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Assessing tungsten transport in the vadose zone: From dissolution studies to soil columns

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ABSTRACT

This study investigates the dissolution, sorption, leachability, and plant uptake of tungsten and alloying metals from canister round munitions in the presence of model, well characterized soils. The source of tungsten was canister round munitions, composed mainly of tungsten (95%) with iron and nickel making up the remaining fraction. Three soils were chosen for the lysimeter studies while four model soils were selected for the adsorption studies. Lysimeter soils were representatives of the typical range of soils across the continental USA; muck-peat, clay-loamy and sandy-quartzose soil. Adsorption equilibrium data on the four model soils were modeled with Langmuir and linear isotherms and the model parameters were obtained. The adsorption affinity of soils for tungsten follows the order: Pahokee peat > kaolin-ite > montmorillonite > illite. A canister round munition dissolution study was also performed. After 24 d, the measured dissolved concentrations were: 61.97, 3.56, 15.83 mg L⁻¹ for tungsten, iron and nickel, respectively. Lysimeter transport studies show muck peat and sandy quartzose soils having higher tungsten concentration, up to 150 mg kg⁻¹ in the upper layers of the lysimeters and a sharp decline with depth suggesting strong retardation processes along the soil profile. The concentrations of tungsten, iron and nickel in soil lysimeter effluents were very low in terms of posing any environmental concern; although no regulatory limits have been established for tungsten in natural waters. The substantial uptake of tungsten and nickel by ryegrass after 120 d of exposure to soils containing canister round munition suggests the possibility of tungsten and nickel entering the food chain.

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1. Introduction

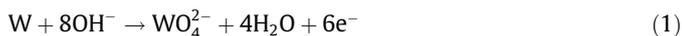
Tungsten is a transition metal with several unique physical and chemical properties (i.e. high melting and boiling points and a density of 19.1 g cm⁻³ (Lassner and Schubert, 1999)). Despite its widespread use, information on the fate and transport of tungsten is limited. The prediction of tungsten behavior in the geoenvironment is a significant challenge due to its unique chemistry, as compared to most metals of environmental concern. It has been established that tungsten and accompanying metals are released from tungsten-containing military munitions under environmental conditions (Seiler et al., 2005; Koutsospyros et al., 2006). Tungsten small-arms munitions have been used at a limited number of Army installations. A detailed study was conducted by Clausen et al. (2007) on the environmental fate and transport of tungsten from tungsten-nylon 5.56 mm munitions on small-arms firing ranges at Camp Edwards on the Massachusetts Military Reservation. Surface and subsurface soils contained tungsten concentrations

of up to 1500 and 3500 mg kg⁻¹, respectively, and pore-water and groundwater concentrations up to 287 mg L⁻¹ and 560 µg L⁻¹, respectively (Clausen et al., 2007; Clausen and Korte, 2009). A comprehensive understanding of tungsten geochemistry is needed since it determines its interactions with the soil matrix, and therefore mobility, bioavailability, and toxicity (Bednar et al., 2008). Particle size and environmental conditions play an important role on leaching kinetics of heavy metals from military hardware, while the mobility of heavy metals depends on the interaction between dissolved heavy metal (in the percolating water traveling through the vadose zone) and soil surface (i.e. sorption-desorption processes), preferential flow paths created by the presence of plant roots and root-heavy metal interactions. This study investigates the solubilization and sorption of tungsten and alloying metals from canister round munitions in the presence of model soils. The canister round munitions were composed of 95% tungsten, nickel and iron making up the remaining fraction and had an average weight of 8.3 g. They are part of the XM1028 120 mm canister tank round and were provided by the US Army Research, Development and Engineering Center, Picatinny Arsenal, NJ. A detailed description of the canister round is included elsewhere (Felt

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et al., 2011). Once in solution, the concentrations of tungsten can be affected by adsorption processes. The sorption isotherm is a common approach to describe a great diversity of retention/release phenomena. This is very useful and often unavoidable to understand and predict the mobility of sorbing substances in the environment (O'Connor et al., 2009). Adsorption-related processes play a significant role in controlling subsurface aqueous tungsten concentration and mobility (Dermatas et al., 2004). Dermatas et al. (2004) performed experiments on the solubility of tungsten and its effects on soil respiration. They reported dissolved concentration of tungsten as high as 490 mg L⁻¹ depending on associated metal combinations as well as depletions in pH and dissolved oxygen. These results agreed with the results of Clausen and Korte (2009) who studied the leaching of tungsten from tungsten-nylon rounds at the Massachusetts Military Reservation. It is worthy to point out that dissolution traditionally refers to a physical reversible process involving no change in oxidation states; however, the release of metals from their elemental states into solutions involves a chemical process which is irreversible along the same path (Ogundipe et al., 2009). Dermatas et al. (2004) reported that, the dissolution process of tungsten in water can be described by the anodic oxidation of metallic tungsten and the cathodic reduction of dissolved molecular oxygen:



It is believed that a combination of galvanic effect and availability of hydroxyl ions is responsible for the dissolution of tungsten when released into the environment in a composite metallic formulation (Ogundipe et al., 2009).

