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Impact of leaching conditions on constituents release from Flue Gas Desulfurization Gypsum (FGDG) and FGDG-soil mixture

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Highlights

- This is the first study to use the new EPA leaching methods 1313-1316.

- The new EPA methods were tested on FGDG and soil-FGDG mixture (SF).

- Leaching based on new EPA methods were compared to traditional methods 1311 and 1312.

- TCLP and SPLP underestimate Se leaching from FGDG and SF compared to the new EPA methods.

- FGDG leached significantly high amount of B compared to that observed from SF.

Abstract

The interest in using Flue Gas Desulfurization Gypsum (FGDG) for land applications has increased recently. This study evaluates the leaching characteristics of trace elements in "modern" FGDG (produced after fly ash removal) and FGDG-mixed soil (SF) under different environmental conditions using recently approved EPA leaching methods (1313-1316). These methods employ various pH and liquid-solid (LS) ratios under batch leaching, column percolation and diffusion controlled release scenarios. Toxicity Characteristic Leaching Protocol (TCLP) and Synthetic Precipitation Leaching Protocol (SPLP) were used for comparison. The data obtained from new EPA methods provide broad insight into constituent release from FGDG and SF when compared to TCLP and SPLP. The release of toxic elements such as Hg, As, Pb, Co, Cd and Cr from SF was negligible. High release of B from FGDG was observed under all tested conditions; however, its release from SF was low. Both FGDG and SF released Se under all pH conditions (2-13) and LS ratios (1-10) in low concentrations (0.02 – 0.2 mg/L). The data from this study could be used to investigate potential use of "modern" FGDG for new beneficial land applications.

1. Introduction

Coal combustion in coal power plants generates about 120-140 million metric tons of coal combustion residues (CCR) annually [1, 2], which include fly ash, bottom ash, flue gas desulfurization (FGD) material and flue bed combustion ash. Most U.S. coal power plants use the FGD process to meet SO_2 emission reduction requirements under the Cross-State Air Pollution Rule (CSAPR) [1, 3]. The wet scrubbing method, which uses limestone slurry to scrub gases, is one of the most commonly used FGD methods in the U.S. SO_2 in flue gas reacts with $CaCO_3$ in the slurry to produce $CaSO_3.2H_2O$, which can be converted to $CaSO_4.2H_2O$ (gypsum) by forced oxidation [4, 5]. This synthetic gypsum is known as flue gas desulfurization gypsum (FGDG). According to the American Coal Association (ACA) annual report, 24,400,000 tons of FGDG was produced in 2013 [6]. The FGDG produced post fly ash removal ("modern" FGDG) was reported to have low pH and low concentrations of toxic elements compared to the FGDG produced without fly ash removal ("Old" FGDG) [7]. However, concentrations of some elements such as Hg, Se and Sr are still higher in "modern" FGDG compared to U.S. natural soil [7, 8].

FGDG has been used for several beneficial purposes due to its abundance, particle size, chemical and physical properties, and the purity of the material [9, 10, 11] either in encapsulated or non-encapsulated forms. According to the ACA annual report, 36% of the total FGDG production in 2013 was used in encapsulated applications such as cement, concrete and wallboard production, while 12.8% was used in non-encapsulated applications such as structural fills/embankments, agricultural practice, soil stabilization, and mining reclamation [6]. The remaining 52% (12,688,000 tons) was disposed as waste in industrial landfills. Element leaching from FGDG is a great concern in both beneficial use and waste disposal scenarios. As large amounts of FGDG are being generated every day, beneficial applications that use FGDG at high rates will be a

proper approach to waste management. The use of non-encapsulated FGDG in land applications needs to be monitored thoroughly as FGDG is directly in contact with soil and ground/surface water sources. Therefore, it is important to study the leaching behavior of elements in FGDG after incorporation in soil, either as a beneficial use or as a waste, under different environmental conditions.

A number of studies have been performed to assess the effectiveness of using FGD products, FGDG (both "Old" and "Modern") as soil amendments [12-18]. Several recent studies have evaluated the efficiency of CCR products (including FGDG) in mine reclamation [19-21], soil stabilization [22, 23] and as a structural fill in embankments/dams [24, 25]. Toxicity characteristic leaching protocol (TCLP) was the most common leaching test used in most studies. Others used column leaching tests [17, 23, 24] or leachates from the field and pots [13, 14, 22] to analyze metal concentrations. A few studies used acid digestion procedures to obtain the elemental composition in soil after the application of FGD products [15, 26]. Most studies reported elevated B leaching from FGDG mixed soils (0.5 - 9 mg/L). In addition, some studies reported higher concentrations of Hg (2.78 – 65.8 µg/kg), As (12.8 mg/kg) and Se (0.47 mg/kg) in soil [14 -16, 23]. However, to date, there have been no reports on element leaching from FGDG or FGDG added soil under multiple pH and liquid-solid ratio (LS) conditions. It is important to study element leaching from soil that is in contact with FGDG under different conditions as the soil pH and LS can vary over a wide range due to climatic changes, addition of chemicals, presence of plants, rainfall and soil moisture content. Even though the "modern" FGDG has low concentrations of toxic elements, the chemical changes likely to occur in soil after FGDG addition may affect the leaching behavior of some elements present in soil. For example, high Ca^{2+} and SO_4^{2-} released from FGDG could change the leaching behavior of Al,

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Mn and P in soil [27-29]. Therefore, it is important to understand the leaching patterns of elements in "modern" FGDG thoroughly under different leaching conditions before and after incorporating with soil. For this purpose, recently approved (2012 - 2013) EPA methods (1313-1316) proposed by Kosson *et al*. [30] is used. These methods allow us to evaluate fundamental leaching properties of materials under a wide variety of conditions, including i) liquid-solid partitioning as a function of pH (EPA-1313), ii) liquid-solid partitioning as a function of LS in a batch extraction (EPA-1316) or column percolation (EPA-1314), and iii) mass transport based release under saturated conditions (EPA-1315). In contrast, the most commonly used leaching method, TCLP (EPA-1311), represents a single scenario that is intended to mimic landfill leaching conditions, and hence does not provide information on element release under environmental scenarios different from the one being simulated [30, 31]. Therefore, TCLP may sometimes cause misinterpretation of element leaching from FGDG-incorporated soil when used in other applications such as for agricultural purposes, soil stabilization, structural filling and mining reclamation. In addition, Hooper [32] showed that TCLP underestimates the concentrations of oxy-anion forming elements. In contrast, the synthetic precipitation leaching protocol (SPLP) – (EPA-1312), which mimics leaching under acid rain conditions, provides elemental leaching only under slightly acidic conditions.

The main objectives of this study are to understand the fundamental information provided by new EPA leaching methods 1313-1316 on element leaching from FGDG and FGDG mixed soil, and compare with TCLP and SPLP. As, B, Ba, Cd, Cr, Hg, Mo, Mn, Ni, Pb, V, Se and Zn are the target elements as some of these are highly toxic (As, Hg, Pb, Cd, Cr) or cause serious health effects (Ba, Ni, Se, Zn) in human beings and animals. In addition, accumulation of B, Mn, and Zn can be phytotoxic. The results from this study can be useful to determine the proper approach

for using FGDG in future beneficial applications, which in turn prevents accumulation of FGDG

in landfills.

2. Experimental

2.1 Materials

2.1.1 FGD gypsum (FGDG)

Commercially available FGDG was obtained from GYPSOIL[TM] Company (Fremont, OH, U.S.).

