Leaching and phytoavailability of trace elements in soils amended with coal-combustion fly ash and fly ash treated biosolids

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Abstract

The aim of this study is to assess the leachability and phytoavailability of trace elements contained in fly ash (FA) and mixed FA and lime-treated biosolids (N-Viro Soil, NVS). This will be done in pots packed with mixtures of these FA products with two Israeli soils that constitute a wide spectrum of chemical, mineralogical and physical properties. Pots will be drip-irrigated at the soil surface and drained from the bottom. They will be either not planted or planted with the test plants lettuce as a leafy vegetable or fruiting bell-pepper. The following parameters will be determined: (i) plant development; (ii) leaching of trace elements; and (iii) content of the elements in plant parts (root, canopy, and fruit).

The experimental substances (soils, FA, NVS and their mixtures) also will be characterized and evaluated by US-EPA Methods 1313 (liquid-solid partitioning as a function of eluate pH using a parallel batch extraction procedure) and 1314 (liquid-solid partitioning as a function of liquid-to-solid ratio using an up-flow percolation column procedure). The pots leaching data will be compared to the EPA leaching data to evaluate FA and NVS contribution to the leaching properties of the potting media. The out coming assessment will enable future applications to be examined in a much quicker and simpler manner.

Introduction

The use of coal ash in Israel in general and fly ash (FA) in particular spans various application fields including infrastructure, construction and agriculture depending on its definition as "usable ash" and resulting ash-derived materials from the perspective of environmental safety. This criterion is application dependent and can be determined by evaluating the environmental impact of the FA use such as the extent of metal leaching or plant uptake under specific application scenarios. In the various applications in which FAs are utilized, the FA comes in contact with other substances which could influence its characteristics. Therefore, FA characterization (e.g., chemical composition and leaching properties) alone is not sufficient in characterizing FA for environmental applications without understanding scenario-specific constituent retention and transfer mechanisms. For example, when FA is blended with soil as part of a soil supplement, the leaching characteristics of the resultant material could be different than the component materials. Consequently, the basic approach of this research proposal is to understand the FA mixtures as a whole by studying the raw

materials, including the FA used in addition to the typical blended mixtures. In this way, it will be possible to estimate the actual contamination potential subject to the agricultural application.

Over 20 years of collaboration between United States and European research teams in the field of leaching, environmental assessment, and test standardization resulted in the joint scheme "Leaching Environmental Assessment Framework" (LEAF). The framework recommends a collection of four leaching tests that follow the tiered approach of leach testing as published in literature (Kosson et al., 2002) with applicability to a wide range of materials and uses. A premier achievement of LEAF was an extensive documentation of the technical basis (Garrabrants et al., 2010) and interlaboratory validation process of four new United States Environmental Protection Agency (EPA) methods in parallel with EU methods that resulted in common practice characterization tests of wastes in general and FA in particular (EPA, 2012a; EPA, 2012b). These tests can be used to develop a characteristic leaching profile of the subject material under equilibrium- and mass transfer-controlled release. Each test is designed to vary a critical release-controlling parameter (e.g., pH, liquid-to-solid ratio, leaching time) to provide leaching data over a broad range of test conditions. The leaching tests include (EPA, 2013):

- Method 1313: Liquid-Solid Partitioning (LSP) as a Function of Eluate pH Using a Parallel Batch Extraction Procedure (PrEN 14429 or PrEN 14997)

- Method 1314: Liquid-Solid Partitioning (LSP) as a Function of Liquid-to-Solid Ratio Using an Up-Flow Percolation Column Procedure (PrEN 14405)

- Method 1315: Mass Transfer Rates in Monolithic and Compacted Granular Materials Using a Semi-dynamic Tank Leaching Procedure (PrEN 15863)

- Method 1316: Liquid-Solid Partitioning (LSP) as a Function of Liquid-to-Solid Ratio Using a Parallel Batch Extraction Procedure (EN 12457)

LEAF includes the program LeachXS Lite™ for database management, enabling comparisons of leaching data for different tests or materials, including outputing data to Microsoft Excel®. LeachXS Lite is available for free licensing and is based on the LeachXS™ platform. The full-featured software in LeachXS Pro allows for advanced modeling and data management capabilities beyond the features included in LeachXS Lite and is licensed for an annual fee.

The results of the LEAF tests can be used empirically or in combination with chemical speciation and scenario-specific mass transport models to estimate constituent leaching for a wide range of application scenarios. Application- and scenario-specific evaluations that consider regional or local geographic conditions (i.e., precipitation, hydrology, soil types, etc.) then can be used to establish decision or acceptability criteria for on-going use of ash based on simplified LEAF testing.