The objective of the current study was to investigate fate and transport of tungsten from canister round munitions in the vadose zone. To achieve this objective, a wide variety of laboratory experimental approaches were used: (i) investigation of adsorption behavior of tungsten onto four different types of soils (montmorillonite, kaolinite, Pahokee peat and illite) from canister round munitions, (ii) dissolution study of tungsten from canister round munitions over 24 d, and (iii) study of fate and transport of tungsten by using soil lysimeters. This study addresses tungsten partition amongst three environmental compartments: (1) aqueous phase, (2) soil and (3) plant tissue. No attempt was made to replicate the potential fragmentation of the canister rounds upon being shot and released into the environment. Although the fragmentation will certainly have a strong impact on the rate of release of munitions constituents, the results of this study are still of importance for assessing the fate and transport of tungsten once it is released to the geoenvironment. Information on tungsten transport in the geoenvironment can also serve as the basis for establishing environmental standards for tungsten, one of the least regulated heavy metals, and it is in line with the concerns raised by the EPA regarding the outstanding issues on the characterization of metals and metal compounds (Koutsospyros et al., 2006).

2. Materials and methods

2.1. Dissolution study

A detailed description of the canister round is included elsewhere (Felt et al., 2011). This study was performed to assess the leaching kinetics of metals from canister round munitions in simulated rainwater with a pH of 4.58 (average pH of the rainwater used for the three soils tested). Preliminary kinetic experiments suggest that 20 d is enough time to achieve a dissolution plateau with the canister round munitions tested. One canister round mu-

munition was placed in a plastic bottle with 60 mL of simulated rainwater. The setup was left static for 24 d at 23.5 ± 1 °C under normal laboratory conditions. Samples were taken on a daily basis initially and using larger intervals after the 10th day. The choice of static conditions was an attempt to mimic environmental conditions where canister rounds leach out metals components without mixing. The experiment was run in triplicates. Approximately 5 mL of liquid aliquots were taken out daily from each bottle for analyses of the different element concentrations. Aqueous phase concentrations of tungsten were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Varian Vista MPX, Varian, and Palo Alto, CA, USA) following modifications of EPA Method 6010B (USEPA, 1996a). The dissolved concentrations of the companion elements (i.e., nickel, iron), were also determined by ICP-OES. To minimize spectral interferences the following wavelengths (Ung Bae et al., 1997) were used in the determinations: 207.911 nm (W), 231.604 nm (Ni), and 238.204 nm (Fe). The instrument was calibrated using a blank and series of six calibrations standards (1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 mg L⁻¹) with typical linear correlation coefficients (*R*²) greater than 0.9999. Blank samples and standards were run periodically as part of QC/QA protocols.

2.2. Adsorption isotherms

This study was conducted to investigate the adsorption of tungsten onto four different types of model soils (montmorillonite, kaolinite, Pahokee peat and illite) from tungsten canister round munitions. The amounts of model soils used in the experiment were chosen to have a similar amount of tungsten in the liquid and solid phases once equilibrium has been reached and they are as follows: 50 mg of Pahokee peat (International Humic Substances Society), 500 mg of IMt-1 illite, 350 mg of Saz-1 Ca-montmorillonite, and 350 mg of kaolinite KGa-1b (The Clay Minerals Society). Details for the soils used can be found in Dermatas et al. (2004) and at <http://www.clays.org/SOURCE%20CLAYS/SCdata.html>. Stock solution was prepared by placing one tungsten canister round munition in 500 mL glass bottle, filled with DI water. The solution was equilibrated for 15 d in planetary shaker operating at 100 rpm (Environmental Shaker model G-24, New Brunswick Scientific, Edison, NJ, USA). This stock solution was then analyzed for the metals of interest by ICP-OES as previously described. The initial concentration range of the metals for the canister round munition in the stock solution were 18.99 mg L⁻¹ for tungsten, 1.88 mg L⁻¹ for iron and 5.60 mg L⁻¹ for nickel respectively. Batch adsorption experiments were conducted by placing the solutions in 50 mL polypropylene centrifuge tubes in contact with four different types of model soils and rotating them “end over end” at 50 rpm in a controlled temperature environment (23.5 ± 1 °C) for 7 d. Equilibration time was chosen based on kinetic experiments (data not shown). Vials containing stock solutions free of soils were also prepared as control to assess metal losses. After 7 d, the vials were centrifuged at 25 °C for 20 min at a speed of 2200 rpm using an IEC HN-SII centrifuge (IEC, Northern Highs, MA, USA); the aqueous phase was carefully removed and filtered through 0.45 μm pore size filters (25 mm GD/X filter, Fischer Scientific). Filtered solutions were analyzed for total tungsten using ICP-OES using the same method cited in the previous section. Analysis of the control vials showed not lost of metals to the tubes materials.