This FGDG was produced in a coal power plant in mid-western U.S. by burning high sulfur coal

and synthesized by forced oxidation after fly ash removal. The soluble ions have been removed

from these FGDG by rinsing with deionized water. The composition of FGDG produced after fly

ash removal was less variable compared to the "Old" FGDG produced before fly ash removal

(Table 1). Hence, a single type of FGDG was used in this study.

2.1.2 Soil

Xenia series silty loam soil (17% Clay, 74% silt and 9% sand) was collected from Wilmington,

OH, U.S. [33]. Soil samples were air-dried and aggregates were broken and sieved to obtain a

particle size of < 2 mm.

2.1.3 Soil-FGDG mixture (SF)

The soil: FGDG ratio can vary over a wide range depending on the scenario (12 T/A to over 125

T/A for beneficial purposes or even higher in a disposal scenario [12]). Therefore, a single rate of

290 T/A, which is equivalent to 71:29 w/w, was used in this study to mimic a worst-case

scenario. Air dried and crushed soil (< 2 mm size) and FGDG were mixed at a ratio of 71:29

w/w, homogenized by tumbling in a closed drum overnight followed by mixing using the cone

and quarter method [34] to make the Soil-FGDG mixture, herein named as SF.

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2.2 Material characterization

The moisture content, the natural pH and the average particle size of the samples were measured following ASTM D2216 -10, EPA Method 9045 D and ASTM D6913-04, respectively; these data are shown in Table 2.

Total element content in each material was measured by acid digestion using EPA Method 3052 followed by ICP-AES analysis (EPA Method 6010 B using an IRIS Intrepid Inductively Coupled Plasma-Atomic Emission Spectrometer, Thermo Electron Corporation, CA). Hg content was measured following EPA Method 7473, using a Direct Mercury Analyzer (DMA- Milestone, Inc., Shelton, CT). National Institute of Standards and Technology (NIST) references, 1633b (trace elements in coal fly ash) and 2709a (San Joaquin soil) were used for quality control purposes (Table S1 (supplemental information)). Sequential extraction was performed to identify element fractionation in FGDG as previously reported [35]. A detailed description of the procedure is given in Table S2. All analyses were performed in triplicates.

2.3 Leaching tests

The following leaching tests were performed in triplicate using the three materials described in Section 2.1.

2.3.1 EPA-1313

EPA-1313 batch test was performed to study element release at different pH (2, 4, 5.5, 7, 8, 9, 10.5, 12 and 13), which was adjusted using appropriate volumes of 2 N HNO_3 and 1 N KOH. Samples were tumbled at 30±2 rpm for 24±2 hours for FGDG and 48±2 hours for soil and SF. Different contact times and initial weights of the materials were selected, considering the particle

size distribution of each material and the appropriate method requirements as shown in Figure S1 and Table S3, respectively. LS of 10 mL/g was used for all materials.

2.3.2 EPA-1314

Element leaching through percolation as a function of LS was studied using EPA-1314 column test. Deionized water was used as the extraction fluid, and a constant upward flow through the column was maintained. Sampling events occurred at 0.2, 0.5, 1, 1.5, 2, 4.5, 5, 9.5 and 10 LS.

2.3.3 EPA-1315

EPA-1315 was performed to study mass transfer based leaching from a compacted sample under completely saturated conditions. Samples were compacted in cylindrical plastic molds made of high-density polyethylene, which were then immersed in sealed vessels filled with deionized water. Liquid to exposed surface area ratio of 8.1 mL/cm^2 was maintained for all the materials. Leachates were collected at 0.8, 1, 2, 7, 14, 28, 42, 49 and 63 day time intervals. Additional information of the test is provided in Table S4.

2.3.4 EPA-1316

EPA-1316 batch test was used to determine element leaching as a function of LS (1, 2, 5 and 10 mL/g). Deionized water was used as the leaching solution, and the samples were tumbled at 30±2 rpm for 24±2 hours for FGDG and 48±2 hours for soil and SF. Different contact times were selected considering the particle size distribution of materials as described in Table S3.

2.3.5 Toxicity Characteristic Leaching Protocol (TCLP) – EPA-1311

TCLP batch test uses an extraction fluid of pH 2.88 ± 0.05 prepared by mixing 5.7 mL of glacial acetic acid with deionized water and diluted to 1 L. LS of 20 mL/g was maintained for all experiments. Samples were tumbled at 30±2 rpm for 18±2 hours.

2.3.6 Synthetic Precipitation Leaching Procedure (SPLP) – EPA-1312

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An extraction fluid prepared by adding 40/60 weight percent mixture of H_2SO_4 (18.4 N) and HNO$_3$ (15.6 N) acids to deionized water until it reached the target pH of 4.20 ± 0.05 was used in the SPLP batch test. LS of 20 mL/g was maintained. Samples were tumbled at 30±2 rpm for 18±2 hours.

All leachates were filtered through 0.45 μm polypropylene membrane filters, preserved with HNO$_3$, and stored at 4 °C and analyzed for dissolved elements and total mercury as described in Section 2.2. Method blanks (Deionized water), analytical blanks, replicates, blank spikes and sample spikes (10% spike level) were analyzed for quality control purposes.

3. Results and Discussion

3.1 Elemental composition and maximum potential for release

The total element content of FGDG, soil and SF is given in Table 3 along with their respective maximum potential release in mg/L, calculated using the LS of 10 L/kg [30]. The leachate concentrations were compared with the US EPA recommended regulatory levels for solid wastes under the Resource Conservation and Recovery Act (RCRA) [36] and the Maximum Contamination Levels (MCLs) for drinking water sources [37] (Table 3). However, the comparisons to the aforementioned reference indicators are considered only as an initial screening assessment. Leachate concentrations of the target elements below their relevant MCLs may be used as a guide of environmental safety; however, concentrations above MCLs should not be considered as an environmental concern as the elements may undergo attenuation during transportation through surface and sub-surface soil. Dilution, sorption, redox reactions, ion exchange, precipitation and biodegradation are some of the natural attenuation processes, which can potentially reduce the contaminant concentrations in aqueous phase leached from soil [38].

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None of these possible attenuation factors has been applied to the leachate concentrations obtained in this study.

Although the FGDG used in this study contained many trace elements, including As, B, Cd, Co, Cr, Cu, Mo, Mn, Ni, Pb, Sb, Se, V, Zn and Hg, their concentrations were relatively low compared to those reported in the literature [1, 7, 26, 39, 40] and in U.S. natural soils [7, 8] (Table 1). The maximum potential release of As, Ba, Cd, Cr, Pb, Se and Hg from FGDG were below the RCRA levels for solid wastes; however, As, Cd, Cr, Mn, Pb, Se and Hg were above the MCLs for drinking water. Nevertheless, the total amount present in each material may not be released as it varies with pH, redox conditions, metal associations and their solubility, LS, temperature and hydrological conditions [41]. Therefore, assessing the element leaching under relevant conditions will be more appropriate than predicting from the total element content.

3.2 Constituent release under equilibrium as a function of pH (EPA-1313)

Elements such as As, Cd, Cr, Ni and Zn in FGDG and SF showed their maximum leaching at the lowest pH (pH=2), whereas Se, Mo and Sr showed their maximum leaching at the highest pH (pH=13), which are highly unlikely to occur in soil (Table 4). The elemental concentrations of the leachates of FGDG, soil and SF at any pH were below the EPA regulatory levels for solid wastes. Elevated Cd and Se concentrations were observed in FGDG at extreme pH (Table 4), which are slightly above the respective MCLs for drinking water. The Mn leaching from FGDG, soil and SF at both acidic and neutral pH were above the national secondary water regulation (0.05 mg/L). However, this may not be an environmental concern, as the natural attenuation is not considered in this study. For all the materials, Hg levels in the leachates at all pH were below the method detection limit (MDL) of 0.046 ppb. Other studies reported similar results [13, 42,

43, 44], and this could be mainly due to the insoluble mineralogical associations of Hg in iron oxides, hydroxides, sulfides and phyllosilicate minerals [39, 43, 45].