The proposed research is based on national and international collaboration of a team with relevant experience and expertise in the proposed field of study. The research program will be overseen by a Scientific Advisory Committee comprised of representatives from NCAB, Israeli regulatory authorities and EPA.

Objectives

The specific objectives of the proposal are to:

1. Determine the uptake of constituents of potential concern (COPC) by certain crop plants and extent of leaching from soil application of (i) fly ash, (ii) fly ash-sewage sludge treated mixture, and (iii) sewage sludge. Two soil types will be considered.
2. Determine relationships between COPC availability for crop plant uptake and LEAF testing. The goal is to be able to use LEAF testing as a rapid surrogate for pot and field studies to determine the safety of use of fly ash-sewage sludge mixtures for agricultural soil applications. This may be accomplished either through direct empirical use of LEAF testing data and/or through chemical speciation modeling of soil-sludge/fly ash interactions.

The main questions to be answered are the effects of FA on contaminants' availability, hence: (i) what is the effect of soil type and intrinsic properties and processes on trace elements availabilities; (ii) does sludge reduce/increase them; (iii) does FA reduce/increase sludge-derived contaminants' availability.

Materials and Methods

Soils: Two soils that constitute a wide range of chemical, mineralogical and physical properties will be used. These are dune sand from the Coastal Plains and a clayey soil from the Pleshet (Revadim). These soils were extensively used in former experiments (especially in lysimeters on the effect of NVS and other sludge types on lettuce; Fine et al., in preparation). Prior to use in experiments, the soils will be sieved (2 mm) to exclude stones and homogenized by cone and quartering or riffle splitting. The two soils will be chemically analyzed for major and trace element concentrations, total organic carbon (TOC) and total inorganic carbon (TIC), cation exchange capacity and clay content.

Plants: Uptake, accumulation and translocation depend on plant properties and on the plant organ. Lettuce and bell-pepper will be used as test plants because (i) they are widely grown in Israel; (ii) they represent a leafy vegetable and a fruiting one, and (iii) they grow vigorously and readily respond to water and nutrient minerals status in the growth medium. Lettuce is often used as an indicator plant for metal bioavailability.

FA, NVS and raw sludge (RSS): An approximate worst case scenario will be tested by using FA characterized by high concentrations of contaminants (i.e., Colombian ash)[1]. The chosen Columbian ash is high in many trace elements and is also suitable for NVS production. A comparison between the Columbian ash and the range of Israeli fly ash types will be developed once the available data is entered in LXS. This FA will be used for producing NVS at the SHAFDAN wastewater treatment plant. NVS will be taken from the mixer outlet and the dewatered raw sewage sludge (RSS) will be sampled at the mixer inlet. All three materials will be chemically analyzed for major and trace

[1] It is not possible to know what will constitute truly a worst case scenario in the future given the range of coals used in Israel, but the Columbian ash represents a high contaminant loading case which can be used to provide an upper bound for future use.

element concentrations, total organic carbon (TOC) and total inorganic carbon (TIC). Soil-FA-sludge mixtures will be allowed to age for 1 month prior to testing (moist, atmospheric exposure) to mimic field conditions of the time between NVS spreading and planting.

Pots: Two liter pots will be used. They will be packed with the following media: (i) soils (two), (ii) NVS-Soil mixtures (at two rates), (iii) FA-Soil mixtures (at two rates), (iv) RSS-soil mixtures (at two rates). The NVS-soil mixing ratios will be according to the total N content of the NVS, to provide a loading rate equivalent to 500 and 2500 kg N ha^{-1}. The former is the ceiling loading rates allowed in Israel and the latter is an extreme case of five times this maximum value. The loading rates of the other materials will be derived as follows:

Loading rate	NVS	FA	RSS
"Normal"	500 kg N ha^{-1}	amount in NVS at 500 kg N ha^{-1}	amount in NVS at 500 kg N ha^{-1}
Five-times the normal load	2500 kg N ha^{-1}	amount in NVS at 2500 kg N ha^{-1}	amount in NVS at 2500 kg N ha^{-1}

The amount of NVS will be added to the 2-liter pots in order to provide the 500 kg N ha^{-1} loading rate. It will be calculated assuming that this NVS is ploughed into the upper 20-cm layer of a 'typical' field soil having a specific density of 1.25 kg L^{-1}. Thus, the weight of the plough layer equals to 250 kg m^{-2} and at 500 kg N ha^{-1} the N concentration in the soil is 0.2 g kg^{-1}. The "Normal" loads of FA and RSS are the respective amounts of FA and RSS that are contained in the NVS dose of 500 kg N, and same applies for the higher rates. Hence, 25 g NVS (at 10 g N kg^{-1} w/w dry) will be mixed into the potted soil (1.25 kg) to provide the "Normal" loading rate (equivalent to 500 kg N ha^{-1}).