2.3. Column study

2.3.1. Soil lysimeter

The transport of tungsten from canister round munition in the vadose zone was studied using laboratory scale soil lysimeters, ryegrass and simulated rainfall events with artificial rainwater to

mimic half year rainfall volume over a four month period. The composition of synthetic rainwater (US Air Force Research Laboratory, 1998) can be found in the Supplementary information (Table A.2). Lysimeters have been used to monitor fate and transport of heavy metals to address the relations between soil, water and plants (Larson et al., 2005). Eight lysimeter columns were constructed using 20.3 cm internal diameter white schedule 40 PVC pipe. The columns were 50 cm in length and sealed at the bottom with a schedule 40 PVC white end cap. A small drainage hole was made at the bottom of each column for sample collection. A small piece of 250 μm polypropylene mesh was placed inside each column over the drainage hole. The columns were then filled with clean gravel (Quikrete All Purpose Gravel #1151) at the bottom, followed by 5 cm layer of clean silica sand (Quikrete Premium Play Sand #1113) and approximately 25 cm layer of sample soils (muck peat, clay loamy and sandy quartzose). The set up of the columns is shown in the schematic (Fig. 1). Four ceramic mini-lysimeters (Rhizosphere Research Products, NL-6700 AN, Wageningen), 5 cm in length and 2 mm in diameter, were placed along the soil profile (2, 9, 16 and 23 cm below the surface). They were used to collect aqueous samples during the transient stage of the study.

Mini-lysimeter samples were taken using a vacuum provided by a 20 mL plastic syringe. Only PTFE tubing was used inside the column. Once the soils were in place, the lysimeter columns were each watered with 200 mL of tap water every day for a week to allow for settling and equilibration. Ryegrass seeds (50–100) were planted into the soils in each column and watered with approximately 200 mL tap water until the germination for 2 weeks. After ryegrass plants were fully developed, three munition pieces were placed in triangular pattern on top of the soil layer in each column. Each canister round was 1 cm in diameter. Watering of the lysimeters was performed as described in the Supplementary information section. At the end of the experiment, the soil columns were disassembled and core samples were taken using a hand held auger. Soil profiles were extracted at specific points to derive a better transport profile of the munitions through the column. The auger penetrated halfway through the soil columns hence soil samples were extracted from two halves of each column; the top half and the bottom half directly above the sand layer. Soil samples and profiles were collected from the following areas; the area attached to the canister round munitions, the center of the columns, and the area

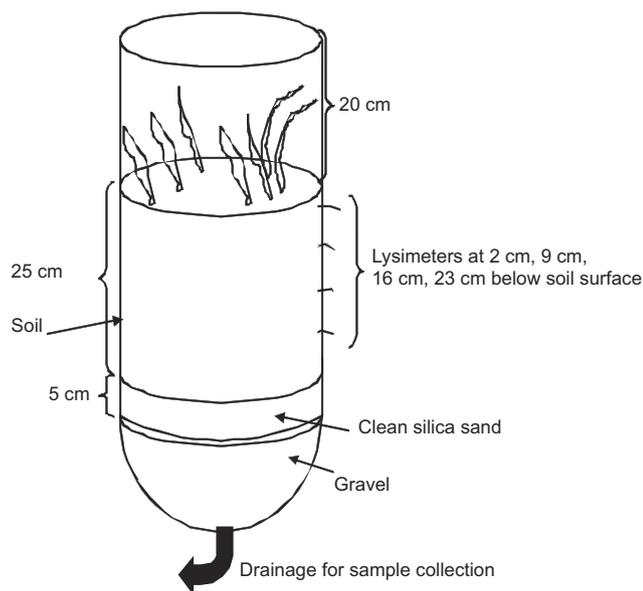


Fig. 1. Lysimeter schematic.

directly beneath the munition samples. Soil core samples were visually examined and matched with the soil depths. Soil samples were digested following a modification of USEPA method 3050B (USEPA, 1996b). After the test was finished, all collected soil samples were dried for 12 h in an oven at 80 °C. Dried samples were weighed and placed in 50 mL digestion vials (SCP Science Inc.) and 1 mL of concentrated phosphoric acid was added at the beginning of the digestion procedure. Between 3 mL H_2O_2 up to 6 mL H_2O_2 were added during the digestion as necessary. The addition of phosphoric acid helps to stabilize tungsten species in the acid digestion solution as stated in method ID-213 of the US Occupational Safety and Health Administration (OSHA, 1994). The inclusion of phosphoric acid in the digestion process was also addressed by Griggs et al. (2009). All acid digestions were conducted in duplicates (except for the soil attached to the munitions pieces where sample amount did not allow for replication) on a DigiPrep hot block digestion system (SCP Science, Champlain, NY); using fluoropolymer digestion vessels to prevent tungsten polymerization onto borosilicate glass vessel walls. The digestion vessels were left open on the hot block digestion system for 2 h at 90–95 °C. The digestate was then cooled to room temperature and filtered through a filter paper (Whatman 42 paper, Fischer Scientific) and diluted to 50 mL with DI water. Montana soil NIST-2710 reference material as well as matrix-spikes was used throughout the acid digestion analyses to check for the recovery of metals of concern.