Only B, Ba, Mo, Mn, Se, Sr and Zn in FGDG and SF leachates showed concentrations above MDLs at the neutral pH, probably due to their higher availability. Se leaching from FGDG and SF was observed under all pH conditions studied (Table 4). According to sequential extraction data, the majority of Se in FGDG is associated with amorphous Fe-Mn oxides (Figure 1). With regard to leaching pattern of FGDG (elevated leaching at alkaline pH (>8) compared to acidic pH) and the sequential extraction data, Se leaching at alkaline pH can be attributed to the desorption of selenite adsorbed onto the iron oxide phase [46] while Se leached at acidic pH could be due to the dissolution of carbonates and oxides containing Se. Al-Abed *et al*. [39] reported selenite (Se (IV)) as the major Se species in FGDG by XAS analysis. Unlike Se, B is released only from FGDG at all pH. Its concentration in SF leachates were <MDL. The majority of B presents as exchangeable and soluble fraction of FGDG, which explains its release at all pH. However, after mixing with soil, the B concentration of the leachate is governed by the B adsorption capacity of soil. For instance, Al and Fe oxide can adsorb B onto their crystal lattices reducing B leaching [47]. Organic compounds and clay minerals also have a great affinity for B; hence, it is not easily desorbed from soil [48].

As the LS used in EPA-1313, TCLP and SPLP are different, the element leaching is given as a percentage of the total concentration in each material (Figure 2). The important observation to note here is the low levels of Se and Mo in TCLP for FGDG and SF compared to EPA-1313 (pH=4 extract). As mentioned before, the Se associated with carbonates and oxides might have dissolved at the acidic pH (pH= 4) of EPA-1313. However, under TCLP (pH=5.5), the carbonate and oxide dissolution may not be as prominent as in EPA-1313, due to the relatively high pH. In

addition, partially dissociated acetic acid of TCLP leachate may not be strong enough to dissolve these mineral associations compared to HNO_3. Hooper [32] also reported that TCLP underestimates the leaching of elements that form oxyanions such as Sb, As, Mo, Se and V. Since these elements are unlikely to form complexes with acetate ions, their concentrations in TCLP leachates are very low [32].

Except for Se and Mo, release of all the other elements in all three materials was higher in TCLP compared to pH 7 extract of EPA-1313. This illustrates that the use of TCLP to determine the element leaching from a material under conditions unlike landfills is an overestimation, which is also reported in other studies [31, 49]. Higher leaching of B, Ba, Cu, Sr, Ni and Zn was observed in TCLP compared to EPA-1313 at acidic pH for all three materials. These elements may form complexes with acetic acid, leading to elevated concentrations in the TCLP extract. The Cd released from FGDG was higher at pH 4 in EPA-1313 compared to TCLP. Twenty two percent of Cd in FGDG is associated with carbonates (Figure 1), which are more soluble in HNO_3 compared to acetic acid, leading to increased Cd concentration in the EPA-1313 extract. This trend was reversed for soil and SF. Organic complexes in soil, which may already be chelated to Cd ions, may have dissolved more in acetic acid compared to HNO_3, increasing the Cd concentration in TCLP. Therefore, the use of TCLP may misestimate the release of certain elements depending on its total concentration, the speciation and their association with organic complexes.

SPLP extracted only B, Ba, Mn, Sr and Zn from all the materials. SPLP underestimated the release of Se and Mo compared to EPA-1313 extract of similar pH (pH=7), especially in FGDG and SF. However, B, Ba, Mn, Sr and Zn released from all three materials were high in SPLP compared to the EPA-1313 leachates at similar pH. This may be due to the dissolution of

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carbonate minerals containing those elements in H_2SO_4 and HNO_3 used in the SPLP. Cd and Ni

released only at acidic pH, and were not observed in SPLP from all three materials, probably due

to the higher final pH of the leachates (Figure 2; FGDG - pH 8, Soil - pH 6.2 and SF - pH 7.4).

While SPLP provides a more realistic idea about element leaching under acid rain conditions, the

use of this test alone does not provide a better insight into element leaching behavior. Both

TCLP and SPLP do not control the material's acid/base neutralizing capacity to achieve a target

pH. However, in EPA-1313, the acid/base neutralizing capacity of a material is controlled to

attain the final target pH of the leachate. Therefore, EPA-1313 is expected to provide more

accurate leaching information for an element under specific pH condition.

3.3 Constituent release under equilibrium as a function of Liquid-Solid ratio (EPA-1316)

The only elements released from FGDG and SF at different LS at equilibrium are B, Ba, Mo,

Mn, Se, Sr and Zn (Table 5). Low LS typically represent the pore water conditions. Elements

such as B and Mo in FGDG reached their maximum release at low LS and remained more or less

the same with increasing LS. For instance, 24.9%, 27.7%, 25.5% and 23.8% of total B was

released at LS of 1, 2, 5 and 10, respectively. This is probably due to the leaching of all soluble B

in FGDG (2.66 mg/kg) (Figure 1) at low LS.

At high LS, the leaching solution is under-saturated with the element of concern, which results in

higher percent release. For example, 1.4%, 1.7%, 2.6%, and 3.5% of total Se in FGDG was

released at LS of 1, 2, 5 and 10, respectively. This may be due to the release of exchangeable

fraction of Se (1.04 mg/kg) as more water enters into pore spaces. A similar trend was observed

with Ba, Mn, Sr and Zn.

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SPLP and TCLP used single LS (20 mL/g) to analyze the element release. However, as shown in Table 5, leaching behavior depends on the LS, which amplifies the significance of the use of EPA-1316 to understand the leaching characteristics of an element.

3.4 Constituents release through percolation as a function of LS (EPA-1314)

Similar to EPA-1316, EPA-1314 measures the constituent release as a function of LS. However, unlike EPA-1316, the equilibrium between solid and liquid phase exists only at the beginning of the EPA-1314. Non-equilibrium conditions occur after prolonged leaching [50]. In this scenario, only the concentrations of B, Ba, Mn, Mo, Se, Sr and Zn were found to be above MDLs for LS from 0.5 to 10. These elements were released in higher concentrations at the natural pH of the material. Figure 3 shows the typical release pattern of elements under the percolation-controlled scenario. Most constituents showed higher concentrations at low LS and the concentrations decreased with increasing LS probably due to dilution effect. It could also be a result of depletion of soluble/exchangeable form of a particular element with time as shown by the plateau that was reached at higher LS (Figure 3). Some constituents like B and Mo reached their maximum release at lower LS as observed in EPA-1316. This could be the release of soluble/exchangeable fractions present in FGDG, especially for B. According to the sequential extraction data, soluble/ exchangeable fractions of B add up to 31% of the total B in FGDG. A significant release of B (24%) was observed from FGDG while soil and SF showed relatively low release, 0.06% and 2.8%, respectively (Table 6) probably due to the higher affinity of B onto soil constituents as explained before. Therefore, B release from SF is most likely due to leaching from FGDG. At low LS, the B leaching from FGDG (4.3 - 10.3 mg/L) was above the "Boron guideline value for drinking water quality" (2.4 mg/L) set by the World Health Organization (WHO) [51]. However, B concentrations (< 0.04 mg/L to 0.78 mg/L) in SF leachates were much

below that level. Pasini and Walker [42] also reported relatively high release of B from FGDG (24% of the total B content; 4.31 mg/kg), which was, however, below the WHO guideline.

