORM method L 1087 and samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8300pv, Perkin Elmer).

The soil organic carbon was determined via loss on ignition using a modification of a method by Ben-Dor and Banin (1989). The soils samples were first dried in an oven at 105 °C overnight and then left in the muffle furnace at 550 °C for 16 hours. We then let the samples dry in a desiccator and calculated the weight of the ignited sample by subtraction.

Total amounts of amorphous and crystalline iron and aluminum in the soils were determined through acid ammonium oxalate (AAO) and citrate-bicarbonate-

dithionite (CBD) extraction respectively as described by Loeppert and Inskeep (1996)

The cation-exchange capacity (CEC) of the soils was known from a previous experiment done at our laboratory and was measured following ÖNORM L 1086-89.

The maximum water holding capacity (MWHC) was measured by placing approximately 5 g of the soils on filter paper and oversaturating them with water. The soils were then left for drainage overnight in a gas tight container to avoid water losses by evaporation. The maximum amount of water held against gravity by the soil was then determined by measuring the weight loss of a subsample dried at 105 °C over 48 h.

Investigated soil characteristics are shown in the results section of the thesis.

3.3 W analysis in soil extracts - Matrix tests

Before starting sequential extraction, we tested the performance of W measurements in different matrices using inductively coupled plasma mass spectrometry (ICP-MS). We prepared soil-water extracts with a SSR of 1:10 from the sandy experimental soil and the "Moosbierbaum" soil following ÖNORM method L 1092-93. This was achieved by first weighing in 5 g of dry soil into acid washed PE bottles (100 mL) and adding 50 mL of distilled water. We then shook the samples by hand and left them to stand overnight at room temperature. On the following day the samples were shaken again for 1 hour in an overhead shaker and afterwards filtrated using syringe filters (Whatman GDX 0.45 μm, Nylon). We created pool samples from the replicates for each of the soils as well as for the blank. Finally we acidified one batch of the samples with 65 % HNO_3 to

a final concentration of 2 % HNO_3 and another one with a home-made solution of 64.5 % HNO_3/0.4 % HF to a final concentration of 2 % HNO_3 / 0.01 % HF.

We also added different concentrations of W (10, 50 and 100 $\mu g\ L^{-1}$) to the samples using for one batch an ICP-MS standard solution (1000 $mg\ L^{-1}$, in 5% HNO_3 with 0.1% HF) and for another a self-made spike solution produced from Na_2WO_4 salt with a concentration of 1000 $mg\ W\ L^{-1}$.

Finally the recovery of W isotopes ^{182}W, ^{183}W, ^{184}W and ^{186}W in the soil suspension was measured using ICP-MS.

In another test we spiked water blanks with an ICP-MS standard solution (1000 $mg\ L^{-1}$, in 5% HNO_3 with 0.1% HF) to final W concentrations of 10, 50 and 100 $mg\ L^{-1}$ and tested the following four different acidification treatments:

- acidifying the samples to a final concentration of 2 % HNO_3 / 0.01 % HF using a home-made solution of 64.5 % HNO_3/0.4 % immediately after spiking the blanks;
- acidifying the samples with a self-made solution of 64.5 % HNO_3/0.4 % to achieve a final concentration of 2 % HNO_3 / 0.01 % HF on the same day as spiking the blanks (i.e. several hours after blank spiking);
- acidifying the samples to a final concentration of 2 % HNO_3 / 0.1 % HF using first 65 % HNO_3 and then concentrated HF added separately on the same day as spiking the blanks;
- acidifying the samples first with concentrated HF to a final concentration of 0.01 % HF and later adding 65 % HNO_3 on the same day as spiking the blanks to achieve a final concentration of 2 % HNO_3.

Afterwards we again measured the recovery of W in the samples using ICP-MS.

3.4 W Adsorption

To determine the pH-dependent adsorption behavior of W in soils with contrasting texture we added five concentrations of $CaCO_3$ (0%, 0.1%, 0.5%, 2.5%, 5%) to subsamples of the sandy and clay experimental soils. After an incubation time of one week at 35 % MWHC, different concentrations of tungstate (1, 2.5, 5, 7.5 mg W kg^{-1}) were added as Na_2WO_4 in a 1:10 soil to solution ratio (mass:volume) including 5 mM KCl as background electrolyte.

The samples were then put in an overhead shaker for 4 hours and centrifuged for 5 minutes with 3,836 x g relative centrifugal force. Afterwards we filtered the decanted solution through syringe filters (Whatman GDX 0.45 μm, Nylon). The samples which were used for immediate measurement were acidified with 65% HNO_3 to a total concentration of 2% HNO_3 while the rest was stored at -20 °C. Samples were analyzed for concentrations of W, Cu, Zn, Mn, Co, Mo, Al and Fe by ICP-MS as described above.

3.5 Determination of total W concentrations in soil – Acid Digestions

For the last step of the sequential extraction as well as for the matrix tests the soil samples were subjected to acid digestion in the fume cupboard. For this the air dried soil samples were ground with a ceramic mortar to achieve sufficient homogeneity for the digestions. We used two standard reference soils (Standard Reference Material 2710a Montana Soil from the National Institute of Standards and Technology and European Reference Material CC141 from the Institute for Reference Materials and Measurements) as reference material. As an internal reference a contaminated Swiss soil from a firing range with a known concentration of W (105 mg kg^{-1}) was also used.

As a preliminary experiment we first tested digestions with aqua regia according to ÖNORM method L 1085. Since Bednar et al. (2009) achieved a better recovery of W using acid digestions with phosphoric acid we also tested a modified version of their method by adding 0.5 mL H_3PO_4 to the ÖNORM method. The details of the method developed by Bednar et al. as well as the two methods we used in our experiment and two other examples from literature are shown in Table 3.1.

	soil [g]	HCl [ml]	HNO$_3$ [ml]	H$_2$O$_2$ [ml]	H$_3$PO$_4$ [ml]	digestion time	W recovery
Bednar et al.[1]	0.5		12.5	5	1	5 h 25 min at 95 °C (digestion block)	76 to 98 %
ÖNORM L 1085	2	15	5			20 – 30 min at 60 °C 2 h at 140 °C (digestion block)	20 to 50 %
ÖNORM modified (our study)	0.5	4.5	1.5		0.5	20 – 30 min at 60 °C (digestion block) 3 h at 150 °C	88 to 105 %
Griggs et al.[2]	0.5		8	6	2	10 minutes at 175 °C (microwave)	88.2 %
Clausen et al.[3]	2		8		2	16 hours at 85 °C (microwave)	80 to 120 %

Table 3.1: Comparison of different acid digestion procedures discussed in this work.

[1] Bednar et al. (2010)

[2] Griggs et al. (2009)

[3] Clausen et al. (2007)

3.6 Sequential extraction

For chemical fractionation of W we adapted a sequential extraction method originally developed for arsenic by Wenzel et al. (2001). We hypothesized that the method should also be applicable to W since it should behave similar to other oxyanions in soil. The extraction targets W bound to five different fractions:

(1) Non-specifically adsorbed

(2) Specifically sorbed

(3) Amorphous and poorly-crystalline hydrous oxides of iron and aluminum

(4) Well-crystallized hydrous oxides of iron and aluminum

(5) Residual phase

3.6.1 Pre-experiment

Before doing the sequential extraction we performed a preliminary experiment to see whether or not it would be necessary to also include steps targeting W bound to (1) the organic matter phase or (2) the carbonate phase in the soil. If W was bound to these phases, these steps would have to be included into the final extraction procedure. The methods for these two experiments were originally developed by Han and Banin (1995) and Zeien and Brümmer (1989).

(1) W bound to the organic matter phase (Zeien and Brümmer, 1989)

To see whether or not it was necessary to include this step, we took the sand and clay soils (W concentration 500 mg kg^{-1}, metal powder spike) in their unlimed and limed versions, dried them in an oven at 105 °C overnight and left them in the muffle furnace at 550 °C for 16 hours to destroy all organic matter. We then used these soils as well as the original untreated soils for the extraction step to see if there would be any differences in W recovery.

For the extraction step we weighed in 1 g of soil and added 25 mL of 0.025 M NH$_4$-EDTA with a pH of 4.6 to achieve a SSR of 1:25. We prepared the extractant by dissolving 7.31 g of EDTA in 1 L of distilled water and adding approximately 2.47 mL of ammonia solution (25 %). The samples were then shaken for 90 minutes and afterwards centrifuged for 10 minutes with 15,344 x g relative centrifugal force. The suspension was filtrated using syringe filters (Whatman GDX 0.45 μm, Nylon) and thereafter 25 mL of 1 M NH$_4$OAc with a pH of 4.6 were added to the soil for a washing step. The extractant for the washing step was prepared by weighing in 77.08 g of NH$_4$OAc and adding 50 mL of acetic acid. We then shook the samples again for 10 minutes and centrifuged and filtrated them as described above. The filtrate from the washing step was added to the already filtrated samples. Samples, which were not acidified immediately, were stored at -20 °C until acidification.

(2) W bound to the carbonate phase (Han and Banin, 1995)

To see whether or not substantial amounts of W can be extracted together with carbonates during this step we used the limed and unlimed versions of the sandy and clay soil (W concentration 500 mg kg^{-1}, metal powder spike) and compared the results.

We weighed in 1 g of soil and added 25 mL of a 1 M sodium acetate/acetic acid (NaAC/HAc) buffer with a pH of 5.5. We prepared the extractant by weighing in 82.038 g of sodium acetate and adding approximately 9.5 mL of acetic acid. Afterwards we shook the samples for 6 hours and centrifuged and filtrated them as described above in the first preliminary experimental step. Samples, which were not acidified immediately, were stored at -20 °C until acidification.

To sum it up the preliminary experimental extraction steps were done as described in Table 3.2:

Step	Extractant	Procedure	Centrifuge	SSR	wash step
organic matter phase	NH_4-EDTA (Titriplex II) 0.025 M; pH 4.6	shaken for 90 minutes	10 minutes, 15,344 x g rcf [a]	1:25	NH_4Ac (1 M); pH 4.6; SSR 1:25; 10 minutes shaking
carbonate phase	NaAc/HAc buffer (1 M); pH 5.5	shaken for 6 hours	10 minutes, 15,344 x g rcf [a]	1:25	

Table 3.2: Extraction steps targeting W bound to organic matter phase and carbonate phase

[a] rcf refers to relative centrifugal force (x g)

After the extraction procedure we acidified the samples to a final concentration of 2% HNO_3 / 0.01 % HF using a self-made solution of 64.5 % HNO_3/0.4 % HF. W concentrations were then analyzed by ICP-MS.

3.6.2 Sequential extraction of W in different soils

The final sequential extraction procedure, in which we used all available versions of the sandy and clay soils as well as a Swiss soil (W2) with a known concentration of W of 105 mg kg^{-1}, was carried out following Wenzel et al. (2001) and targeted these factions:

(1) Non-specifically adsorbed W

We weighed in 1 g of soil into 50 mL polyethylene tubes and added 25 mL of 0.05 M $(NH_4)_2SO_4$. To prepare the extractant 6.607 g $(NH_4)SO_4$ were dissolved in 1 L of distilled water. After adding the extractant to the soil, the samples were shaken for 4 hours and centrifuged for 10 minutes with 15,344 x g relative centrifugal force. We then filtrated the supernatant using syringe filters (Whatman GDX 0.45 µm, Nylon). The filtrated extracts were stored in a freezer at -20 °C and later acidified to a final concentration of 2% HNO_3 / 0.01 % HF as described above. The remaining soil was used for the next extraction step.