2.3.2. Reagents

All chemicals used were of reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of 18.3 $\text{M}\Omega\text{ cm}$. The acids used for the soil and plant digestion, nitric (HNO_3), hydrochloric (HCl), and phosphoric (H_3PO_4), were all trace metals grades and were purchased from Fischer Scientific Inc. Single element standards for tungsten and other metals were purchased from Sigma Aldrich (St. Louis, MO). All other chemicals were obtained from Fischer Scientific Inc.

2.3.3. Plant uptake studies

Ryegrass (Ward's Biology catalog, No. 86V8130, Rochester, NY, USA) was planted into the soil columns and watered daily with 200 mL of tap water for approximately 2 weeks for germination. However the first batch of planted rye grass did not germinate well in some of the columns due to the lumpy texture of some of the soil samples which affected roots growth. The lumpy soils were slightly pulverized by hand and another batch of rye grass was planted and watered for 2 weeks. A third rye grass plant sowing was performed after 5 weeks of column set up. This time, 40 seeds were added to the lysimeters to increase plant density due to the low plant density achieved with the first two sowings. Extra sowings (using between 40 and 60 seeds) were performed in the following weeks to increase rye grass density. Each column was amended with three canister round munitions after the ryegrass plants were fully developed. The canister round munitions were placed on top of the soil layer in triangular pattern at the center of the column. Ryegrass plants (shoots) were harvested after 52 d to monitor the heavy metals uptake. After running the test for 4 months, all plants (shoots and roots) were removed from the columns; dried, weighted and acid digested as described in the Section 2.3.1. Finally, the samples were analyzed for the metals of interest by ICP-OES.

2.3.4. Leaching studies

Leaching tests play an important role in assessing the potential environmental impacts of the munition components when utilized or deposited in soil. Leaching results from the lysimeter experiments may be taken to represent results obtained under field-resembling conditions, and they may thus be very useful for

predicting the fate and mobility of heavy metals. The synthetic rainwater with the adjusted pH for each region was passed through the columns twice a day during week days (as described in the [Supplementary information](#) section), leaving weekends to normal dry out. The leaching experiment was run for 4 months. Effluent from the columns was collected on a daily basis, and the leached volume was recorded to perform a water mass balance at the end of the experiment. The pH of the liquid samples was measured immediately by using an Accumet AR25 digital pH-meter with Accumet 13-620-285 pH electrode from Fischer Scientific, Pittsburg, PA, USA). Then sample aliquots were analyzed to assess the release of tungsten by ICP-OES following approved analytical method.

3. Results and discussion

3.1. Dissolution study

Three replicates were run for this experiment. Results from the ICP analysis of liquid samples from the dissolution study are presented in Fig. 2.

The results are the mean concentrations of three liquid samples, taken out daily from canister round munition solutions. Two of the munitions show a very similar leaching pattern while a third one displayed a lower rate of leaching of the metals. The reason for this difference is not clear; perhaps canister round munitions used in the test presented different surface roughness making some of them more prone to leach out metals than the others. The initial mean concentrations of tungsten, iron and nickel were 6.72, 0.55 and 0.71 mg L⁻¹ respectively. At the end of day 24, the maximum concentrations for the metals of interest were: 61.97, 3.56, 15.83 mg L⁻¹ for tungsten, iron and nickel respectively. These results are in agreement with previous studies (O'Connor et al., 2009; Clausen et al., 2010) in which the dissolved concentration of iron is smaller compared to tungsten and nickel. Fig. 2 shows that considerable amounts of tungsten and nickel may be leaching out from the canister round munitions due to interactions with rainwater, although as it will be shown in the following section, this will not specifically translate into a widespread transport through the vadose zone. The relatively large dissolved tungsten concentrations obtained, the fact that at pH < 6.2 the monomeric tungstate ion starts to polymerize to form isopolytungstates (Lassner and Schubert, 1999) and the pH of the simulated rainwater (pH ~ 4.58) suggest the possibility of formation of condensed polytungstates during the dissolution test.