Experimental pots design: The variable experiments will be as follows: 2 soils: sand and clay; three matrixes: NVS, FA, RSS; 3 mixing ratios: 0, 500 kg N ha^{-1} and 2500 kg N ha^{-1}; two test plants: lettuce and bell-pepper. The experiment will be conducted in 4 replicates. In order to decrease the number of treatments, the RSS and the FA controls will only be tested at the higher mixing ratio (2500 kg N ha^{-1}) and with one crop (lettuce). Lettuce was selected for these cases because leafy vegetables are prone to accumulate available heavy metals. Hence, the summary of treatments is as follows:

Additive	Soils	Mix. rates	Plants	Treatments	# of pots
NVS	2	2	2	8	24
FA	2	1	2	4	16
RSS	2	1	2	4	16
None	2	1	2	4	16
Total					72

Deionized (by reverse osmosis) water will be used for irrigation of the pots, and N (83 mg L^{-1}), P (16 mg L^{-1}), and K (60 mg L^{-1}) ('Raviv' concentrated fertilizer solution at 1:1000 dilution) will be added through the irrigation water. This fertigation system will be computer controlled. Four pots will be mounted on scales for continual weight monitoring. The amount of drainage from each pot

will be manually monitored on a frequent basis (daily if necessary), and drainage samples will be collected from each pot on a weekly (1^{st} month), bi-weekly (2^{nd} month), or monthly (3^{rd} month on) basis, with each collected leachate sample analyzed as indicated below. Controlled deficit irrigation will be employed, only prescribed drainage will be allowed, and the drainage will be collected immediately. Computer controlled drip irrigation will be used and adjusted based on the plant water uptake. Typical irrigation rate will be intermittent (i.e., once per week) to excess to 20 percent leaching.

Estimated growth periods are: lettuce - 60 days, bell-pepper - 120 days.

In order to eliminate atmospheric effect on the leachate at all times (namely, from the drainage stage) the following methodology will be applied. Leachate will be collected and sampled by attaching a plastic bag (10 L) to the lysimeter drainage outlet. Sampling in sealed bags under confined atmosphere will prevent degasification and pH changes, and possible co-precipitation of carbonates and heavy metals (Fine et al., 2013). The irrigation head will be gradually increased until leachate will emerge (usually 0.5-5 L). The bags will be weighed to determine the leachate volume and leachate will be subsequently sampled. The irrigation will be then stopped (usually for 1 day) to allow for transpiration to reduce soil water content and restore the deficit irrigation regime.

<u>Chemical analyses of pots experiment:</u> The following parameters and elements will be measured in the drainage: pH, EC, Cl, DOC and DIC, and mineral N forms ((nitrate+nitrite, ammonium; immediately after sampling), then the samples will be acidified (1 percent high purity nitric acid) for sample preservation, and stored at 4°C for further analyses. These will include and P, Ca, Mg, Fe, K, SO_4, and trace elements and heavy elements. The specific list of analyses will be based on results of total content analysis and Method 1313 analyses of the component materials. Analyses will employ adequate methods and instruments.

<u>Plant analyses:</u> These will be performed at the end of the growth season (lettuce) or after the 2^{nd} cycle of fruiting (bell-pepper). Samples of canopy and fruit will be quantitatively treated (weighed, dried, milled) and digested in appropriate media (H_2SO_4 + H_2O_2 for total N; Aqua Regia for all other elements). The digests will be analyzed as above. Lettuce roots will be removed from the Sand-FA medium by washing the potting medium over a screen. An attempt will be made to similarly separate bell-pepper roots from Sand-NVS media.

<u>USEPA methods:</u> In order to characterize the chemical and leaching properties of the substrates used in the pot experiments, each type will be initially tested by Method 1313. Method 1313 is an equilibrium-based leaching test designed to provide eluate solutions representing the liquid-solid partitioning (LSP) curve of constituents as a function of eluate pH (EPA, 2012a). The procedure consists of parallel batch extractions at pH values from pH 2 to pH 13 and one extraction at the natural pH of the material. Extraction is conducted at a solid/liquid (L/S) ratio of 1:10 for 24 hours (fine material). Dilute acid or base is added to each extraction according to a pre-test titration in order to achieve the final extract pH values. Conductivity and pH values of the final extract solution are recorded and leachates are filtered prior to chemical analysis of the eluate. Eluate concentrations for constituents of interest are plotted as a function of eluate pH allowing for comparison to quality control and assessment limits.