Ba, Mn, Sr and Zn were released continuously from all materials throughout the experiment, though the released amount decreased with increasing LS. In each case, the total element content was much higher than the total cumulative release, which implies that the maximum potential release calculated based on the total element content is not reliable. The total Mn content in the soil was approximately 12 times as that in FGDG, whereas soil and SF had similar amounts with a total Mn content of 737 and 506 mg/kg, respectively. However, SF released more Mn through percolation compared to soil. Similar trends were observed in EPA-1313 at the pH range of 4 – 7 and in EPA-1316 at each LS. Although FGDG did not provide significant amounts of Mn to the soil, FGDG addition may have an impact on the release of Mn from the SF. Both Ca and Mn concentrations in SF leachate increased significantly from 570 mg/L to 874 mg/L and 0.45 mg/L to 6.5 mg/L, respectively when pH changed from 7 to 4. Elevated Ca^{2+} content in SF caused by FGDG addition at the pH 7- 4 may have increased the Mn desorption from soil. Moharami and Jalai [29] also made a similar observation.

The cumulative release of Se from FGDG and SF in EPA-1314 as a function of LS and in EPA-1313 as a function of pH are presented in Figures 4a and 4b, respectively. Se was not released from the soil through percolation under natural soil pH. Referring to EPA-1313, we can verify that Se in soil leached only at high alkaline pH, which could be the reason for not observing Se release in EPA-1314 under natural soil pH. According to EPA-1314, Se in SF had reached the maximum release at the end of the experiment (LS of 10); however, Se was continuously released from FGDG at very low concentrations even at the highest LS. Considering the Se association as obtained from sequential extraction (Figure 1) and the pH of the system, the Se

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released from FGDG could be from the exchangeable fraction (8%) as the dissolution of Fe

oxides is highly unlikely at neutral pH. Similar leaching patterns have been reported in other

studies, and similar conclusions on the influence of surface dissolution mechanisms on the

release of oxy-anionic elements like Se have been drawn [39]. Even though the Se

concentrations in the initial leachates (at low LS) from both FGDG and SF were slightly higher

than the drinking water regulatory value (0.05 mg/L), it decreased as the LS increased due to

dilution effect.

3.5 Mass transport-based constituent release (EPA-1315)

Only a few elements (B, Ba, Mn, Mo, Se, Sr, Zn) leached in EPA-1315 with the concentrations

above MDLs. According to the diffusion theory model developed by Groot and Van der Sloot

[52], potential leaching mechanisms of constituents can be predicted by the slope of the curve

between log cumulative release (in mg/m^2) and log leaching time (in seconds). Slope values

closer to 0.5, 1 and 0 signify that the release mechanisms are diffusion, dissolution and wash off,

respectively [52]. Similar plots made for the elements of interest in the three materials are shown

in Figure 5, while their respective slopes and proposed mechanisms are given in Table 7.

Similar to other leaching methods, a significant amount of B was leached from FGDG in EPA-

1315 (Table 6). A slope of 1.06 for B in FGDG (Table 7) potentially indicates dissolution as the

rate-limiting step. Although a significant amount of B was released from FGDG, the B released

from SF was unquantifiable (<MDL).

Although FGDG released some Se (0.02 - 0.03 mg/L), the Se leaching from SF was below MDL

(0.02 mg/L). According to the values in Table 7, the rate-limiting step for Se leaching from

FGDG can be dissolution, whereas for Mn, it could be diffusion. Further, slopes above 1

theoretically indicate dissolution to be the leaching mechanism for Mn in soil and SF. In general, the leaching mechanisms of Mn and Ba in SF were similar to that of in soil. This is likely due to the higher concentration of Mn and Ba in soil compared to FGDG. The prediction of possible leaching mechanisms for a given element in a material should be validated with other parameter such as chemical speciation, total content, the leaching conditions such as pH and redox condition. For example, when a high percent of Se in FGDG is associated with carbonates and Fe-Mn oxides, the most relevant leaching mechanism should be dissolution, which could have been changed to diffusion if more Se is associated with soluble phase than with carbonates or oxides.

3.6 Implications of EPA methods 1313-1316 over traditional leaching methods

TCLP is the most commonly practiced leaching protocol, used to determine the suitability of a waste to be disposed of in a landfill. However, if a waste needs to be re-used, the TCLP may not appropriately determine the consequences of reuse of the particular waste. In that case, data obtained from the EPA-1313 extractions collected at different pH would be more realistic than TCLP. In addition, SPLP, alone may not provide enough information to decide whether the reuse of a particular waste is environmentally benign. Although most trace elements leach at acidic pH, elements such as Se and Mo leached more in alkaline pH than acidic pH. The use of TCLP and SPLP, may not reflect all possible leaching environments encountered during reuse scenarios, including differing pH, moisture content, rain fall and presence of other materials. The use of new EPA methods, 1313-1316, provides proper insight to the behavior of FGDG in soils over different pH and LS, under percolation conditions, and under fully saturated conditions. Performing more than one of these tests in conjunction could prevent misinterpretation of data about element leaching as explained in section 3.4 for Se leaching in soil. In addition, the

leaching mechanism of the constituents of potential interest and the diffusivity of certain elements under fully saturated conditions can also be obtained from these methods. The leaching mechanisms predicted by these leaching tests are based on the models and theories developed and used in the literature. Further, the long-term metal leaching from a waste material can be estimated using both EPA-1314 and 1315. In addition, EPA-1314 can also be used to predict the metal leaching under different LS ratios by extrapolating/interpolating the data. The reliability of these predictions should be verified by other characteristics of the material and the leaching conditions as mentioned in section 3.5.

Sometimes, certain wastes regulated by TCLP may not cause harmful effects on the environment as predicted when used in reuse scenarios or vice versa. Under such circumstances, the use of new EPA methods will provide a more appropriate approach to decide whether a particular waste is to be disposed of or reused. Moreover, detailed information obtained from new methods could be used to identify new beneficial land applications of FGDG such as heavy metal stabilization in contaminated soil or increasing current application rates in existing beneficial reuse scenarios. As element leaching over a wide range of pH is analyzed in EPA-1313, these data will be more useful for such applications. Although the recent EPA methods are more time consuming compared to TCLP and SPLP, the information obtained from these methods is very useful to assess the environmental impacts of waste reuse applications.

4. Conclusions

This study explored the leaching pattern of trace elements from FGDG and SF under different environmental conditions using recently approved EPA methods. Each test provided invaluable information on element release, including leaching at different pH, LS and possible leaching mechanisms for different elements in each material. The comparison between new EPA leaching

tests with the TCLP and SPLP clearly demonstrated the significance and advantage of using EPA methods 1313-1316 to study the element leaching from FGDG over traditional methods.

Although the FGDG used in this study contained many trace elements, only Se, B, Ba, Mn, Mo, Sr and Zn were released under all the tested environmental conditions. The low concentrations of other trace elements in FGDG may be a reason for their low release. Both B and Se in FGDG and SF were released mainly through surface dissolution as implied by the data of EPA-1315. Se leaching from both FGDG and SF increased with increasing pH and LS. The percent release of B from FGDG was significantly higher compared to other elements. However, B release was insignificant in FGDG added soil except at very low LS. Higher Mn leaching was observed in soil after FGDG addition probably due to the release of Ca^{2+} by FGDG into soil in large concentrations.