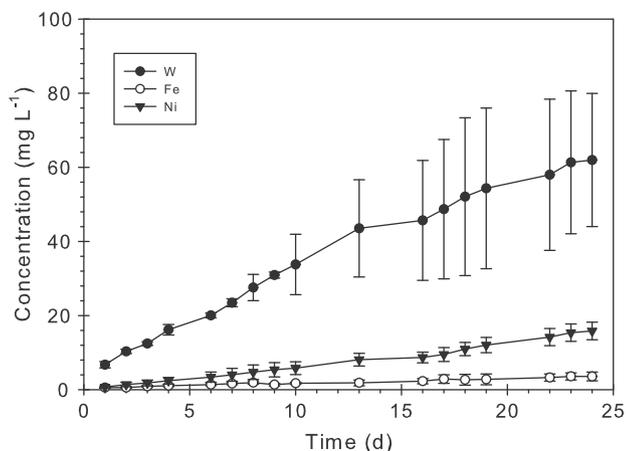
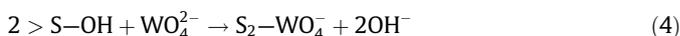


Fig. 2. Dissolved concentrations (mg L⁻¹) of W, Fe and Ni in canister round munition solution.

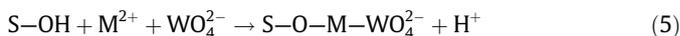
3.2. Adsorption isotherms

After examination of the isotherms curves obtained, the data was modeled using Langmuir and linear adsorption model equations (Pokhrel and Viraraghavan, 2008), via linear regression analysis. Langmuir model was the best fit for kaolinite, while linear model fitted the data the best for montmorillonite, illite and Pahokee peat in the range of concentrations tested. Regression analysis resulted in K_D of 25.01 (0.9935), 344.6 (0.9984) and 2.96 (0.9310) mL kg⁻¹ for montmorillonite, Pahokee peat and illite, respectively. The numbers in the brackets represent the regression coefficient (R^2). The isotherm parameters for kaolinite were as follows: $S_m = 1522$ mg kg⁻¹ and $B_L = 0.97$ L mg⁻¹. The regression coefficient was 0.9416. The isotherm simulations are shown as lines in Fig. 3 together with the experimental data.

Sorption-desorption reactions are important in controlling tungsten mobility in soil systems and the uptake of tungsten by two of the four soils appeared to be significant. As expected, the extent and nature of the adsorptive behavior is strongly influenced by the soil type. The extent of the tungsten uptake is in the following order: Pahokee peat > kaolinite > montmorillonite > illite. Pahokee peat, with 93% organic matter content (TOC 43.9%), adsorbs large amounts of tungsten from solution. The TOC of the other clays used in the experiment is below 0.1%. This high uptake may be related to the formation of complexes of tungsten with humic substances. Dermatas et al. (2004) reported that for the clay soils (i.e., montmorillonite and illite), the release of hydroxyl ions groups to solution suggests the adsorption of tungstate anions to surface hydroxyl groups located at the edge sites of the clay structure. The hysteric sorption-desorption is the characteristic of the chemisorption of anions to variable-charge soils according to the following reactions (McBride, 1994):



where WO_4^{2-} is the tungstate anion and $>\text{S-OH}$ is a reactive metal hydroxyl group. The fact that aqueous solutions originally contain significant amount of cations that were readily sorbed by the clays (i.e., Fe, Ni) suggests that the formation of type A ternary complexes cannot be ruled out. Type A ternary complexes can be described as follows (McBride, 1994):



A maximum tungsten adsorption capacity of 1522 mg kg⁻¹ for kaolinite was estimated from the modeling while a maximum was not

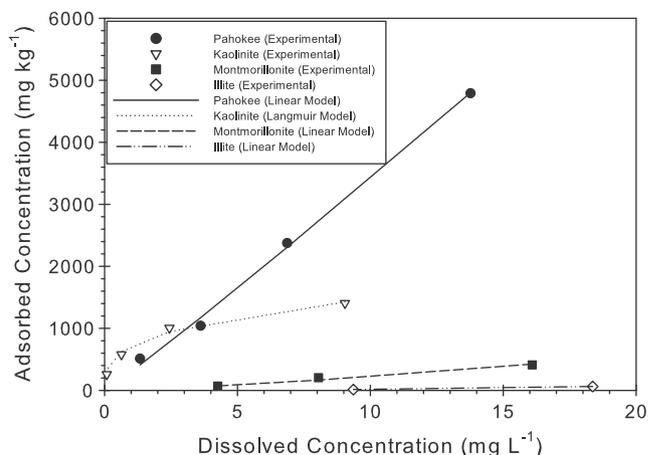


Fig. 3. Sorption isotherms of W onto selected well-characterized soils from canister round munition.

attained for the other three soils due to their linear isotherms in the tungsten concentration range tested. The linear distribution coefficient for Pahokee peat, montmorillonite and illite found in this study are in agreement with the previous research (Dermatas et al., 2004). Dermatas et al. (2004) using a Freundlich model reported capacity values of 856, 27.4 and 22.9 (mg kg^{-1}) (mg L^{-1})ⁿ for the specific tungsten alloy for Pahokee peat, montmorillonite and illite, respectively. The larger difference observed for illite is likely related to the smaller particle size of the illite used in the Dermatas et al. (2004) study. The high affinity of the clays and organic matter for dissolved tungsten species may be responsible for the slow movement in the soil systems. The formation of polytungstates in environmental samples has been shown (Bednar et al., 2008; Clausen et al., 2011) and its influence in transport has been discussed. However, the linear and/or Langmuir shapes of the isotherms in this study, do not suggest that polymerization is occurring.