(2) Specifically sorbed W

For step 2 of the sequential extraction we added 25 mL of 0.05 $(NH_4)H_2PO_4$ to the remaining soil from step 1. We prepared the extractant by dissolving 5.75 g of $(NH_4)H_2PO_4$ in 1 L of distilled water. The samples were then shaken for 16 hours and afterwards treated as described in step 1.

(3) Amorphous and poorly-crystalline hydrous oxides of iron and aluminum

For step 3 of the sequential extraction we added 25 mL of 0.2 M NH$_4$-oxalate buffer with a pH of 3.25 to the remaining soil. We achieved the pH by mixing 0.2 M di-ammonium oxalate monohydrate ($(NH_4)_2C_2O_4 * H_2O$) and 0.2 M oxalic acid di-hydrate ($C_2H_2O_4 * 2 H_2O$) in a ratio of 1:0.6 (62.5 mL 0.2 M NH$_4$-oxalate and 37.5 mL 0.2 M oxalate for a final volume of 100 mL). The samples were then shaken for 4 hours in the dark and afterwards centrifuged and filtrated as described above. After the filtration we added 12.5 mL of the same 0.2 M NH$_4$-oxalte buffer to the soil for a washing step. The samples were shaken again for 10 minutes in the dark and centrifuged for 10 minutes with 15,344 x g relative centrifugal force. Afterwards we filtrated the samples as described in the previous steps and combined the two filtrates. The pooled samples were acidified as described above.

(4) Well-crystallized hydrous oxides of iron and aluminum

For step 4 of the sequential extraction we added 25 mL of 0.2 M NH$_4$-oxalate buffer + 0.1 M ascorbic acid with a final pH of 3.25. We achieved this by mixing 17.612 g ascorbic acid with 680 mL of 0.2 M di-ammonium oxalate monohydrate and 320 mL of 0.2 M oxalic acid di-hydrate. Next we put the samples in a water basin at 96 ± 3 °C for 30 minutes in the light and afterwards centrifuged, filtrated and acidified them as described above. For this step we again did a wash step which was the same as in step 4.

(5) Residual phase

For the last step of the sequential extraction the remaining soil was first dried at 105 °C overnight. We then ground the residual soil and a subsample (0.5 g) was

digested using the modified ÖNORM method. We added 4.5 ml HCl, 1.5 ml HNO$_3$ and 0.5 ml H$_3$PO$_4$ to the sample and digested the soil at 150 °C for 3 h (as described in Figure 3.1). We afterwards acidified the samples as described above. The analysis of the samples was carried out using ICP-MS.

To sum it up the sequential extraction was done as follows:

Step	Extractant	Procedure	Centrifuge	SSR	wash step
1	0.05 M (NH$_4$)$_2$SO$_4$[a]	shaken for 4 hours	10 minutes, 15,344 x g rcf [d]	1:25	
2	0.05 M (NH$_4$)H$_2$PO$_4$ [a]	shaken for 16 hours	10 minutes, 15,344 x g rcf [d]	1:25	
3	0.2 M NH$_4$-oxalate buffer (pH 3.25)[b]	shaken for 4 hours in the dark	10 minutes, 15,344 x g rcf [d]	1:25	0.2 M NH$_4$-oxalate buffer (pH 3.25); SSR 1:12.5; shaken for 10 minutes in the dark; centrifuged for 10 minutes, 15,344 x g rcf [d]
4	0.2 M NH$_4$-oxalate buffer + 0.1 M ascorbic acid [b] (pH 3.25)	30 minutes in a water basin at 96 ± 3 °C in the light	10 minutes, 15,344 x g rcf [d]	1:25	0.2 M NH$_4$-oxalate buffer (pH 3.25); SSR 1:12.5; shaken for 10 minutes in the dark; centrifuged for 10 minutes, 15,344 x g rcf [d]
5	Aqua regia + 0.5 mL H$_3$PO$_4$	open digestion		1:50[c]	

Table 3.3: Sequential Extraction procedure for W, modified after Wenzel et al. (2001)

[a] Modified according to Saeki and Matsumoto (1994)

[b] Zeien and Brümmer (1989)

[c] after the digestion

[d] rcf refers to relative centrifugal force (x g)

3.7 Analysis

For the analysis of the samples ICP-MS (Elan 9000 DRCe, Perkin Elmer) was used. Soil extracts and digestions were diluted using 2 % HNO_3. As an internal standard we used ^{115}In. A certified quality control solution was measured at the beginning and end of every measurement and additional quality controls were measured repeatedly throughout each measurement run using diluted ICP-MS multi-element standard solutions Blanks were also inserted into each measurement in regular intervals. We used multi-point calibrations which were assumed as simply linear and measured before each batch. The results were blank-corrected afterwards.

3.8 Statistics

The statistical analysis was carried out using SPSS Statistics Version 20 (IBM). We used the Compare means procedure to determine significant differences ($p > 0.05$) between treatments using t-test and One-Way-ANOVA.

Graphical illustrations were plotted using Systat Software, SigmaPlot Version 12.

For the experiment on recovery of W from soil water extracts we calculated an Uncertainty budget. For this we estimated the semi-range between the upper and lower limits of uncertainty (a) for each step of the procedure and (assuming a rectangular distribution) calculated the standard uncertainty (u) as follows:

$$u = \frac{a}{\sqrt{3}} \; ,$$

The standard uncertainties of all steps were then combined and multiplied with a coverage factor $k = 2$, providing a level of confidence of approximately 95 %.

4. Results and Discussion

4.1 Soil characterization

Table 4.1 provides an overview of the physico-chemical properties of the experimental soils. The most relevant difference between the soils was the dissimilarity in texture. The clay soil from Litschau had a much higher clay content (260 g kg^{-1} clay, 600 g kg^{-1} silt, 140 g kg^{-1} sand) than the sandy soil from Siebenlinden (10 g kg^{-1} clay, 460 g kg^{-1} silt, 530 g kg^{-1} sand).

Both soils were acidic, with the pH values being 5.03 for the clay soil and 4.5 for the sandy soil (determined in 0.01 M $CaCl_2$).

The maximum water holding capacity (MWHC) and soil organic carbon content (SOC) differed only slightly between the experimental soils.

Fe- and Al-oxides as well as plant-available PO_4 and K were higher in the sandy soil, while the clay soil had a higher cation exchange capacity (CEC).

soil properties		clay soil	sandy soil
MWHC		71 %	63 %
Fe-oxides (AAO)[1]		6.31 g kg^{-1}	7.4 g kg^{-1}
Al (AAO)[1]		3.05 g kg^{-1}	4.25 g kg^{-1}
Fe-oxides (CBD)[1]		8.45 g kg^{-1}	11.3 g kg^{-1}
Al (CBD)[1]		3.46 g kg^{-1}	3.33 g kg^{-1}
texture	sand	140 g kg^{-1}	530 g kg^{-1}
	silt	600 g kg^{-1}	460 g kg^{-1}
	clay	260 g kg^{-1}	10 g kg^{-1} clay
textural class (FAO)		Silt loam	Sandy loam
pH unlimed (CaCl$_2$)		5.03	4.5
pH limed (CaCl$_2$)		7.44	7.02
SOC		33.8 g kg-1	31.4 g kg-1
CEC		94.7 mmolc kg^{-1}	58.7 mmolc kg^{-1}
PO$_4$ (CAL extract)[2]		22.2 mg kg^{-1}	58.2 mg kg^{-1}
K (CAL extract)[2]		8.00 mg kg^{-1}	266 mg kg^{-1}

Table 4.1: Chemical and physical properties of the experimental soils

[1] Loeppert and Inskeep (1996)

[2] ÖNORM L 1087

4.2 W analysis in soil extracts – Matrix tests

4.2.1 Water extracts

The results of the preliminary experiment to test the recovery achieved by ICP-MS with different matrices and W spikes (described in section 3.3) are shown in Figure 4.1. The spiking treatment using an ICP-MS standard solution and 2 % HNO$_3$ produced a significantly lower recovery of W in all variants. Between the

two treatments using Na_2WO_4 there were significant ($p < 0.05$) differences in the higher concentrations of the soil extracts from the sandy soil as well as in the lower concentrations of the HNO_3 blank. Generally W recovery was between 75 and 112 %.
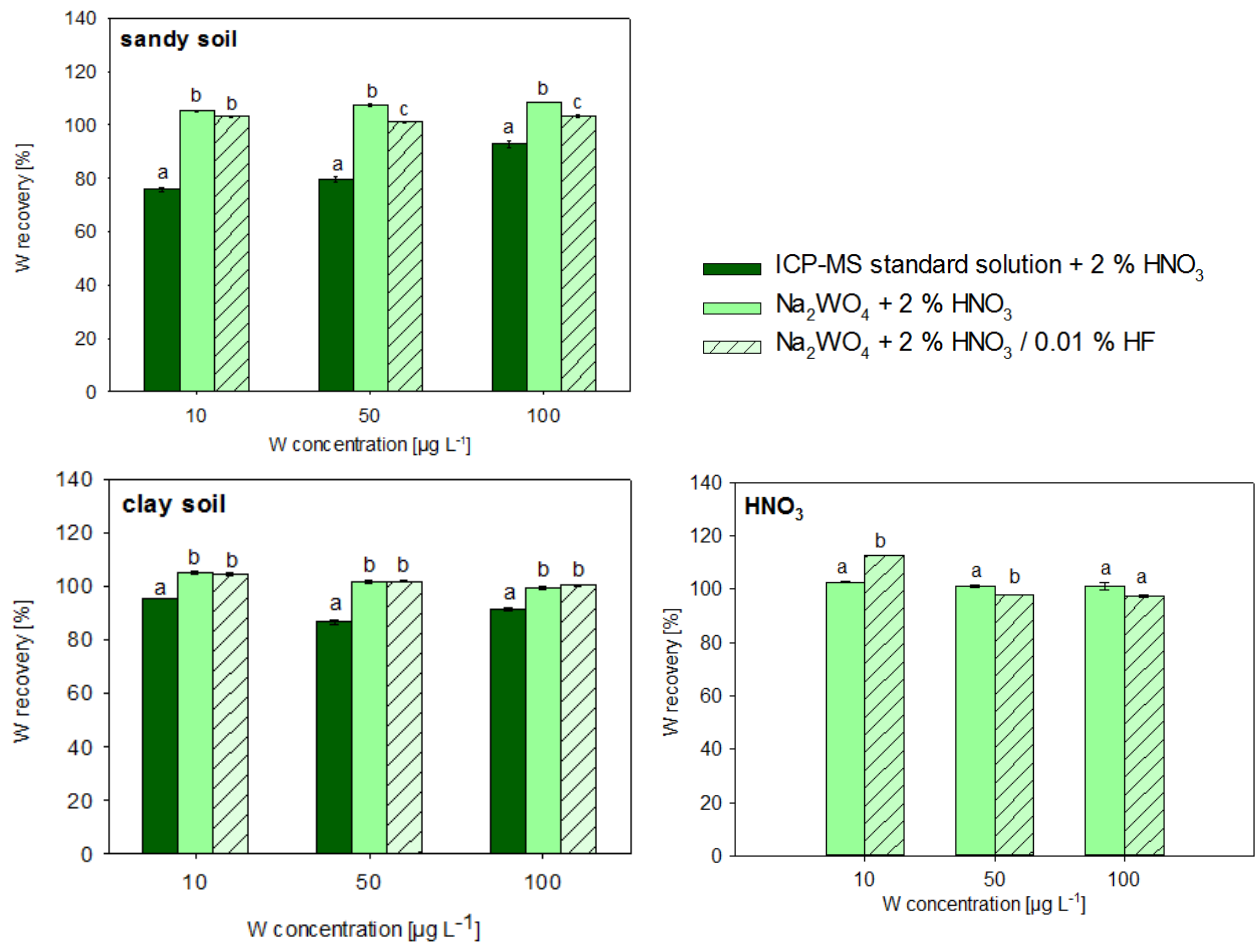
Figure 4.1: Recovery of W [%] in soil water extracts treated with different W spikes and acidification treatments. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same W concentration (One-Way ANOVA, $p > 0.05$, n = 3).