As element leaching was not a major concern at the higher FGDG application rates used in this study, the data from this study could be used to potentially increase current application rates of "modern" FGDG in beneficial land applications as well as to identify new beneficial land applications. This has the added benefit of reducing the amount of FGDG sent to landfills for disposal. Future studies will include additional experiments with different types of soils and application rates.

Acknowledgements

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Figure Captions

Figure 1: Elemental fractionation of B, Cd and Se in FGDG as obtained from sequential extraction.
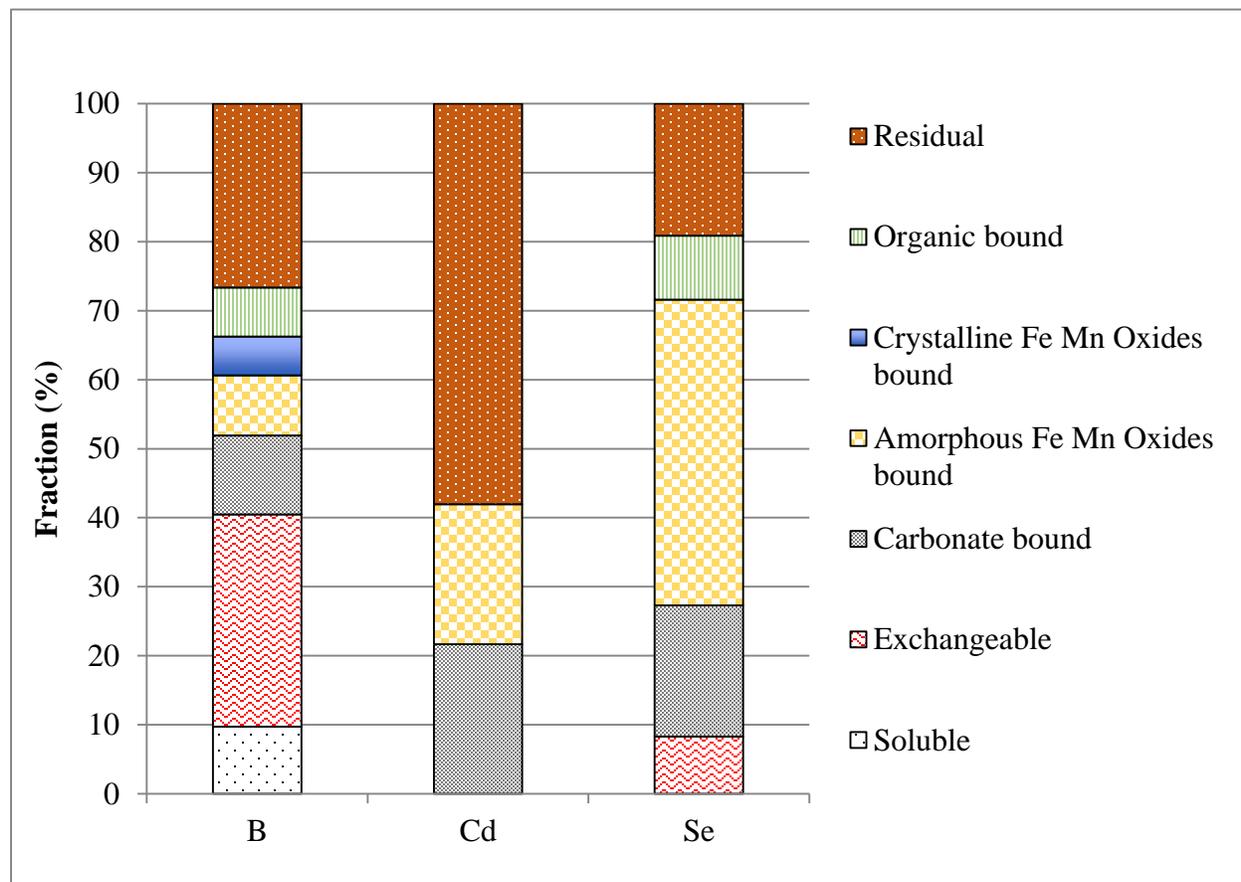
Figure 2: Elements leached from FGDG, soil and SF at different pH under EPA-1313, TCLP and SPLP.
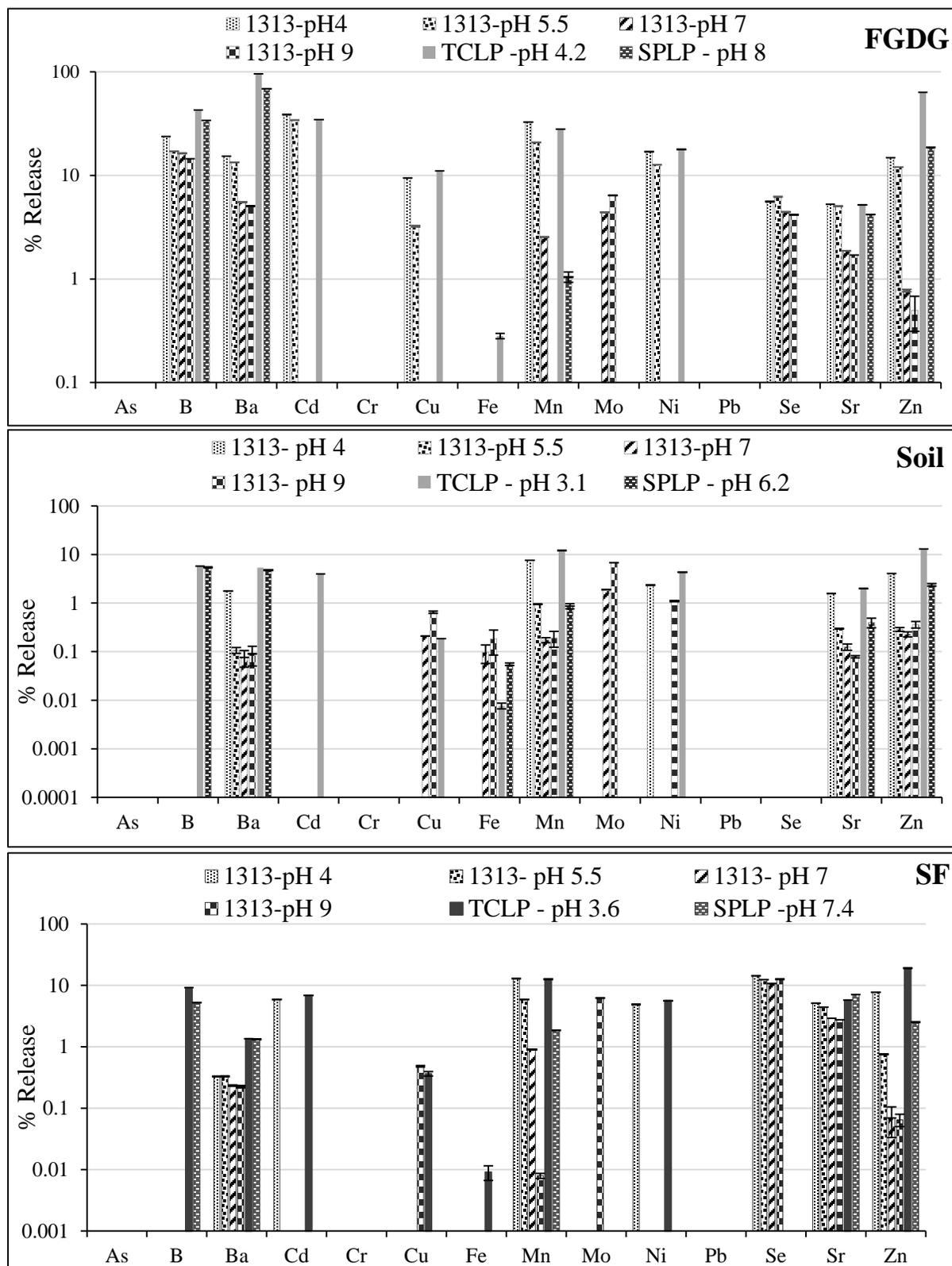
Figure 3: Cumulative release of Ba, Mn, Sr, Zn and B in FGDG, soil and SF from EPA-1314 as a function of cumulative LS. The total content of each element is represented in dashed lines.
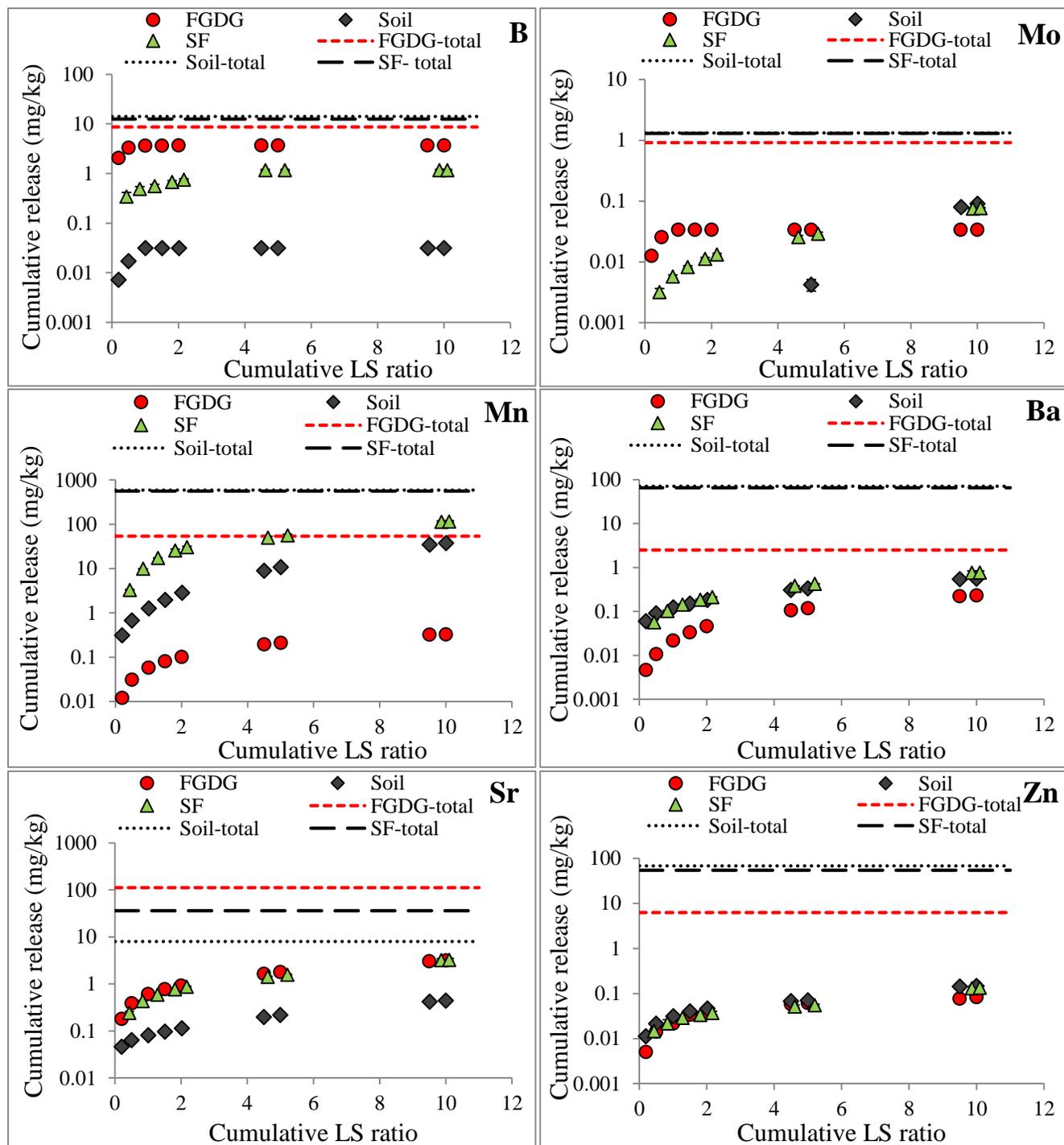
Figure 4: **(a)** Cumulative Se concentration leached from FGDG, soil and SF from EPA-1314 as a function of cumulative LS. The total Se content in each material is represented in dashed lines. **(b)** Se concentration of leachates of FGDG, soil SF as a function of pH.