3.3. Column study

3.3.1. Liquid samples

The effluent from the columns was collected on a daily basis and the volumes of the effluent were recorded. The total volume of rainwater influent during the experiment was 11.50 L for muck peat, 10.05 L for clayey loamy and 10.76 L for sandy quartzose columns. The amounts of leachate collected from the lysimeters were 9.16 L, 7.94 L and 8.80 L from muck peat, clay loamy and sandy quartzose columns respectively. The total amount of the effluent collected by the mini lysimeters was 90 mL from muck peat, 50 mL from clay loamy and 60 mL from sandy quartzose. These values suggest a water unbalance due to accumulation in the soil and/or evapotranspiration of 20.4%, 21%, and 18.2% for muck peat, clay loamy and sandy quartzose respectively over four months. These values are reasonable considering the size of surface area of the top of the lysimeters and that the experiments were run at a fairly constant room temperature (23.5 ± 1 °C).

The daily pH of the leachate was recorded for each sample. The results are presented in Fig. 4.

As it can be seen, for muck peat and clay loamy soils and for a given sampling time, there was not a significant difference between the pH of the effluent of the non-amended control column and the pH of the canister-amended columns. The sandy quartzose effluent showed a larger difference between the control and amended columns compared with the other two soils. The differences were more significant during the first 20 and last 24 d of

the experiment. The control column showed a higher pH of the effluent leachate for sandy quartzose. The pH of the simulated rainwater used was more acidic than the pH of the three soils tested (Tables A.1 and A.3). For amended columns the pH values of the leachates from the first day of the experiment were 6.37, 7.40 and 4.18 for muck peat, clay loamy and sandy quartzose columns, while the final pH values were 7.78 for muck peat, 7.56 for clay loamy and 5.18 for sandy quartzose columns respectively. This increase in pH value is likely due to the soil buffering capacity (Fig. A.1). Leachate from all soils showed an increased pH with respect to the simulated rainwater and the corresponding soil pH). Sandy quartzose soil columns with the smallest buffering capacity show a smaller increase in pH as compared with the other two soils. The buffering capacity of the soils helps neutralizing the acid pH of the rainwater. The pH of the soils were 6.75 for muck peat, 5.12 for clay loamy and 5.48 for sandy quartzose respectively. The final pH of the leachates showed an increase for all three soils tested. This may be due to the interchange of tungstate for hydroxyl ions in soil edges (Dermatas et al., 2004).

Dissolved tungsten concentrations of the leachates are presented in Fig. 5. Tungsten concentrations in liquid soil aliquots appears to be low in terms of posing any environmental concern; although no regulatory limits have been established for W in natural waters and soil. The results indicate that, while tungsten concentration is highly variable for clay-loamy and muck peat soils, the leachate from sandy-quartzose columns shows a much smaller tungsten concentration compared with the other two soils. A lower dissolved tungsten concentration in the leachate associated with a soil may indicate that tungsten mobility was reduced in that soil system, but a lower dissolved tungsten concentration does not preclude tungsten transport. For all three types of soils, tungsten concentration in the leachates was always smaller than $50 \mu\text{g L}^{-1}$ (Fig. 5). It is important that, the detection limit for dissolved tungsten concentration by ICP-OES is around $15 \mu\text{g L}^{-1}$ and the quantification limit is around $45 \mu\text{g L}^{-1}$. Thus, the low tungsten concentrations should be taken cautiously although these do not change the fact that very limited leachability was observed. The affinity of soil components (i.e., clay and soil organic matter) for tungsten and pH may be the reasons for variation in concentration. The interaction between the pH of the influent rain water, the pH changes induced by the leaching of metals from the canister rounds and their adsorption by soil, and the buffer capacity of soils determine the final pH of the effluent and of the water percolating through the system which impacts tungsten leachability. Dermatas et al. (2004) mentioned that, dissolution of tungsten is favored at alkaline pH and the effluent from the sandy quartzose soil columns

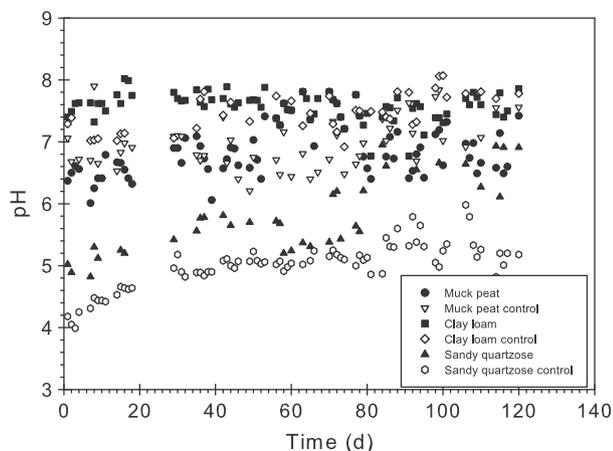


Fig. 4. pH of the leachate collected at the bottom of the lysimeters amended with canister round munitions.