Parallel to the pots experiments, Method 1313 will be applied to 15 cases: the two soils with no treatment (none), the three treatment agents NVS, RSS, and FA alone, and six mixtures (2 soils x 3 treatments) at the high load of mixture and three mixtures with NVS at the low mixing rate. The summary of application is as follows:

Additive	Substrate	Soils	Mix. rates	Treatments
NVS	1	2	2	5
FA	1	2	1	4
RSS	1	2	1	4
None	-	2	-	2
Total				15

For comparison with the plant studies, Method 1314 (EPA, 2012b) will be carried out for each of these cases. Method 1314 is an up-flow percolation column procedure used to evaluate the release of constituents from solid materials as a function of cumulative liquid-to-solid ratio (L/S). Approximately 300-600 grams of "as is" or air-dried solid material is packed into a 5-cm diameter x 30-cm long column. Layers of clean silica sand are used at the top and bottom of the column to provide flow regulation on the inlet side and coarse filtration at the outlet. Leaching solution (eluent) is pumped upward through the material and collected as nine discrete volume fractions of the continuous elution volume. The pump flow rate is adjusted to provide a volume of eluent equivalent to 0.75 ± 0.25 L/S per day. For the inorganic materials, deionized water is used as the eluent for testing; however, a 1 mM solution of $CaCl_2$ may be used when testing certain materials (e.g., organic soils, clayey materials) where deflocculation of clay layers or dissolution of organic carbon may be a concern. The collection bottle is placed above the column to provide sufficient hydraulic head to ensure saturated column flow while avoiding siphoning as well as to minimize backpressure which can cause leaks in the system. The eluates are collected at specified L/S values of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10 mL/g-dry. The eluate pH, conductivity and oxidation-reduction potential (ORP) are recorded for each fraction prior to filtration through a 0.45-µm membrane for further analysis. Cumulative release from the column is calculated based on eluate concentrations at each liquid-solid interval. The outputs of Method 1314 include eluate concentration for each L/S ratio and cumulative release plotted as a function of L/S. This approach illustrates changes in leaching that develop as percolation progresses and L/S increases.

Analysis of aqueous extracts from both standard methods will include major and trace elements, dissolved organic and inorganic carbon, pH, ionic strength (conductivity), and redox. The specific trace elements to be analyzed will be screened based on the pH 2 extraction step from Method 1313 and a reduced analytic set will be developed. Mercury will only be analyzed selectively as part of the study (limited number of samples; specific samples to be analyzed to be specified). All leaching and pot testing data will be managed in LeachXS. A statistical package will be used to evaluate correlations and analysis of variance. Results will be compared with leachate samples from the pots and plant uptake. This comparison will determine whether the standard EPA method (1314) is a good short term estimator of performance for plant uptake. The combined results from both standard methods (1313 and 1314) will enable development of a geochemical model of the leaching and uptake processes.

Geochemical Speciation Modeling: Early results from leaching tests on soil, fly ash and sludge components will be used to develop chemical speciation liquid-solid partitioning models of the material mixtures and provide initial indications of expected results from leaching and pot studies. Geochemical speciation modeling will be further applied to develop and verify models of leaching and plant uptake from the mixtures of materials under the test conditions considered (i.e., pH dependent leaching, percolation scenarios including Method 1314 and pot studies). All geochemical speciation modeling will be carried out using LeachXS-Orchestra as described in van der Sloot et al. (2008, 2010), , Carter et al. (2009) and EPA (2014).

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Time schedule and work-plan

a. Stage 1 – April – October 2014
    i. Development of a quality assurance project plan (QAPP) along with EPA review [DSK, NT, PF, HvdS]
    ii. Collection of component materials (2 soils, 1 fly ash, 1 sewage sludge, 1 NViro mixture prepared with fly ash and sludge), sieving (pass 2mm) and homogenization of each component material. Collect ca. 150 L of each material. Provide 2 L of each homogenized material to GSI. [PF]
    iii. Characterization of 6 component materials (total content, Method 1313) [NT].
    iv. Develop characterization report [NT, DSK]. Preliminary modeling of component materials and mixtures [HvdS, DSK].
    v. Selection of mixtures for pot studies [all]
    vi. Preparation of selected mixtures for study (blend, repetitive cone and quartering), age for 30 days (moist, open air, shallow pans) [PF].
    vii. Pot studies (5 weeks, Lettuce; 14 weeks, peppers) [PF]
        1. Initial set up
        2. Pot eluate collection
        3. Fruit and plant sampling
        4. Chemical analysis

b. Stage 2 – November 2014 - June 2015
    i. Leaching characterization [NT] – Oct. 2014 – June 2015
        1. Components (soils) – Method 1314
        2. Mixtures for pot studies – Method 1313, 1314
    ii. Modeling mixtures and column studies – Jan. – July 2015 [Hvds]

c. Stage 3 – July 2015 – Feb 2016
    i. Data analysis and Report preparation – June – Oct. 2015
    ii. Report Review Draft – Nov. 2015
    iii. Report Review Complete – Dec. 2015
    iv. Final Report submission – March. 2016