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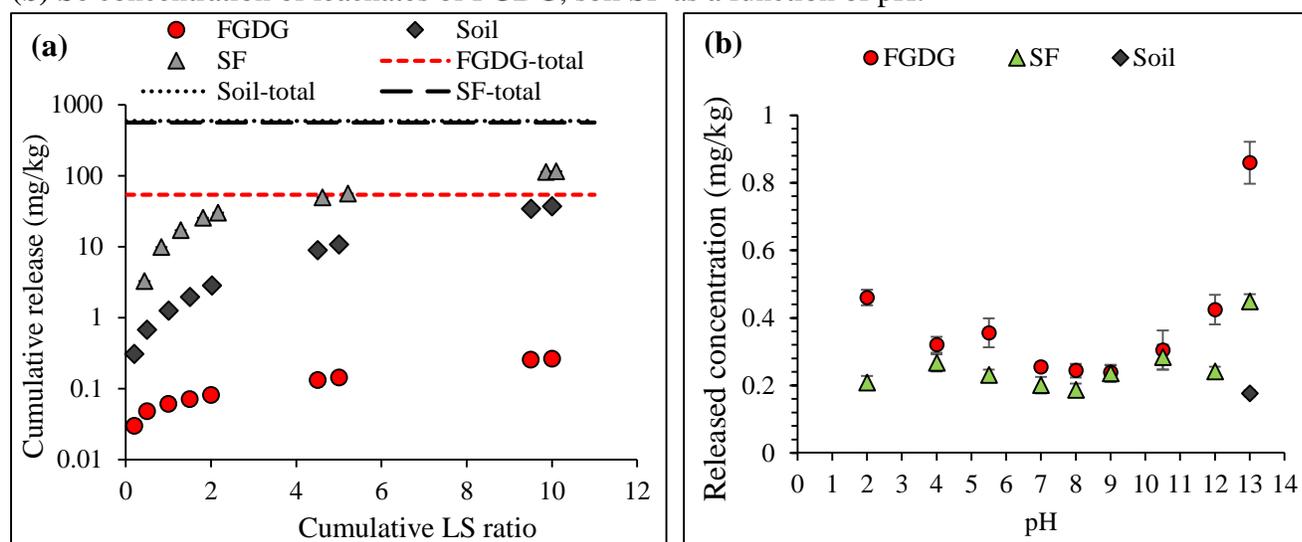
Figure 5: Cumulative release of elements as a function of contact time for FGDG, soil and SF in EPA-1315.
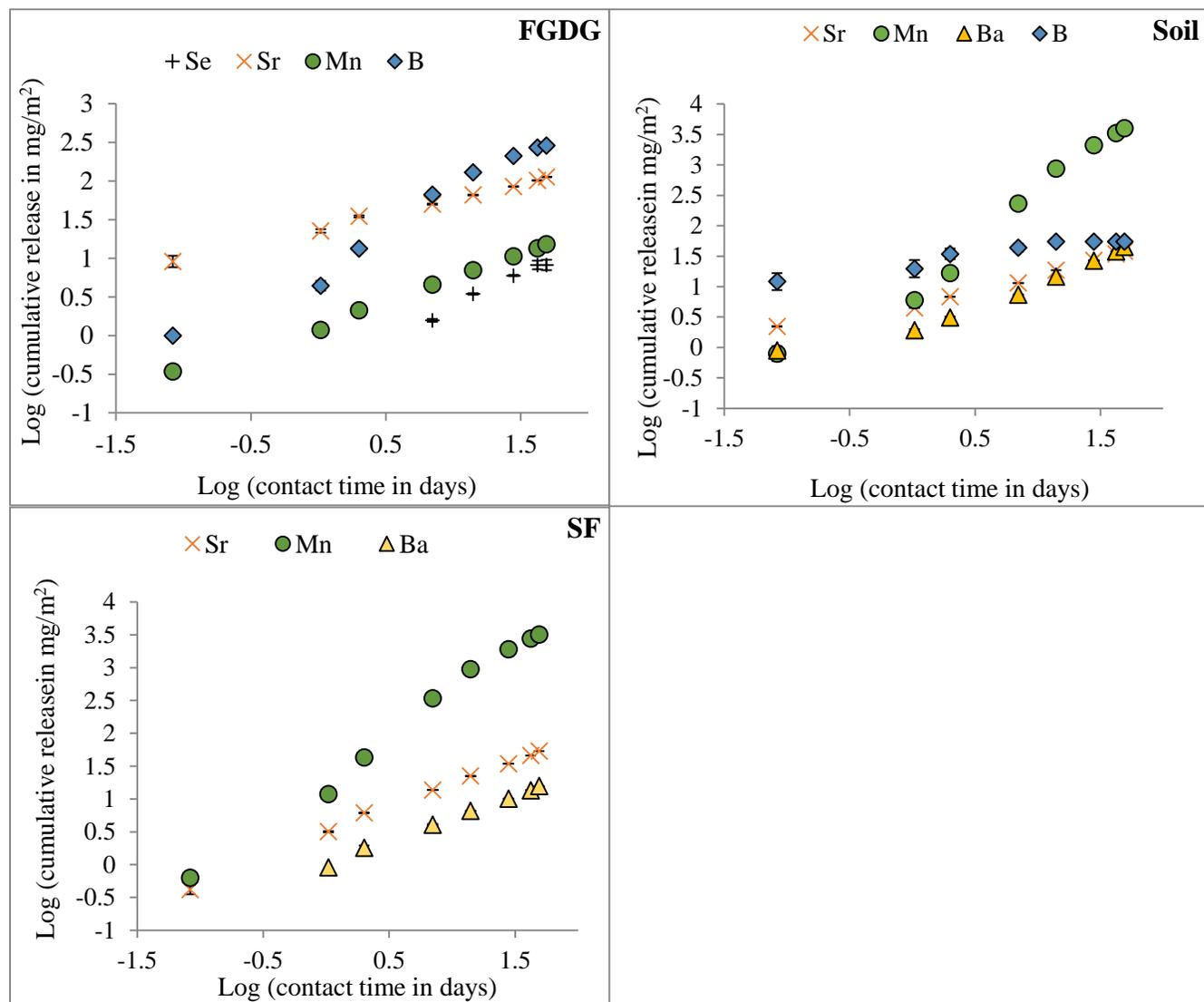
Table 1: Elemental composition of "Modern" and "Old" FGDG and U.S. natural soil