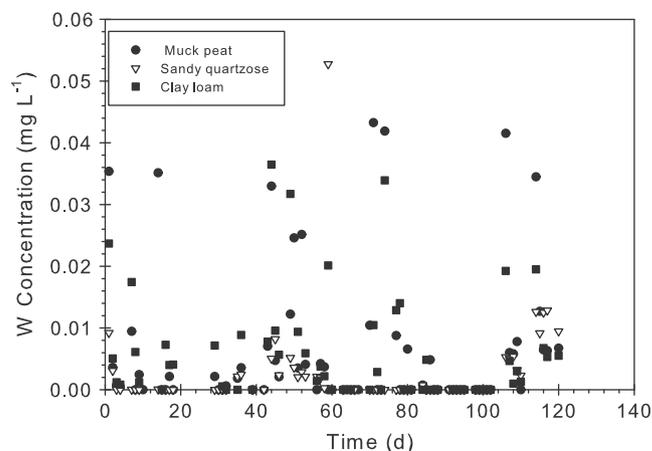


Fig. 5. Dissolved tungsten (W) concentrations of the leachate collected at the bottom of the lysimeters amended with canister round munitions.

was consistently acidic ranging between 4.2 to 6 (Fig. 4). From these experiments, it is clear that acidic conditions generally reduce the mobility of tungsten in soil. This may be due to decreased leachability and enhanced adsorption (Eqs. (3) and (4)), whereas alkaline conditions tend to promote mobility, likely due to protonation and deprotonation, respectively of soil particle surfaces involved in sorption reactions where the mechanism described in Eq. (5) is not controlling the adsorptive behavior. Furthermore, the above discussion is valid for the type of tungsten source used in this study (i.e., canister munitions) as sources allowing larger tungsten leachability may result in higher tungsten concentrations in the leachate.

The leaching behavior of Ni and Fe is presented in Figs. A.2 and A.3 in the Supplementary information section. The concentration of all three metals (tungsten, iron and nickel) appears to be low in terms of posing any environmental concern; although no regulatory limits have been established for tungsten in natural waters (Koutsospyros et al., 2006).

3.3.2. Soil samples

Tungsten concentrations in the three different soil samples were compared to each other to identify any effect caused by the soil type. Duplicate samples were extracted. The adsorbed concentration of tungsten onto three different types of soils along the column profile is summarized in Fig. 6. Moreover, the results of metals (i.e., Fe, Ni, and W) concentrations in the soils that were attached to the canister round munitions pieces are also discussed. For all three soil samples, the concentration profiles of tungsten show substantial difference in values and shape (Fig. 6). Tungsten concentration was measured at different column depths from 1 to 30 cm and for all three soils, maximum concentrations of metals of interest were detected in the soil samples which were taken from 2 cm column depth. The lowest concentration values for the metals of interest were observed for clay loamy columns. This may be attributed to the higher fines (smallest soil particle size) content of the muck peat and clay loamy soil compared to sandy quartzose soil. The highest W concentration for clay loamy soil at 2 cm depth was 10 mg kg⁻¹. This result is in agreement with the results of soil samples from the soils attached to the munitions pieces discussed below. The variation of the metal concentration with depth for this soil was much smaller than for muck peat and sandy quartzose soils. Muck peat and sandy quartzose soils show higher tungsten concentration, up to 150 mg kg⁻¹ in the upper layers of lysimeter and a sharp decline with depth suggesting strong retardation process along the soil profile. Tungsten concentrations at 2 cm column depth were 177 mg kg⁻¹ for sandy quartzose and 137 mg kg⁻¹ for

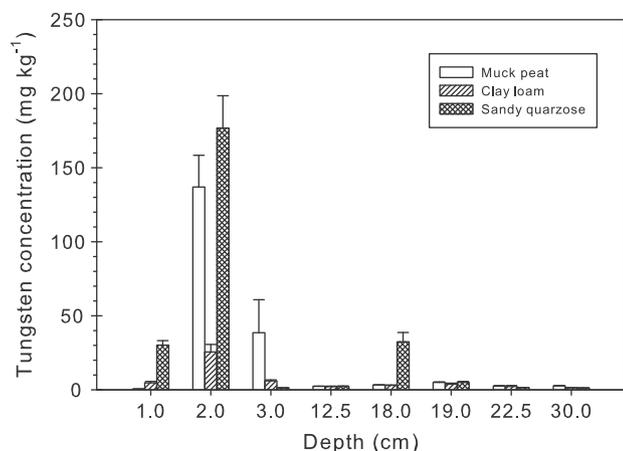


Fig. 6. Average W concentration (mg kg⁻¹) along the clay loamy, muck peat and sandy quartzose columns profile. Average and standard deviation of two replicates.

muck peat soils respectively. There is less environmental concern about the Fe and Ni in the canister round munitions used in this study. Iron is commonly found in most soils and was present in all three test soils. Nickel is not likely to transport through an environmental system because of its low solubility in water.