Bednar et al. (2007) used ICP-MS to measure samples containing molybdenum and W. They found that while both W isotopes they worked with (182 and 184) could potentially be susceptible to interferences by various oxides (e.g. of holmium, dysprosium, erbium, ytterbium), there would generally be low

concentrations of these elements in regular samples. Since our samples also most likely didn't contain any of these elements, it may be safe to assume that there were no interferences in our experiment either.

Clausen et al. (2010) did a study on the use of ICP-MS for measurements of W in water and soil samples and found the technique to be well-suited for the task with a limit of quantification (LOQ) of 0.04 µg L^{-1} for water samples containing W. The mean values observed in our measurements were 0.27 µg L^{-1} (ranging from 0.02 µg L^{-1} to 0.81 µg L^{-1}) for LOD (limit of detection) and 0.81 µg L^{-1} (ranging from 0.06 µg L^{-1} to 1.77 µg L^{-1}) for LOQ. Both Clausen et al. (2010) and Bednar et al. (2007) found no significant differences between the W isotopes used in their experiments (182 and 184). This was confirmed in our experiments, in none of which we ever found a significant difference between our measured W isotopes (182, 183, 184 and 186).

Another study in which ICP-MS was successfully used to measure W concentrations in water was done by Seiler et al. (2005) who measured W concentrations in water samples and achieved a detection limit of 0.09 µg L^{-1}.

While W recovery in the two treatments using Na_2WO_4 was satisfactory, the recovery in the variants using the ICP-MS standard solution was significantly lower. A possible explanation for this could be that the water matrix of this ICP-MS standard solution was not acidified and it was also past its expiration date and might not have been stable anymore.

We decided to apply a 2 % HNO_3 / 0.01 % HF matrix for all our samples of the main experiment. Table 4.2 shows an uncertainty budget of the entire procedure. The differences between the two treatments using Na_2WO_4 as well as the observed recovery above 100 % in some samples (Figure 4.1) were most

likely the result of inaccuracies during measurement, as they fall within the range of uncertainty calculated in this procedure.

	Component of Uncertainty	Uncertainty	Distribution	Divisor	Std Unc	
1	Weighing of soil	0.1	Rectangular	1.73	0.06	%
2	Filtration	3	Rectangular	1.73	1.70	%
3	Spiking	1	Rectangular	1.73	0.58	%
4	Spike preparation	0.1	Rectangular	1.73	0.06	%
5	Sample preparation	1.2	Rectangular	1.73	0.69	%
6	Calibration	1	Rectangular	1.73	0.58	%
		combined standard uncertainty			2	%
		coverage factor k			2	
		expanded uncertainty			**4**	**%**

Table 4.2: Uncertainty Budget for the experiment on recovery of W from soil water extracts

So while the addition of HF most likely did not make any difference for W recovery, we anticipated a positive effect on the measurability of Si, which was measured for use in further experiments. According to studies by Gaines (2011) and Dean (2003) the complexation with F- promotes stability of the element. Therefore we kept using HF for the further experiments.

4.2.2 Aqua regia

The comparison of the results of the two methods for soil digestion tested (described in section 3.5) shows a significant difference between the different digestion methods applied (Figure 4.2). The method using H_3PO_4 to prevent polymerization of W achieved a recovery of W around two times higher than the traditional ÖNORM method and resulted in a total recovery between 88 and

105 %. W recovery with the ÖNORM method on the other hand was only between 20 and 50 %.
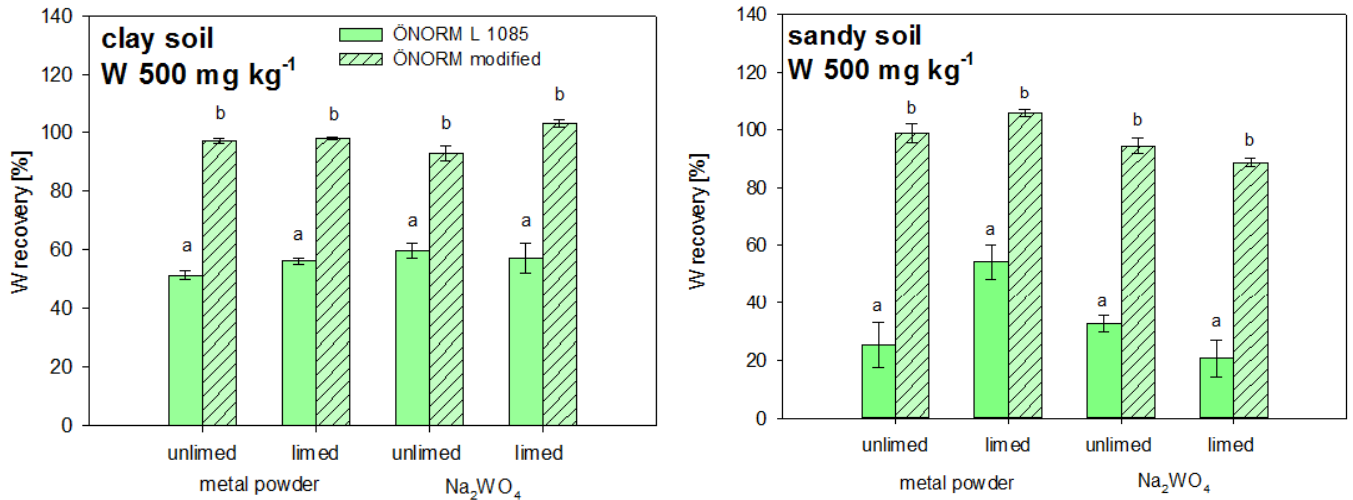
Figure 4.2: Recovery of W [%] after acid digestions following different methods. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant (Independent Samples t-test, $p > 0.05$, n = 2).

Bednar et al. (2010) originally developed their digestion method based on US norms. Based on this method we modified the ÖNORM method, since traditional digestion techniques have been shown to insufficiently extract W from soil because of precipitation of insoluble tungstates and the polymerization of tungstates onto soil particles. The phosphoric acid used in the method developed by Bednar et al. (2010) is likely to polymerize with W and form acid soluble W species for measurement by ICP-MS. Bednar et al. (2010) observed significantly increased W recovery of between 76 and 98 % compared to traditional digestion techniques, which only yielded between 25 and 56 % W recovery. Additionally the same authors found only little influence on the measurability of other elements using this method. The same was also true for the other elements measured in our samples (Mg, Al, Si, Ca, Mn, Fe, Mo; data not shown). The slightly higher recovery of W in our experiment might have been

due to aging effects, since our soils were incubated only for two months, while Bednar used soils incubated for three years as well as long-term contaminated soils from military sites.

Similar results were also found in the studies conducted by Griggs et al. (2009), in which again phosphoric acid was added to a standard digestion procedure. The recovery of W using the modified digestion method in this experiment was greatly increased, going from an average recovery of 10.2 % up to 88.2 %.

Clausen et al. (2010) also suggest using a HNO_3-H_3PO_4 acid mixture as an alternative to more difficult-to-handle procedures involving HF. Their results showed that most of W could be dissolved using a HNO_3-H_3PO_4 dissolution procedure.

Based on the obtained results and the information from the available literature we decided to use the modified ÖNORM method adding H_3PO_4 to the standard aqua regia solution. Compared to the method described by Bednar et al. (2010) the biggest difference was the addition of HCl while adding less HNO_3 for our digestion. This however didn't seem to change the positive effect on the measurability of W in any way.

4.2.3 Acidification test

The results of the experiment in which we used different acidification treatments on spiked water blanks (described in section 3.5) are shown in Figure 4.3.

The samples with HF added before HNO_3 had a significantly higher W recovery than all other treatments at the 10 and 100 µg L^{-1} W concentrations.

The treatment with a higher concentration of HF (0.1 %) showed a significantly lower recovery than all other treatments at all treatments except for the lowest W concentration.

There were no significant differences between the acidification treatment with 2 % HNO_3 and 0.01 % HF added simultaneously and the treatment with HNO_3 and HF added simultaneously immediately after spiking at any concentration. Generally W recovery was ranged between 90 and 100 % with only two exceptions (10 µg L^{-1} W with 2 % HNO_3 / 0.01 % HF added immediately after spiking, 100 µg L^{-1} W with 2 % HNO_3 / 0.1 % HF added) showing a higher or lower recovery of 116 % and 84 % respectively.
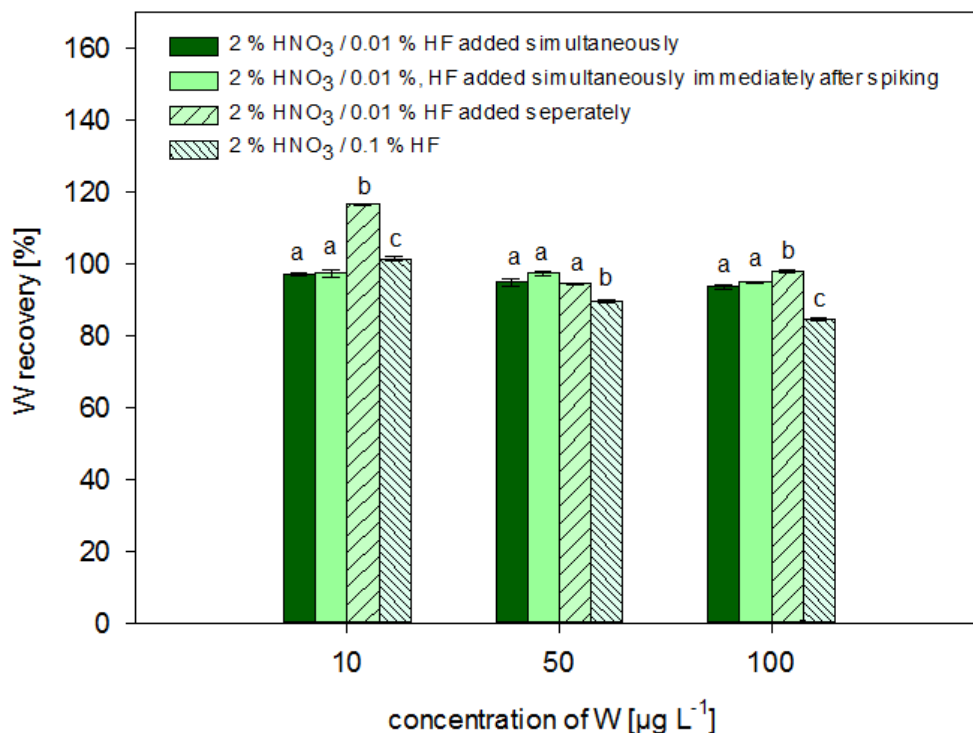
Figure 4.3: Recovery of W [% of spike] in soil water extracts using different acidification treatments. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same W concentration (One-Way ANOVA, $p > 0.05$, n = 3).

Since even the significant differences between the treatments were for the most part rather small we chose the treatment using 2 % HNO_3 / 0.01 % HF added

simultaneously using a mixture of 64.5 % HNO_3 / 0.5 % HF for our further experiments, because it was the easiest treatment to handle. The results of this experiment seem to indicate that the order in which the acids are added is most likely of no relevance for W recovery and that there is no need to add more than 0.01 % HF to the samples.