| Element	Soil A horizon, conterminous United States [*] (mg/kg)	"Old" FGDG[+]		"Modern" FGDG[‡]
		Mean	**Range**	
As	6.6	74.7	5.4 - 213	5.0
B	n.r.	145	68 - 302	n.r.
Ba	522	n.r	n.r.	100.0
Ca	1.61[#]	312	241- 412	n.r.
Cd	0.3	2.30	0.5 - 3.9	1.0
Co	9.1	8.90	3.8 - 27.3	n.r.
Cr	37	16.9	11.7 - 25.3	5.0
Cu	19.9	177	16.5 - 913	n.r.
Fe	2.19[#]	16	7 - 27	n.r.
K	1.46	1.20	0.8 - 1.5	n.r.
Mg	0.59[#]	91.8	3.8 - 162	n.r.
Mn	622	207	63 - 625	n.r.
Mo	1.02	8.60	0.02 - 25.3	n.r.
Ni	18.5	33.0	16.4 - 58.2	n.r.
P	632	141	59 - 235	n.r.
Pb	22.2	11.3	5 - 28	5.0
S	0.06	126	82 - 183	n.r.
Sb	0.84	n.r.	n.r.	n.r.
Se	0.3	3.60	2.3 - 4.6	1.0
Sr	163	308	98 - 895	n.r.
Ti	0.27[#]	n.r.	n.r.	n.r.
V	61	20.1	0 - 41.6	n.r.
Zn	64	119	45 - 245	n.r.
Hg	0.04	<5	<5	0.2

n.r.: not reported, * Values obtained from Smith *et al.* [8], +Values obtained from Kost *et al.* [40], ǂValues obtained from Rufus *et al.* [7], # Units are in weight percent (wt%)

Table 2: Physical characteristics of materials

Property	FGDG	Soil	SF
Moisture Content (%)	5.9	1.6	5.5
pH	8.46	6.10	7.26
D 50 particle size (µm)	60	525	160

Table 3: Total element content of the materials, the maximum release potential and the maximum contamination level of each element for drinking water sources and for solid wastes.

Element	Total content (mg/kg)			Maximum potential for release (mg/L)			Maximum contamination level (MCL) for drinking water [‡] (mg/L)	Resource Conservation and Recovery Act (RCRA) regulated levels for solid wastes* (mg/L)
	FGDG	Soil	SF	FGDG	Soil	SF		
As	1.53	13.3	9.99	0.15	1.33	0.99	0.01	5.0
B	15.5	52.1	41.5	1.55	5.21	4.15	n.r.	n.r.
Ba	3.77	351	270	0.38	35.1	27.0	2.0	100.0
Ca	26.9[#]	0.29[#]	6.29[#]	n.c.	n.c.	n.c.	n.r.	n.r.
Cd	0.15	0.79	0.65	0.02	0.08	0.06	0.005	1.0
Co	0.35	7.20	4.48	0.04	0.72	0.45	n.r.	n.r.
Cr	4.28	41.7	32.6	0.43	4.17	3.26	0.1	5.0
Cu	4.16	64.9	46.8	0.42	6.49	4.68	1.3	n.r.
Fe	0.11[#]	2.22[#]	1.62[#]	n.c.	n.c.	n.c.	n.r.	n.r.
K	495	1.27[#]	1.07[#]	4.95	n.c.	n.c.	n.r.	n.r.
Mg	0.14[#]	0.21[#]	0.19[#]	n.c.	n.c.	n.c.	n.r.	n.r.
Mn	62.4	737	506	6.24	73.7	50.6	0.05[‼]	n.r.
Mo	0.97	1.63	1.4	0.10	0.16	0.14	n.r.	n.r.
Ni	1.79	11.2	8.72	0.18	1.12	0.87	n.r.	n.r.
P	51.9	623	484	5.19	62.3	48.4	n.r.	n.r.
Pb	35.3	21.1	n.a.	3.53	2.11	n.c.	0.015	5.0
S	18.4[#]	201	4.97[#]	n.c.	20.1	n.c.	n.r.	n.r.
Sb	1.83	1.08	0.77	0.18	0.11	0.08	n.r.	n.r.
Se	5.73	n.a.	1.87	0.57	n.c.	0.04	0.05	1.0
Sr	135	78.3	84.9	13.5	7.83	8.49	n.r.	n.r.
Ti	41.6	0.39[#]	0.32[#]	4.16	n.c.	n.c.	n.r.	n.r.
V	3.30	59.3	45.4	0.33	5.93	4.54	n.r.	n.r.
Zn	8.86	76.3	58.2	0.89	7.63	5.82	5.0[‼]	n.r.
Hg	0.06	0.01	0.03	0.006	0.001	0.003	0.002	0.2