There were three munitions pieces in each column. The analysis of soils attached to the nine canister round munitions (three per each soil lysimeter) show high tungsten and nickel concentrations up to the thousands mg kg⁻¹ (i.e., highest tungsten concentration 8000 mg kg⁻¹, highest nickel concentration 16300 mg kg⁻¹) and iron concentration up to 50000 mg kg⁻¹. The concentration values are very scattered which is another confirmation of the different metal leaching behavior among different munitions pieces. As expected, the highest tungsten concentration (8000 mg kg⁻¹) was observed in muck peat soil sample. Tungsten concentration in soil samples attached to munition pieces varies between 1050 and 8000 mg kg⁻¹, between 456 and 6547 mg kg⁻¹, and between 28 and 1065 mg kg⁻¹ for muck peat, sandy quartzose and clay loamy soils, respectively. For the muck peat soil, just two results were computed as the soil sample that was attached to munition #3 was lost during the acid digestion. Low and high metal concentrations in a given lysimeter are associated to the same canister munition. These results are in agreement with our results on adsorbed tungsten concentrations along the column profile. Clay loamy soil was the one with the lowest tungsten concentration compared with the other two.

In summary, due to soil buffer capacity and adsorption-desorption processes it appears that three soils tested severely retarded the movement of tungsten. The corrosion-based leaching of metals from tungsten munition pieces in the soil system appears to be slower than in direct aqueous leaching experiments. This is a different behavior than the one found by other authors (Clausen and Korte, 2009; Clausen et al., 2010, 2011) but agrees with the findings of Dermatas et al. (2004) and the US Air Force Research Laboratory (1998).

3.3.3. Plant uptake studies

It was observed that, the uptake of the metals of concern by the ryegrass depends on the type of soil and the metal. Iron is the metal that shows the highest concentration in plant tissues, however, this may not be related with the canister round munitions' corrosion. This result is in agreement with the concentration of iron in the leachates. Iron is a normal constituent of soils and the high uptake may be the result of normal plant physiological behavior. Tungsten uptake is also larger than nickel uptake in 5 of 6 samples analyzed and this behavior is certainly related to the larger amount of tungsten present in the canister round munition. As expected, metal uptake appears to be directly related with the time of exposure as all samples taken after 120 d show higher concentrations of metals in the plant tissue than the samples taken after 52 d (see Table A.6 in the Supplementary information section). Final tungsten concentration in the plant tissue at the end of the experiment is; 355 mg kg⁻¹ for clay loamy, 252 mg kg⁻¹ for muck peat, and 202 mg kg⁻¹ for sandy quartzose columns. The values of tungsten in the ryegrass after 120 d suggest some concerns related to tungsten entering into the food chain at significant concentration levels and needs further study.

4. Conclusions

To date, tungsten has been the subject of less extensive toxicological and/or fate and transport studies than other heavy metals of concern and remains one of the least regulated metals. The information provided in this study fills a substantial gap in information regarding the fate and transport of tungsten in the vadose zone.

Dissolution, sorption, and mobility of tungsten in the vadose zone from canister round munitions are reported. The concentrations of all three metals (tungsten, iron and nickel) in liquid and soil aliquots were too low in terms of posing any environmental concern; although no regulatory limits have been established for tungsten in natural waters and soil. The adsorption of tungsten appears to be the strongest on the soil with the highest organic content (Pahokee peat), possibly indicating interactions with humic substances, an area worthy of additional attention and study. This behavior appears to significantly retard tungsten mobility. The interaction between the pH of the influent rain water, the pH changes induced by the leaching of metals from the canister rounds and their adsorption by soil, and the buffer capacity of soils determine the final pH of the effluent and of the water percolating through the system which impacts tungsten leachability. The corrosion-based leaching of metals from canister round munition in the soil system appears to be slower than in direct aqueous leaching experiments. Increased metal dissolution could potentially increase metal transport and leaching, affecting metal concentrations and in the case of tungsten/nylon rounds reported by Clausen and Korte (2009).

The length of time soils are exposed to the canister round munition (residence time) in the laboratory is relatively short compared with the much longer residence times that exist in the environment. Long term field lysimeter studies are likely to yield more reliable results. Lastly, the uptake of tungsten by ryegrass after 120 d may suggest some concerns related to tungsten entering into the food chain at significant concentration levels and needs further study.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2011.11.036](https://doi.org/10.1016/j.chemosphere.2011.11.036).

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