The unrealistically high W recovery (116 %) of the treatment with HF and HNO_3 added separately at the lowest concentration of W was most likely a result of either a mistake during sample preparation or an error during measurement.

4.3 W Adsorption

The results of the adsorption test investigating the effect of lime-driven pH changes and the effect of soil texture on W solubility (described in section 3.4) are shown in Figure 4.5.

Prior to the adsorption test we measured the pH of the different soil treatments used in the experiment (Figure 4.4) in a 0.01 M $CaCl_2$ solution at an SSR of 1:2.5. The pH of the unamended soils were 4.5 for the sandy soil and 5.03 for the clay soil. The highest pH values of the soils, with 5 % $CaCO_3$ added, were 7.44 for the sandy soil and 7.02 for the clay soil.
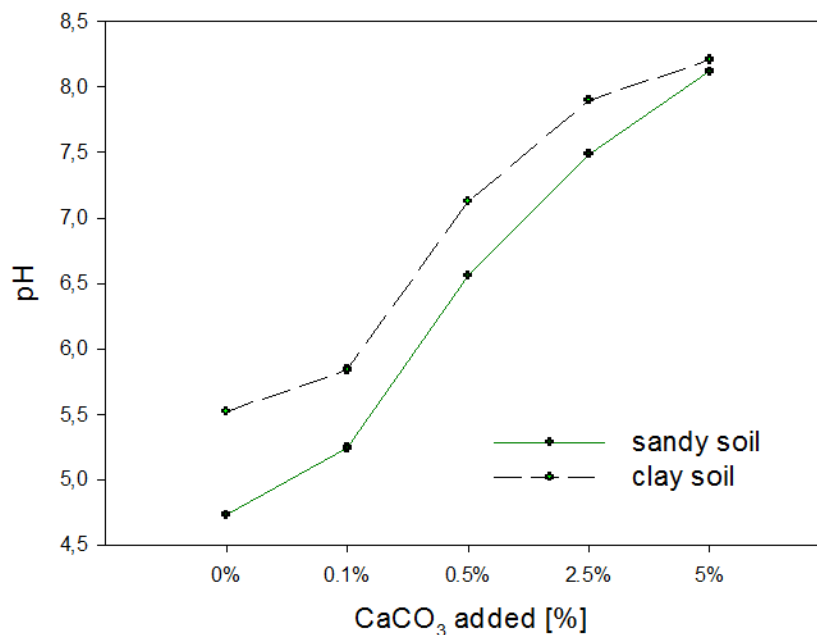
Figure 4.4: pH values of soils measured in 0.01 M CaCL$_2$ suspension according to ÖNORM method L 1083-80 after addition of different concentrations of CacO$_3$.

At all concentrations W was significantly stronger bound to the soils in the low pH range. In the soils with no CaCO$_3$ added nearly 100 % of the W were held by the soil matrix, irrespective of concentration added. Comparing the experimental soils, significantly more W was adsorbed at higher levels of pH in the clay soil than in the sandy soil. At the highest level of lime addition (5 % CaCO$_3$ added) the adsorption of W was around 60 % in the clay soil and around 20 % of the total W added in the sandy soil.

There were no significant differences in the relative fraction of W adsorbed between the different W concentration levels in the sandy soil. In the clay soil however, the relative amount of W adsorbed was 10-15% higher in the soils with lower W additions, especially at high pH (2.50 % and 5 % CaCO3).

The detailed statistical results of the adsorption test are shown in Appendix Tables A1, A2 and A3.
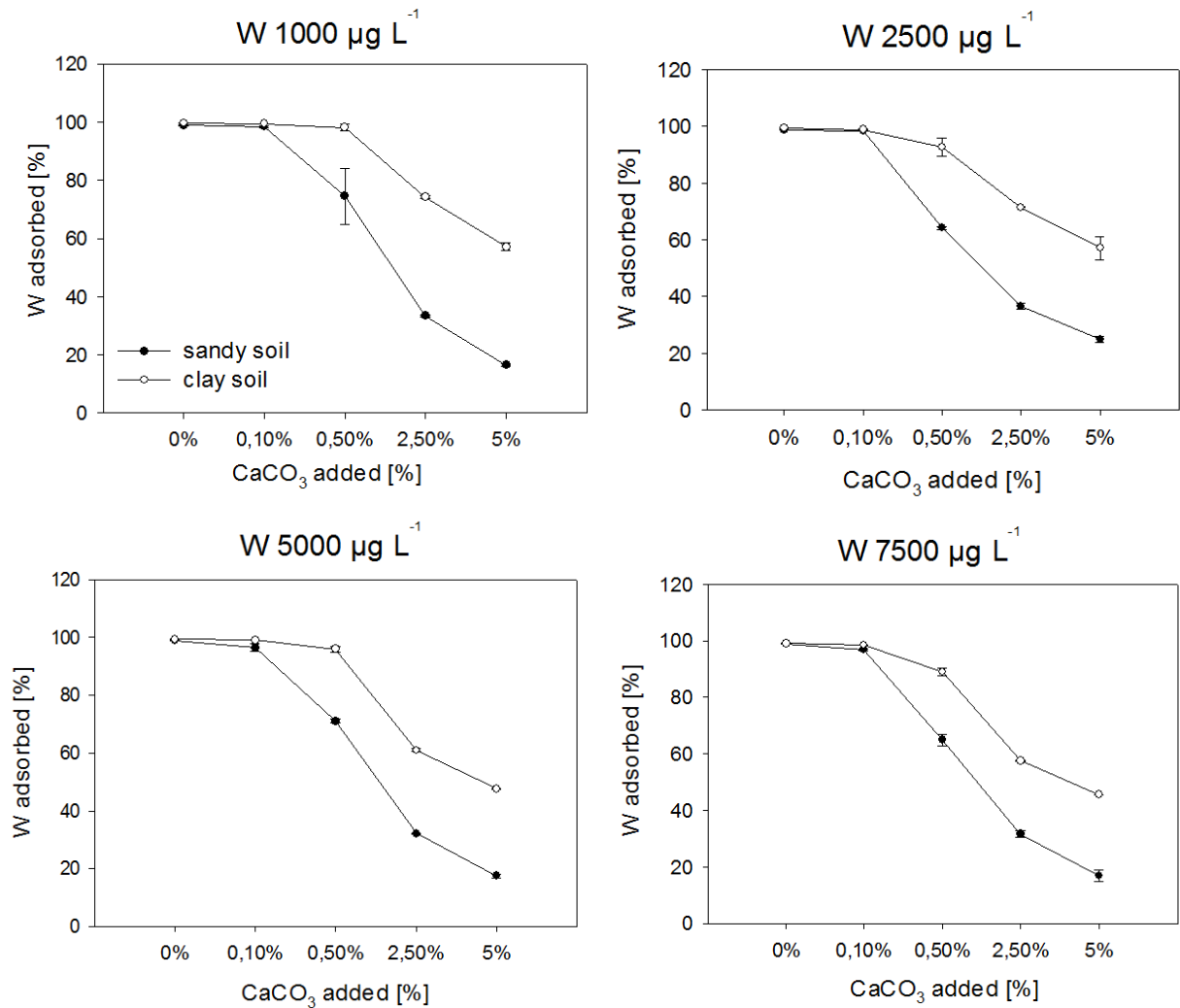
Figure 4.5: Adsorption of W in soils with different concentrations of W and different amounts of $CaCO_3$ added. Error bars indicate the standard error of the mean. n = 2

It is generally known that anions are bound more strongly to the soil at lower levels of pH due to the greater presence of positively charged adsorption surfaces as protons bind to Al- and OH-groups in the soil. (Scheffer et al. (2010,p. 144), Zeitz (2005)). This was very clearly the case in this experiment and matches our assumption that W behaves like other anions in soil.

Gustafsson (2003) did an experiment on the adsorption of MoO_4^{2-} and WO_4^{2-} to ferrihydrite. The results of his study closely match our findings, with nearly all of the W adsorbed at pH levels below 6 and a steady decline at higher levels of pH.

Goldberg et al. (1996; 1998) did two studies on the topic of molybdate adsorption on soils and minerals. The results of these experiments also show a strong adsorption at low pH levels and decreasing adsorption at higher levels of pH with only very little Mo adsorbed at pH > 9. Other factors, such as particle concentration, solution ionic strength, temperature and competing ion concentration, seemed to play only a limited role in controlling molybdenum adsorption. Gustafsson (2003) also used MoO_4^{2-} in his experiment and found a similar pH dependency, although molybdate seemed to be less strongly adsorbed to ferrihydrate than tungstate.

For other anions like arsenate and phosphate the effect of increasing adsorption with decreasing pH is also well known (Antelo et al. (2005), Gao and Mucci (2001)). In an experiment done by Gao and Mucci (2001) phosphate adsorption to synthetic goethite in 0.7 M NaCl solution went from 57 % at pH 4 down to 20 % at pH 10. Arsenate showed a similar pattern in this experiment with adsorption varying between 48 to 100 % at pH 4 and 20 to 45 % at pH 10 depending on the initial concentrations added. In the experiment done by Antelo et al. (2005) adsorption of phosphate and arsenate on synthetic goethite also increased with decreasing pH in a similar way.

Apart from the pH dependency of W sorption, another important factor to consider when looking at the results of this experiment is the texture of the soil. Since clay has a higher specific surface area than sand, it will generally have a higher capacity for binding ions (Scheffer et al., 2010 ,p. 135). This is also the case in our adsorption test, where W at higher levels of pH was more strongly bound to the clay soil than to the sandy soil. Despite the overall negative surface charge of clay minerals, positive charges at edges can significantly contribute to anion binding. Therefore the higher clay content compensates for the higher metal

oxide (Fe & Al, Table 4.1) concentrations in the sandy soil, resulting in stronger W adsorption in the clay soil across all W concentrations and lime additions.

4.4 Sequential extraction

4.4.1 Pre-experiment

 (1) W bound to the organic matter phase (Zeien and Brümmer, 1989)

The results of the pre-experiment targeting W bound to the organic matter phase of the soil (described in section 3.6.1) are shown in Figures 4.6, 4.7 and 4.8. There was no significant difference between the soils with intact organic matter and those with the organic matter burned off for three of our four experimental soils. Only in the unlimed sandy soil could we find a significant difference between the two treatments, with the W recovery being higher in the soil without organic matter.
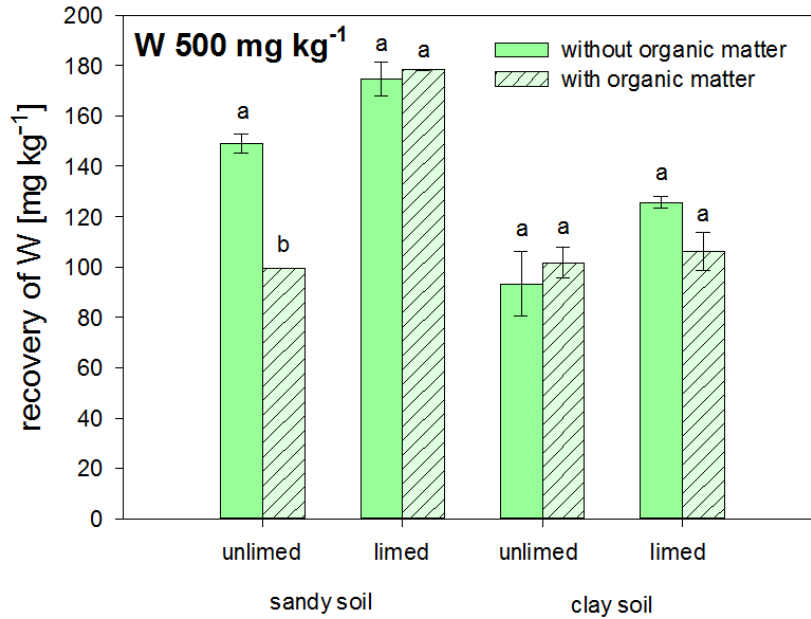
Figure 4.6: Concentration of W in extracts from soils with and without organic matter phase using 0.025 M NH$_4$-EDTA. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant (Independent samples t-test, $p > 0.05$, n = 2).