n.c.: not calculated, n.r.: not reported, n.a.: the values were below method detection limits [‡] Values obtained from US EPA drinking water quality criteria [37], [‼] Values obtained from US EPA National Secondary Drinking Water Regulation [37], *Values obtained from US EPA hazardous wastes characteristics [36], [#] Units are in weight percent (wt%). All the analyses were done in triplicates and reported data have <10% relative standard deviation (RSD)

Table 4: Constituent release at equilibrium as a function of pH (EPA-1313)

		Leachate Concentration (mg/L)															
		As ≠[0.021]	B [0.039]	Ba [0.009]	Cd [0.0004]	Cr [0.019]	Cu [0.011]	Fe [0.435]	Mo [0.003]	Mn [0.002]	Ni [0.009]	Pb [0.013]	V [0.006]	Se [0.017]	Sr [0.003]	Zn [0.002]	Hg* [0.046]
pH 2	FGDG	0.03	0.40	0.07	0.01	0.13	0.08	14.5	0.01	3.06	0.04	n.a.	0.06	0.05	0.74	0.16	n.a.
	Soil	n.a.	n.a.	3.70	0.01	0.02	0.16	10.5	n.a.	19.1	0.10	0.19	0.35	n.a.	0.22	1.12	n.a.
	SF	0.03	n.a.	0.07	0.01	0.04	0.09	5.86	n.a.	14.6	0.07	0.07	0.01	0.02	0.41	0.83	n.a.
pH 5.5	FGDG	n.a	0.27	0.05	0.01	n.a	0.01	n.a	n.a	1.30	0.02	n.a	n.a	0.04	0.68	0.11	n.a.
	Soil	n.a.	n.a.	0.04	n.a	n.a.	n.a	n.a.	n.a.	0.70	n.a	n.a.	n.a.	n.a.	0.02	0.22	n.a.
	SF	n.a.	n.a.	0.09	n.a.	n.a.	n.a.	n.a.	n.a.	2.98	n.a.	n.a.	n.a.	0.02	0.38	0.04	n.a.
pH 7	FGDG	n.a	0.25	0.02	n.a	n.a	n.a	n.a	0.004	0.16	n.a	n.a	n.a	0.02	0.25	0.01	n.a.
	Soil	n.a.	n.a.	0.03	n.a.	n.a.	0.01	2.16	n.a.	0.13	n.a.	n.a.	n.a.	n.a.	0.01	0.02	n.a.
	SF	n.a.	n.a.	0.06	n.a.	n.a.	n.a	n.a	n.a.	0.45	n.a.	n.a.	n.a.	0.02	0.25	0.004	n.a.
pH 9	FGDG	n.a	0.23	0.02	n.a	n.a	n.a	n.a	0.01	n.a	n.a	n.a	n.a	0.02	0.23	0.004	n.a.
	Soil	n.a.	n.a.	0.03	n.a.	n.a.	0.04	4.04	0.01	0.14	0.01	n.a.	n.a.	n.a.	0.01	0.03	n.a.
	SF	n.a.	n.a.	0.06	n.a.	n.a.	0.02	n.a.	0.01	0.004	n.a.	n.a.	n.a.	0.02	0.23	0.004	n.a.
pH 13	FGDG	n.a.	n.a	0.02	n.a	n.a	n.a	n.a.	0.02	n.a	n.a	n.a	0.01	0.09	1.65	0.01	n.a.
	Soil	0.27	n.a.	0.04	n.a.	0.02	0.29	4.41	0.02	0.30	0.06	n.a.	0.35	0.02	0.01	0.05	n.a.
	SF	n.a.	n.a.	0.17	n.a.	n.a.	0.12	n.a.	0.02	n.a.	0.02	n.a.	0.01	0.04	1.11	0.01	n.a.

≠ method detection limit (MDL) of each element is given within parenthesis, *Hg concentrations are in µg/L, n.a: values below the method detection limits. RSD <10%.

Table 5: Percent release of elements as a function of LS (EPA-1316)

Element	% release											
	LS - 1			LS - 2			LS - 5			LS - 10		
	FGDG (7.91)[‡]	Soil (5.82)	SF (6.79)	FGDG (7.90)	Soil (5.86)	SF (6.89)	FGDG (7.90)	Soil (5.85)	SF (7.07)	FGDG (7.87)	Soil (5.79)	SF (7.24)
B	24.9	0.27	0.92	27.7	0.58	1.06	25.5	1.44	1.32	23.2	2.49	n.a.
Ba	0.53	0.02	0.08	1.06	0.03	0.08	2.65	0.06	0.07	5.31	0.06	0.06
Mo	5.15	n.a.	n.a.	6.18	n.a.	n.a.	5.15	n.a.	1.07	4.12	n.a.	n.a.
Mn	0.16	0.19	0.34	0.22	0.20	0.45	0.32	0.28	0.82	0.48	0.32	1.23
Se	1.39	n.a.	2.14	1.74	n.a.	3.21	2.62	n.a.	5.34	3.49	n.a.	10.69
Sr	0.38	0.08	0.52	0.58	0.08	0.87	1.04	0.13	1.71	1.70	0.13	2.94
Zn	0.03	0.03	0.02	0.07	0.03	0.03	0.22	0.13	0.08	0.45	1.31	0.17

n.a. : not applicable as the concentrations were below the method detection limit, ‡ Final pH of the leachate is given in parenthesis. RSD <10%.

Table 6: Boron concentrations released from FGDG, Soil and SF in the column leaching test (EPA-1314) and the tank leaching test (EPA-1315)

Material	Percolation controlled release (EPA-1314)		Mass transport based release (EPA-1315)	
	Cumulative release (mg/kg)	% release from total content	Cumulative release (mg/kg)	% release from total content
FGDG	3.69	23.8	3.02	19.5
SF	1.17	2.82	n.a	n.a
Soil	0.03	0.32	0.50	0.96

n.a.: not applicable as the concentrations were below the method detection limit. RSD <10%.

Table 7: Regression analysis of elements leaching from FGDG, Soil and SF (Figure 5)

Element	FGDG			Soil			SF		
	Slope	R^2	Predicted leaching mechanism	Slope	R^2	Predicted leaching mechanism	Slope	R^2	Predicted leaching mechanism
B	1.06	0.97	dissolution	0.25	0.93	wash off	n.a.	n.a.	
Se	0.86	0.98	dissolution	n.a.	n.a.		n.a.	n.a.	
Mn	0.61	0.99	diffusion	1.45	0.97	dissolution	1.39	0.99	dissolution
Sr	0.39	0.99	diffusion	0.46	0.97	diffusion	0.75	0.99	diffusion
Ba	n.a.	n.a.		0.65	0.95	diffusion	0.71	0.99	diffusion

n.a.: not applicable as the concentrations were below the method detection limits