We also measured a number of other elements (Mg, Al, Ca, Mn, and Fe) during this pre-experiment. Of interest are especially the concentrations of Fe and Al. Soluble iron concentrations were significantly higher in the limed sandy soil when the organic matter was removed, while no significant differences were observed for the natural acidic sandy soil. In the clay soil however, we found the opposite trend, with Fe being more soluble in the unlimed soil with organic matter still intact. The concentrations of aluminum were higher in the treatments without organic matter in all soils.
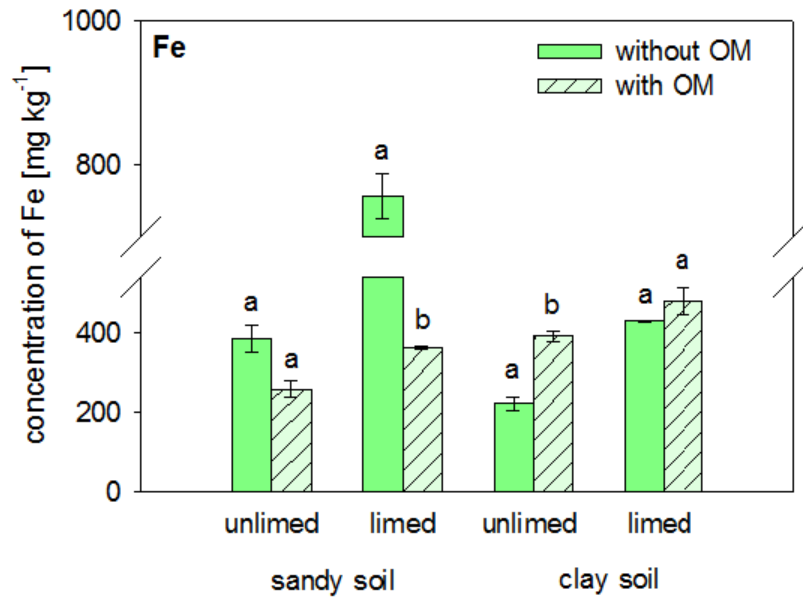
Figure 4.7: Concentration of Fe in extracts from soils with and without organic matter phase using 0.025 M NH$_4$-EDTA. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant. (Independent samples t-test, $p > 0.05$, n = 2)
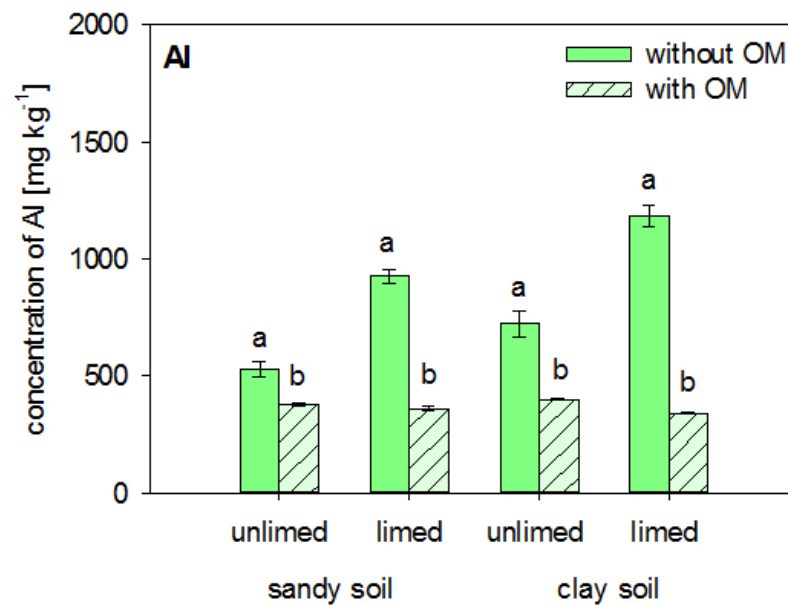
Figure 4.8: Concentration of Al in extracts from soils with and without organic matter phase. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant. (Independent samples t-test, $p > 0.05$, n = 2)

While there was a significant difference in extracted W for one of the soil treatments, we believe this is not because of W bound to the organic matter. Since it is also negatively charged, organic matter in the soil can be strongly adsorbed on mineral surfaces, mainly through chemisorption to hydrous oxide minerals (eg. Fe and Al) (Alloway, 2012 ,p. 57).

When the organic matter is lost, so are the bonds between the organic matter and the metal oxides. In the soils without organic matter Fe, Al and Mg also had for the most part a significantly higher solubility and were recovered in higher concentrations. Since removal of the OM had no effect on W recovery in all soils except the unlimed sandy soil, it seems that W was bound to Fe- and Al-oxides rather than to organic matter. In the unlimed sandy soil W adsorbed to either oxides of Fe or Al might have been set free along with the dissolution of the bonds between the OM and the oxides. Another possible explanation for the higher amounts of Fe and Al recovered from the soils without OM could however be that relevant concentrations of these elements were present in the OM complexes themselves and were released during the incineration of the OM.

Borggaard et al. did various studies on the influence of organic matter and humic substances on phosphate adsorption to aluminium and iron oxides (Borggaard et al. (1990), Borggaard et al. (2005)). They found the phosphate adsorption capacity and the presence of organic matter to be independent of each other. There are however other studies which suggest a decrease in phosphate adsorption in the presence of organic matter (Bhatti et al. (1998), Gerke (1993)). Borggaard et al. (2005) suggest that these different results may be due to differences in experimental setup such as time of equilibration, order of addition of the substances and concentrations. Our own results seem to suggest that W behaves similar to what Borggaard et al. observed for phosphate, with no significant difference with or without organic matter.

Molybdenum adsorption on the other hand has been reported to be closely related to organic matter content in the soil (Karimian et al., 1978). Wichard et al. (2009) also found molybdenum to be bound to both mineral oxides as well as organic matter in their experiments. Jiang et al. (2015) did a study on the effects of soil properties on molybdenum availability and found soil organic carbon to be the most important factor.

Wenzel et al. (2001) also did not use the NH_4-EDTA extraction step in the final version of their sequential extraction for arsenic, which we adopted for our experiment. While in their experiment between 2 and 7 % of the total arsenic was extracted during this step, there was no relation to the soil organic matter content of the used soil and the step was thus eliminated. They also found NH_4-EDTA to be not specific, as it dissolved considerable amounts of Fe and Al from amorphous hydrous oxides, which in turn lead to the dissolution of arsenic bound to this fraction.

Considering that in three of the four soils there is no difference in W solubilization with and without organic matter, it seems reasonable that organic matter and W may have different binding sites to oxides. The increase of Fe and Al in the samples with organic matter burnt away is most likely due to the destruction of the bonds between the organic matter and the oxides. During this reaction W adsorbed to either Fe or Al could possibly also be set free, which is in all likelihood what happened in the unlimed sandy soil. It would however also be possible that the elevated concentrations of Fe, Al, Mg and W were released during the incineration of the OM. However since we only found elevated W concentrations in one of the four experimental soils we decided in the end against including this step in our sequential extraction.

(2) W bound to the carbonate phase (Han and Banin, 1995)

The pre-experiment targeting the carbonate phase of the soil (described in section 3.6.1) showed a significant difference between the limed and unlimed versions of the soils only in the sandy soil (Figure 4.9). There was no significant difference between the limed and unlimed clay soils.
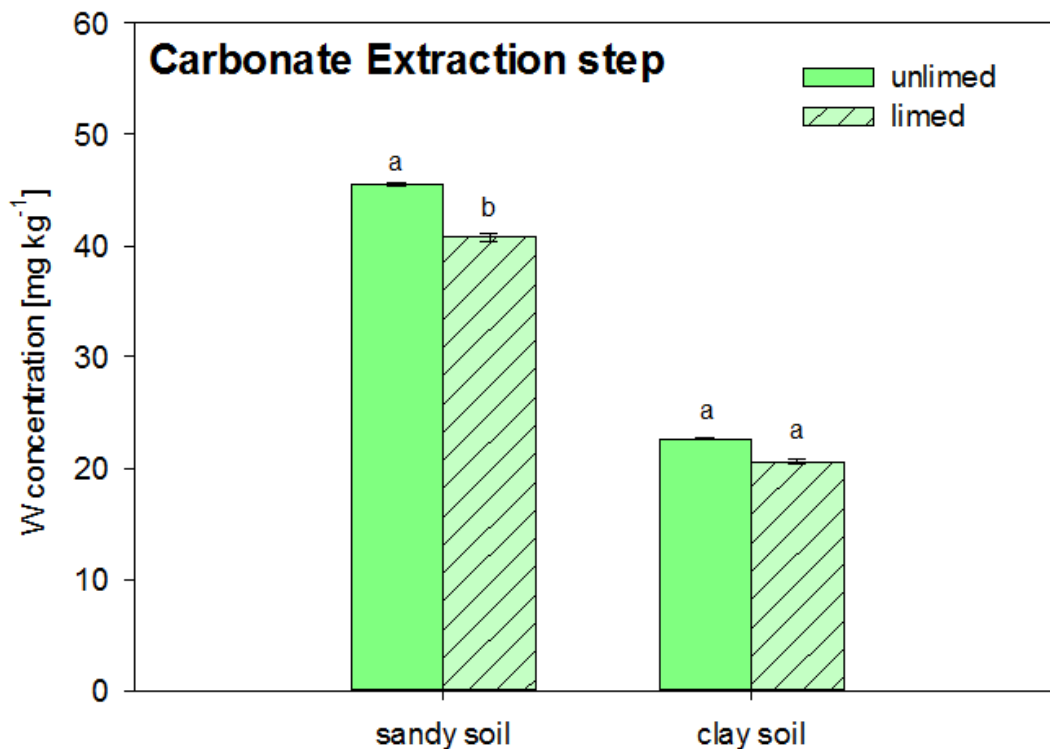

Figure 4.9: Concentration of W in extracts from soil targeting the carbonate phase of acidic and alkaline soils using 1 M NaAC/HAc buffer. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant. (Independent samples t-test, $p > 0.05$, n = 2)

The extraction using 1 M NaAC/HAc with pH 5.5 has been shown in the experiment by Han and Banin (1995) to be able to extract all carbonate from soils with a carbonate content between 10 and 20 %. Since carbonate contents in our soils were lower than that, we decided to test this method in the pre-experiment. In the experiment done by Wenzel et al. (2001) this step was also

initially considered, but dropped after it only extracted negligible amounts of arsenic.

Goldberg et al. (1996) did a study on molybdenum adsorption and its connection to carbonate content of soils, but did not find $CaCO_3$ to be a significant factor controlling adsorption. Phosphate on the other hand is well known to be adsorbed to calcium carbonate in soils (Cole et al., 1953).

Since the difference in W recovery between the limed and unlimed soils in this experiment was relatively low (and there was in fact less W extracted from the carbonate soil) in the sandy soil (around 5 mg kg^{-1} out of 500 mg kg^{-1} added to the soil) and there was no significant difference between the treatments in the clay soil, it would seem that W behaves similar to molybdenum in this aspect. Considering that our soils also contained only low concentrations of carbonate we decided against including this step in the final sequential extraction procedure.

4.4.2 Sequential extraction of W in different soils

The results of the final sequential extraction (described in section 3.6.2) are shown in Figures 4.10, 4.11 and 4.12. Most of the W was recovered during step 3, which was targeting W bound to amorphous and poorly-crystalline Fe- and Al-oxides using 0.2 M NH_4-oxalate for the extraction. This applies for all soils and treatments. The percentage of W that was extracted during this step was for most W concentrations and soil treatment between 40 and 80 %, with the higher oxide associated W concentrations found in the soils spiked with Na_2WO_4 salt.

The main difference between the limed and unlimed soils was the amount of W extracted during the first step (using 0.05 M $(NH_4)_2SO_4$) which targeted non-specifically adsorbed W (Table 4.4). For nearly all soils and treatments

significantly more W was extracted from the limed soils during this step than from the unlimed treatments. For the unlimed soils the percentage of W extracted during this step was generally well below 10 % with only two outliers (clay soil 5000 mg kg^{-1} W and sandy soil 5000 mg kg^{-1} W with Na_2WO_4 spike) being at 14 and 18 % respectively. The limed soils had generally between 10 and 20 % of W extracted from this phase.

soil	spike	W total [µg kg^{-1}]	mean unlimed [µg kg^{-1}]	SE unlimed [µg kg^{-1}]	mean limed [µg kg^{-1}]	SE limed [µg kg^{-1}]	p
sandy	Na_2WO_4	500	3.3	0.02	92.9*	0.15	**0.000**
sandy	Na_2WO_4	5000	923.75	316.90	1161	319.3	0.916
clay	Na_2WO_4	500	1.63*	0.11	56.6	3.24	**0.003**
clay	Na_2WO_4	5000	743.3*		1322	162.6	0.288
sandy	metallic W	50	0.19	0.00	6.20	0.05	**0.000**
sandy	metallic W	500	2.88	0.18	66.8*	4.29	**0.000**
sandy	metallic W	5000	70.8	6.75	564.2	64.6	**0.002**
clay	metallic W	50	0.03	0.00	4.21	0.08	**0.000**
clay	metallic W	500	0.99*	0.01	68.8	2.54	**0.000**
clay	metallic W	5000	33.8*	1.28	989.6	24.3	**0.001**

Table 4.4: Statistical results from the independent t-test comparing the effect of lime within each W concentration soils used in the first extraction step of the sequential extraction with different pH. In soils marked with * there was a significant difference between the two spike variants.

Across all investigated soils and treatments only a small amount of W (below 10 %) was extracted during the second step, which used 0.05 M $(NH_4)H_2PO_4$ to extract specifically sorbed W. The only exception was the unlimed clay soil with 5000 mg kg^{-1} W added (Na_2WO_4 spike) with 16 % W recovery during this step.

During step 4 (well-crystallized Fe- and Al-oxides, 0.2 M NH_4-oxalate + 0.1 M ascorbic acid) and step 5 (residual phase, acid digestion) only smaller

amounts of W (between 5 and 10 % for most soils) were extracted and there were mostly no significant differences between the limed and unlimed soils.

For the majority of the soils we were not able to extract all of the W we added initially. Only two of the soils (limed clay soil 500 and 5000 mg kg^{-1} W with Na$_2$WO$_4$ spike) had all of the added W recovered during measurement. For the rest of the soils between 3 and 30 % of the added W could not be extracted with the final acid digestion step.

Figure 4.10 shows the soil variants in which we found a significant difference between the two different spiking treatments. All in all we found significant differences in ten of the 32 variants during the first four steps of the sequential extraction. Except for one (step 2 of the unlimed sandy soil W 500 mg kg^{-1} soil) in all of them we extracted more W from the soil spiked with Na$_2$WO$_4$. The complete statistics for this comparison are listed in Appendix Table A4.
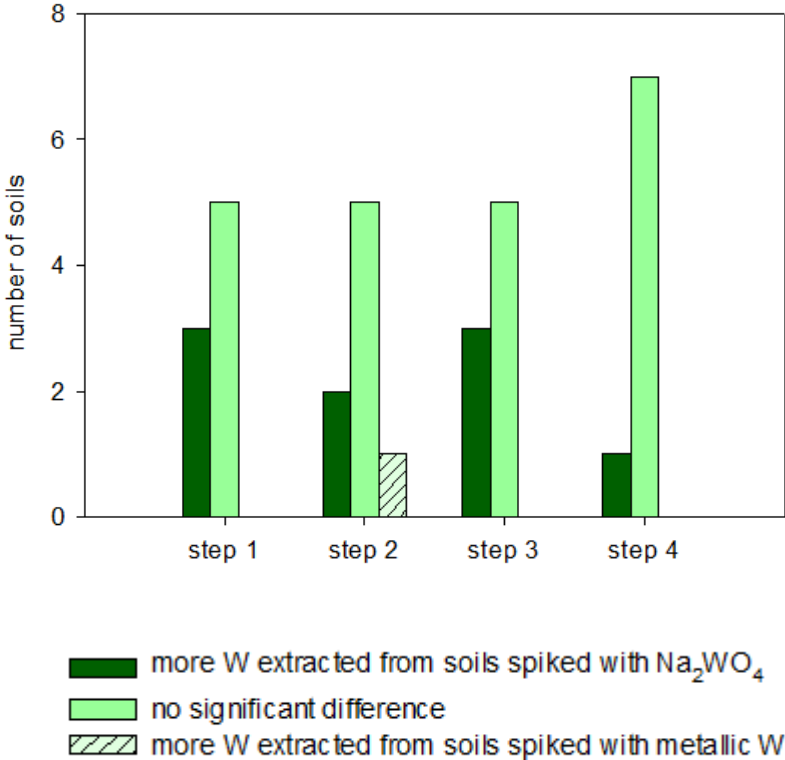
Figure 4.10: Number of soils used in the sequential extraction with or without significant ($p > 0.05$) differences comparing the effect of different W spikes. Results based on One-Way ANOVA. N_{tot} = 8.

Across the soils, there were significant differences ($p < 0.05$) in 22 of the 32 variants for the first four steps of the sequential extraction (Figure 4.11). During the first three steps we extracted significantly more W from the sandy soils in 14 cases. During step 4 more W was extracted from the clay soils in four soil variants. The complete statistics for this comparison are listed in Appendix Table A5.
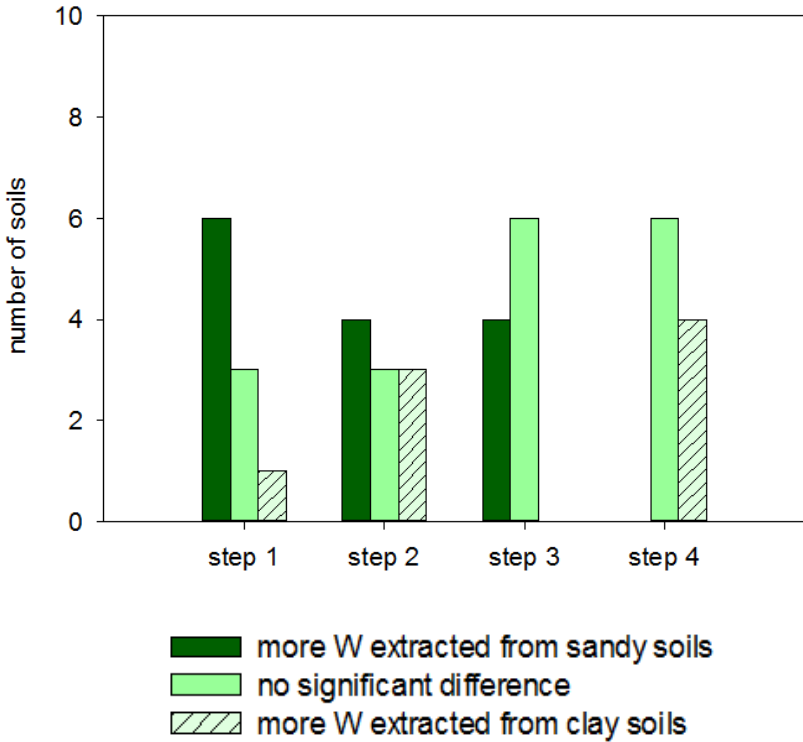
Figure 4.11: Number of soils variants used in the sequential extraction with or without significant ($p > 0.05$) differences comparing the experimental soils. Results based on One-Way ANOVA. $N_{tot} = 10$.
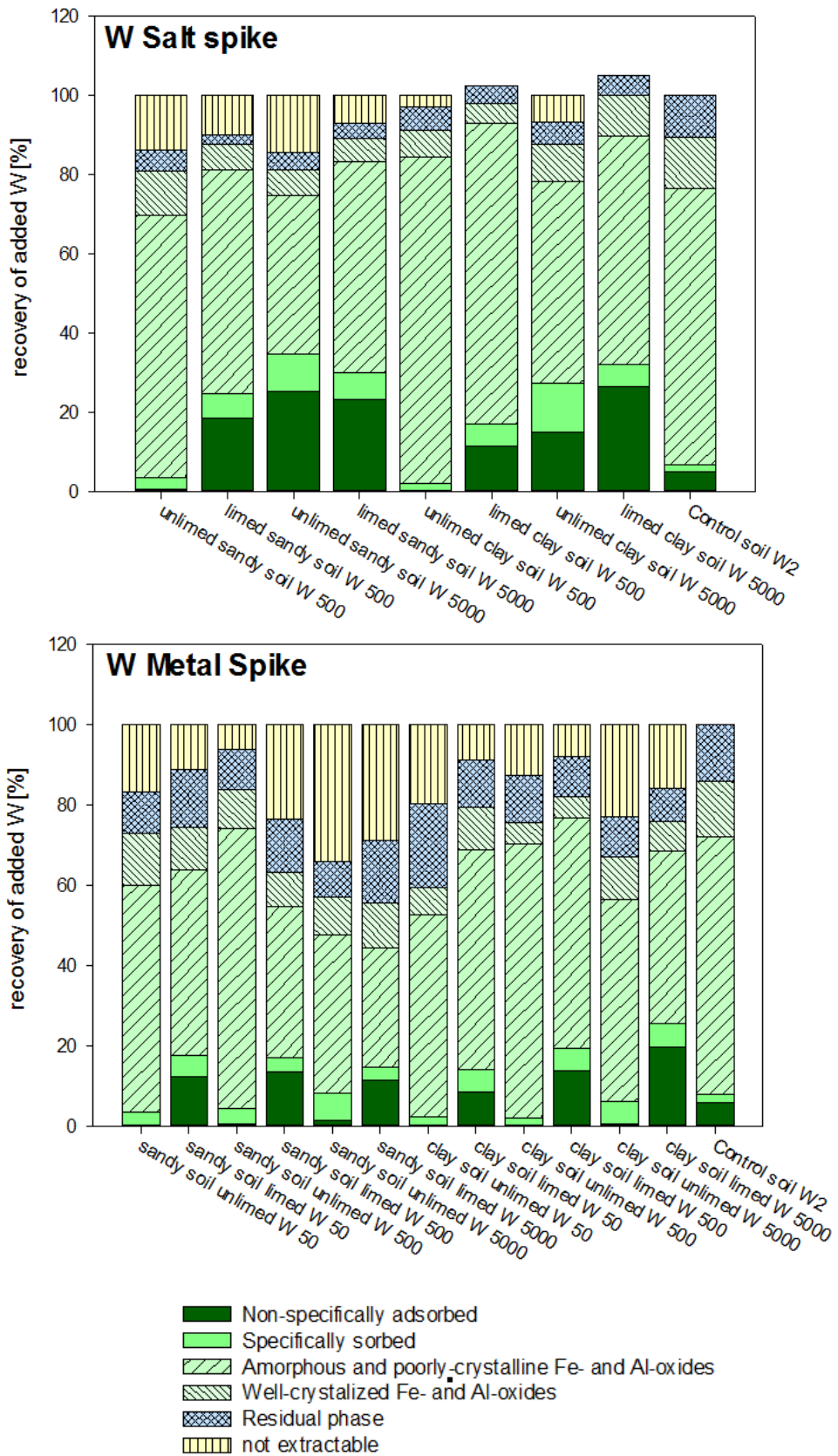
Figure 4.12: W recovered during the five steps of the sequential extraction from soils spiked with Na_2WO_4 and metallic W powder.
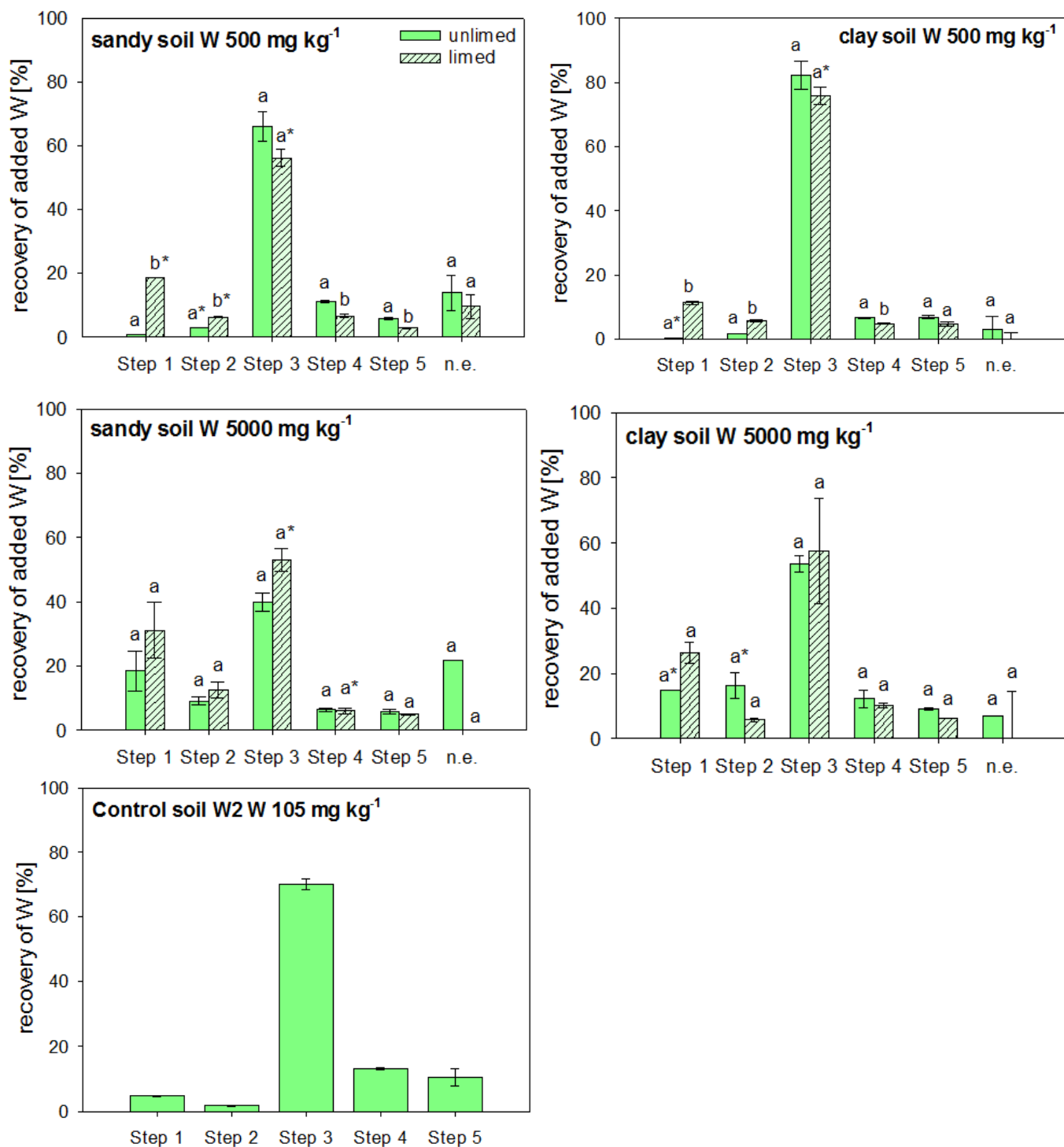
Figure 4.13: W recovered during the five steps of the sequential extraction from soils spiked with Na_2WO_4. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant (Independent samples t-test, $p > 0.05$). In data points marked with * there was a significant difference between the two spiking treatments. n = 2
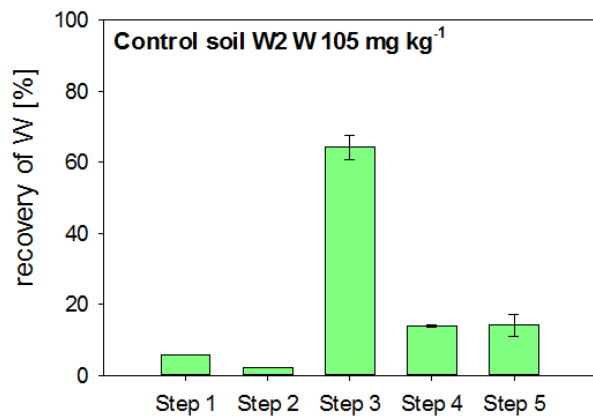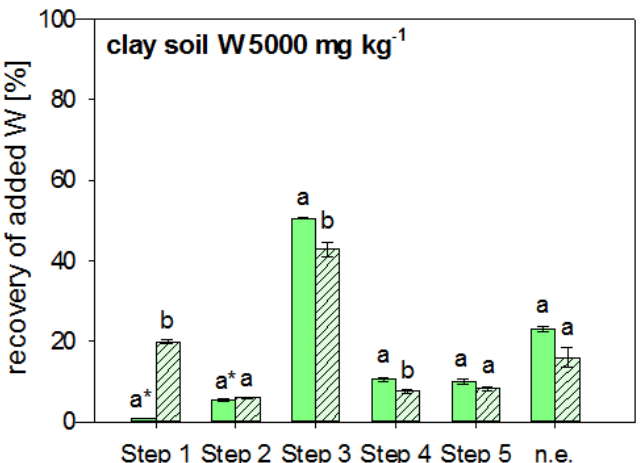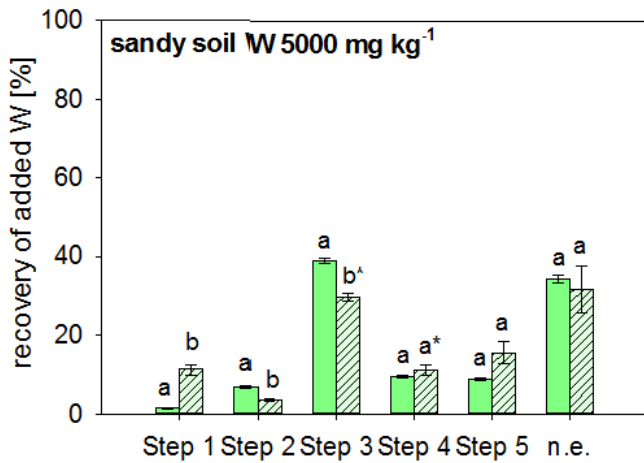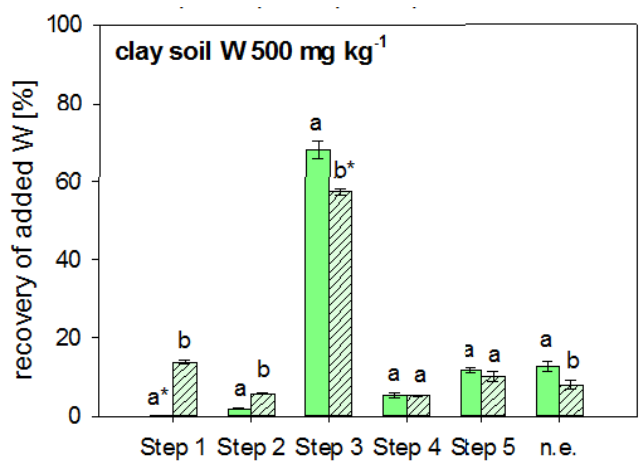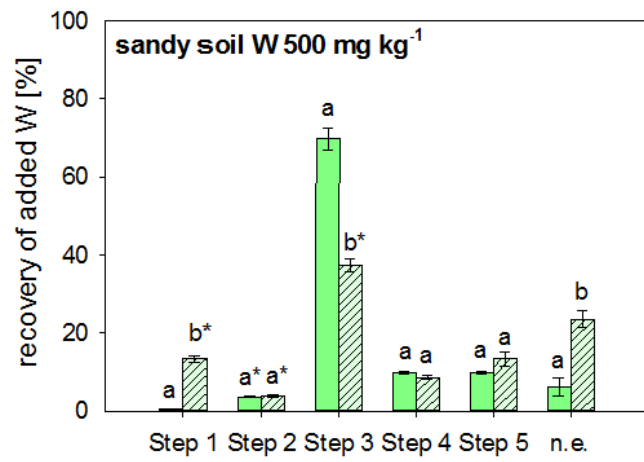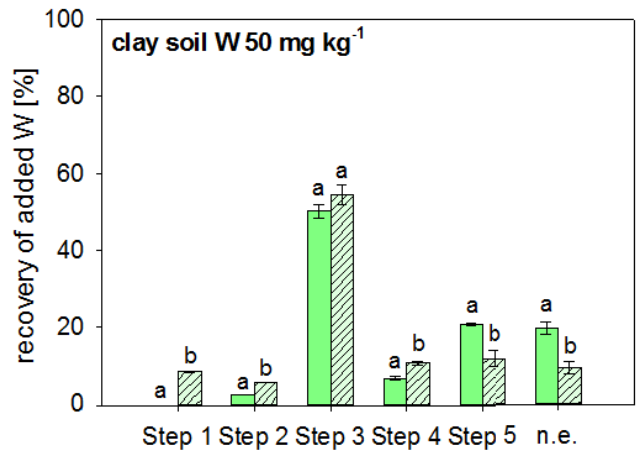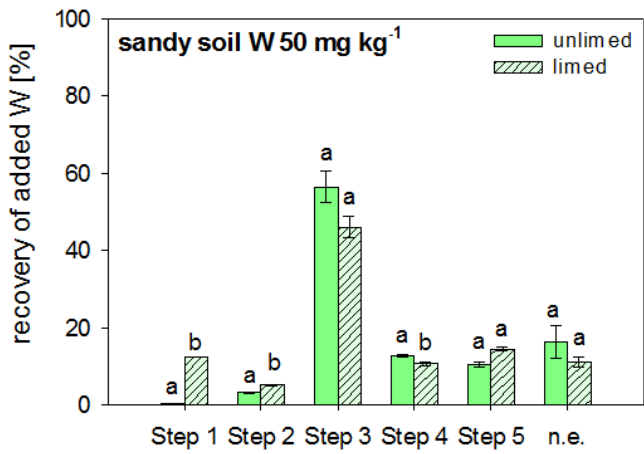
Figure 4.14: W recovered during the five steps of the sequential extraction from soils spiked with metallic W powder. Error bars indicate the standard error of the mean. Letters indicate significant difference within the same soil variant. (Independent samples t-test, $p >$ 0.05). In data points marked with * there was a significant difference between the two spiking treatments. n = 3

Since amorphous Fe and Al (oxy)hydroxides have a high specific surface area as well as a high positive charge density (Scheffer et al., 2010 ,p. 144) they are expected to have a high capacity for binding anions. It is therefore no surprise that we found most of our W bound in the faction which is thought to extract W bound to these (oxy)hydroxides. Gustafsson (2003) measured the adsorption of WO_4^{2-} and MoO_4^{2-} to ferrihydrite over a pH range from 3 to 10. He found W to be strongly adsorbed to ferrihydrite, especially at low pH. Since in our sequential extraction the biggest part of the added W was extracted during the step targeting Fe and Al (oxy)hydroxides, this seems to be in line with our own results.

Comparing the results of our sequential extraction to the partitioning of other known anions we can also observe similarities:

In the study of Wenzel et al. (2001), from which we adapted our sequential extraction procedure, arsenic was found to be distributed among the five extraction steps as shown in Table 4.5.

	As - Wenzel et al. (2001)		W – our experiment	
	median [%]	range [%]	median [%]	range [%]
Non-specifically adsorbed	0.24	0.02 – 3.8	10.2	0.1 – 29.6
Specifically sorbed	9.5	2.6 – 25	5.5	1.8 – 13.4
Amorphous and poorly crystalline hydrous oxides of Fe and Al	42.3	12 – 73	62.3	41.6 – 84.8
Well-crystallized hydrous oxides of Fe and Al	29.2	13 - 39	10.4	4.8 – 15.7
Residual phase	17.5	1.1 - 38	10.9	2.6 – 25.9

Table 4.5: Medians and ranges of As and W distribution during the steps of the SEP in the experiments done by Wenzel et al. (2001) and us.

These distributions are quite similar in their overall pattern. W in our experiment has been extracted in larger portions from the first and third step, while arsenic

was extracted in bigger portions form the last two extraction steps. For both arsenic and W the largest portion of the anion was bound to the Fe- and Al-oxide-fraction. The range of W extracted from the first step was much larger in our experiment, which is the result of the large differences in W recovery between limed and unlimed soils during this step. This however does not necessarily indicate a higher solubility of W compared to arsenic. The soils used in the experiment done by Wenzel et al. (2001) were contaminated for a longer period of time, so the lower recovery might have been an aging effect. This would also be in accordance with other works like for example an experiment done by Broggi et al. (2010) in which the effect of incubation time on phosphorus extraction was determined. They found a decreased recovery of phosphorus after longer incubation periods. The lower recovery of W from some of the soils treated with metal powder compared to those treated with Na_2WO_4 might also be a result of the different incubation times of our soils The detailed effects of the incubation time on the adsorption of W could probably be determined best through a follow-up experiment using the same soils after a longer period of incubation.

Phosphate, another anion, is also mostly bound to Fe and Al (oxy)hydroxides and its sorption has also been shown to be dependent on pH (Scheffer et al., 2010, p. 144; Hinsinger (2001) in a similar way to W in our experiment.

Goldberg et al. (1996) found the dominant molybdenum adsorbing surfaces in soil to be Al and Fe (oxy)hydroxides together with clay minerals and organic matter. Geng et al. (2013) amended soils with Fe (oxy)hydroxides in their experiment and achieved a higher adsorption of Mo through this treatment.

Comparing our results for W with these examples from literature for other, similar anions, the pattern of behavior seems similar. W in our experiment is mainly bound to the Al and Fe (oxy)hydroxides, which is the same for a number

of other anions in the soil. The difference in adsorption between limed and unlimed soils also matches results from other experiments. Keeping this in mind, it seems our hypothesis that W behaves similar to other (oxy)anions in the soil was confirmed.

Higher solubilization of W in the limed soils during the $(NH_4)_2SO_4$ step supports our hypothesis of W being more strongly bound in acidic soils due to the more positive average surface charge. This also fits with the results of the adsorption test, where W was more strongly adsorbed at lower levels of pH (Figure 4.5). The W extracted during this step is expected to be the most readily available portion for plants, although this would have to be confirmed in separate experiments.

As already discussed in section 4.3 molybdate (Goldberg and Forster (1998) (Goldberg et al., 1996)), arsenate and phosphate (Antelo et al. (2005), Gao and Mucci (2001)) also show similar a similar behavior of being adsorbed most strongly at low pH.

5. Conclusion

The first and second objective within the scope of this work was to test and optimize methods for measurement of W in extracts and acid digests targeting total W in soils. The recovery of W in soil water extracts using ICP-MS and a matrix of 2 % HNO_3 and 0.01 % HF was in general between 90 and 100 %. For the acid digestion we modified the ÖNORM method for soil digests following the method developed by Bednar et al. (2010) by adding 0.5 ml H_3PO_4 to the auqa regia digestion solution. The results significantly improved W dissolution from the soil samples, with recovery increasing from 20 to 50 % with the ÖNORM method to nearly 100 % using the modified version. In conclusion both the

digestion method and the acidification treatment worked well and could be used during the rest of the experiments as well as in future experiments done with W.

In the second part of this work we investigated the adsorption of W to soils of different texture and pH. The results from this experiment matched data from literature as well as the behavior of similar anions such as molybdate, arsenate and phosphate. W was more strongly bound to the clay soil and to soils with low levels of pH, which was most likely a result of the higher number of positively charged adsorption sites in soils with low pH and the higher specific surface area of clay.

The final step of our experiment was the adaption of a sequential extraction procedure for arsenic developed by Wenzel et al. (2001) for the use with W. We considered and tested two additional steps targeting W bound to organic matter and carbonate but did not include them in the final SEP as we found only small amounts of W extracted during these steps. In this regard W seems to behave similar to As but different from phosphate, which is also bound to carbonate and OM. In the final sequential extraction most of the W was extracted from the amorphous and poorly crystalline Fe- and Al-oxide phase, which matches literature data as well as the information known from other similar anions. More W was extracted from the non-specifically adsorbed faction of alkaline soils, matching the results from the adsorption test. In conclusion we found the sequential extraction procedure to work well with W.

Compared to molybdate and arsenate there are many similarities concerning for example the influence of pH, texture and the phases to which the ions are bound to in soil. There are also similarities to phosphate (for example influence of pH and adsorption to Fe and Al oxides) but also some differences regarding the adsorption to carbonates and organic matter. Conclusively the sequential extraction procedure, which could be successfully adapted to the use with W, as

well as the methods for W measurement in soil water extracts and for acid digestion of samples containing W should prove useful in further experiments done with soil samples containing W.

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Appendix

Table A1: Statistical results from the ANOVA comparing soils used in the adsorption test with different concentrations of tungsten added. SPSS output from test results

sandy soil		0% CaCO$_3$	0.1% CaCO$_3$	0.5% CaCO$_3$	2.5% CaCO$_3$	5% CaCO$_3$
	ANOVA p	0.995	0.244	0.479	0.080	0.288
W	1000 µg L^{-1}	a	a	a	a	a
	2500 µg L^{-1}	a	a	a	a	a
	5000 µg L^{-1}	a	a	a	a	a
	7500 µg L^{-1}	a	a	a	a	a

clay soil		0% CaCO$_3$	0.1% CaCO$_3$	0.5% CaCO$_3$	2.5% CaCO$_3$	5% CaCO$_3$
	ANOVA p	**0.000**	**0.028**	0.095	**0.000**	**0.026**
W	1000 µg L^{-1}	a	a	a	a	a
	2500 µg L^{-1}	b	ab	a	b	a
	5000 µg L^{-1}	b	ab	a	c	ab
	7500 µg L^{-1}	c	b	a	d	b

Table A2: Statistical results from the ANOVA comparing soils used in the adsorption test with different concentrations of CaCO₃ added. SPSS output from test results

sandy soil		1000 µg L^{-1}	2500 µg L^{-1}	5000 µg L^{-1}	7500 µg L^{-1}
	ANOVA p	**0.000**	**0.000**	**0.000**	**0.000**
	0% CaCO$_3$	a	a	a	a
	0.1% CaCO$_3$	a	a	a	a
	0.5% CaCO$_3$	a	b	b	b
	2.5% CaCO$_3$	b	c	c	c
	5% CaCO$_3$	b	d	d	d

clay soil		1000 µg L^{-1}	2500 µg L^{-1}	5000 µg L^{-1}	7500 µg L^{-1}
	ANOVA p	**0.000**	**0.000**	**0.000**	**0.000**
	0% CaCO$_3$	a	a	a	a
	0.1% CaCO$_3$	a	a	a	a
	0.5% CaCO$_3$	a	a	b	b
	2.5% CaCO$_3$	b	b	c	c
	5% CaCO$_3$	c	c	d	d

Table A3: Statistical results from the t-test comparing soils used in the adsorption test. SPSS output from test results

		sig. 0% CaCO$_3$	sig. 0.1% CaCO$_3$	sig. 0.5% CaCO$_3$	sig. 2.5% CaCO$_3$	sig. 5% CaCO$_3$
clay soil – sandy soil						
W	1000 µg L^{-1}	0.114	0.126	0.137	**0.000**	**0.001**
	2500 µg L^{-1}	**0.003**	0.321	**0.012**	**0.001**	**0.013**
	5000 µg L^{-1}	**0.007**	0.181	**0.002**	**0.001**	**0.001**
	7500 µg L^{-1}	**0.010**	**0.038**	**0.011**	**0.003**	**0.005**

Table A4: Statistical results from the t-test comparing soils used in the sequential extraction. Comparison of different W spikes used. SPSS output from test results

Na_2WO_4 - metallic W	sandy soil				clay soil			
	W 500 mg kg^{-1}		W 5000 mg kg^{-1}		W 500 mg kg^{-1}		W 5000 mg kg^{-1}	
	unlimed	limed	unlimed	limed	unlimed	limed	unlimed	limed
	sig.	sig.	sig.	sig.	sig.	sig.	sig.	sig.
step 1	0.148	**0.026**	0.139	0.099	**0.004**	0.088	**0.000**	0.076
step 2	**0.010**	**0.009**	0.324	0.068	0.104	0.953	**0.033**	0.754
step 3	0.596	**0.033**	0.812	**0.004**	0.143	**0.004**	0.221	0.317
step 4	0.145	0.106	0.064	**0.044**	0.127	0.258	0.465	0.100
step 5	**0.005**	**0.025**	**0.015**	0.123	**0.005**	**0.032**	0.100	**0.025**

Table A5: Statistical results from the t-test comparing soils used in the sequential extraction. Comparison of different soils. SPSS output from test results

sandy soil – clay soil	Na_2WO_4						metallic W			
	W 500 mg kg^{-1}		W 5000 mg kg^{-1}		W 50 mg kg^{-1}		W 500 mg kg^{-1}		W 5000 mg kg^{-1}	
	unlimed	limed	unlimed	limed	unlimed	limed	unlimed	limed	unlimed	limed
	sig.	sig.	sig.	sig.	sig.	sig.	sig.	sig.	sig.	sig.
step 1	**0.004**	**0.008**	0.771	0.696	**0.000**	**0.000**	**0.000**	0.715	**0.006**	**0.013**
step 2	**0.001**	0.263	0.293	0.559	**0.005**	**0.005**	0.000	**0.011**	**0.014**	**0.014**
step 3	0.132	**0.037**	0.070	0.813	0.247	0.084	0.666	**0.003**	**0.001**	**0.008**
step 4	**0.011**	0.111	0.176	0.056	**0.002**	0.996	**0.003**	**0.010**	0.153	0.096
step 5	0.362	0.099	0.218	**0.013**	**0.000**	0.337	0.084	0.223	0.192	0.322