



Geological Survey of Israel
Ministry of Energy

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

Alon Moshe





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This thesis was submitted in partial fulfillment of the requirements for the degree of "Master of Science" to the senate of The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem.

The study was carried out under the supervision of:

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Dr. Pinchas Fine, Agricultural Research Organization, Volcani Center.

This study is dedicated to the late Mr. Omri Lulav, General Director of the Israeli Coal Ash Administration (1995-2018).

Omri was an intelligent, hard worker who with great vision understood and took into consideration the benefits as well as the risks involved with the use of coal ash in a range of applications. He encouraged research in order to ensure optimal coal ash utilization while maintaining protection of human health and the environment. Omri's support was priceless and provided me the ability to complete this work.

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Abstract

The N-Viro Soil[®] (NVS) is a beneficial agricultural soil amendment produced from a mixture of raw sewage sludge (RSS), coal combustion fly ash (FA) and calcium oxide (at ca. 55:40:5 ratio, respectively). The NVS contains plant available essential macro and microelements and enhances biological characteristics and improves physio-chemical conditions of problematic soils. However, the FA component of NVS allegedly increases the release and phytoavailability of toxic elements. The overall aim of this study is to assess the relative role of NVS components, FA and RSS, on potential uptake by test plants and leaching to groundwater of constituents of potential concern.

The research focused on the leachability of As, B, Mo, and Se, and plant uptake of As, Cd and Pb. These studied elements are monitored regularly by the Ministries of Environmental Protection, Agriculture and Rural Development and Health. Leachability was assessed using two tests: (1) The US-EPA test method 1313, which examines elemental liquid-solid partitioning as a function of eluate pH, and (2) a greenhouse mini-lysimeters (ML) experiment. In addition, the latter was carried out to evaluate the plant uptake of the various constituents of potential concern by using lettuce as the test plant. The studied matrices of the two systems include NVS, FA and RSS as additives to two soil types, dune sand (DS) and a clay soil (Vertisol; CS). The NVS mixing ratio was according to its total N load, and was equivalent to application of 500 and 2500 kg N/ha (L and H for low and high loads, respectively). The application rates of the FA and RSS were accordingly. The FA chosen (Colombian La-Loma) represents worst-case scenario as it contains high concentrations of constituents of potential concern. The RSS used was untreated secondary sewage sludge from the SHAFDAN waste water treatment plant. A total of fourteen different soil-additive mixtures (including non-treated plain soil controls) were tested.

Leaching from the raw materials, RSS and FA, as a function of pH indicate that constituents of potential concern were released in high concentrations at various pH values. The FA is the primary source of these elements released from the NVS. Hence, the FA was the source for the elevated element concentrations released from the NVS-soils mixtures throughout the entire pH range. The RSS was no source for these elements.

In the ML loaded with soil mixtures of FA and NVS, the B, Mo, and Se concentrations in the leachate decreased with increasing leachate volume (liquid-solid ratio; L/S), with a “first

flush” leaching pattern. For example, elemental leachability decreased from L/S 0.3 to 5 of the non-planted dune sand amended with high load of NVS (DS-NVS-H): 7.65 to 0.5 mg B/L, 1.65 to 0.03 mg Mo/L, 0.18 to 0.02 mg Se/L and 0.14 to 0.06 mg As/L. Arsenic concentrations were less affected by increasing L/S.

Good correlation existed between the pH dependent test results and the ML data of the NVS-soil mixtures at the high NVS and FA loads of both soils (with the highest correlation for Se). This positive correlation indicates the importance of the pH on constituents of potential concern leachability compared to variability of L/S and soil type.

Mass balance calculations of planted and non-planted, amended and non-amended ML indicate that the FA incorporated in the NVS does not release high quantities of constituents of potential concern and therefore seems safe for agricultural application. The percentage of constituents of potential concern released from FA and NVS additions in the clay soil were much lower than the ones released from amended dune sand. The maximum overall amounts of As, B, Mo and Se released from the FA and NVS amended clay soil over the eight weeks growing season (overall L/S ratios of 0.3-2) were equivalent to <4%, 13%, 34% and <7%, respectively, of their total amounts added. In contrary to the clay soil, the maximum elemental quantities released from the FA and NVS amended dune sand were much higher (11%, 65%, 84% and 29%, respectively).

The lettuces from all the ML treatments, including the excessive NVS and FA loads to the dune sand, were safe for human consumption as none of the monitored elements reached the ceiling concentrations for leafy vegetables of 1 mg Cd/kg, 1.5 mg Pb/kg and 5 mg As/kg. However, NVS and FA increased the As, Cd and Pb concentrations in lettuces compared to control non-amended growth (e.g., DS-NVS-H amendments compared to dune sand alone: 0.55 vs. 0.04 mg Cd/kg, 0.9 vs. 0.5 mg Pb/kg and 0.45 vs. 0.06 mg As/kg). Statistically, except for the high RSS additive, there is no difference between the lettuce yields (i.e., dry weights) between all treatments, although increasing lettuce development was observed for both RSS and NVS treatments.

The leachability of the studied constituents of potential concern is mainly affected by the soil pH and therefore in the future, the US-EPA 1313 pH dependence test could assist in inspecting various amendments.

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List of Abbreviations

AC	– Additive Contribution
COPC	– Constituents of Potential Concern
CS	– Clay Soil
Cum.	– Cumulative
DL	– Detection Limit
DS	– Dune Sand
DWI	– Israel Drinking Water Standard
Econt.	– Element Content
FA	– Fly Ash
GSI	– Geological Survey of Israel
H	– High Load
IWI	– Israel Irrigation Water Standard
L	– Low Load
L/S	– Liquid to Solid Ratio
LEAF	– Leaching Environmental Assessment Framework
LOI	– Loss on Ignition
LSP	– Liquid-Solid Partitioning
ML	– Mini-Lysimeter
NOM	– Natural Organic Matter
NVS	– N-Viro Soil
PB	– Planting Bed
RSS	– Raw Sewage Sludge
TEM	– Total Element Mass
TER	– Total Element Released
UCC	– Upper Continental Crust
UDL	– Under Detection Limit
UNEP	– United Nations Environment Programme
US-EPA	– United States Environmental Protection Agency
VC	– Volcani Center
VU	– Vanderbilt University

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1. Introduction

The Tel Aviv Metropolitan Area wastewater treatment plant (SHAFDAN) is expected to decrease the direct sewage sludge discharge into the Mediterranean Sea. This was supposed to be completed by 1998, in compliance with the United Nations Environment Programme (UNEP) Convention for Protection of the Mediterranean Sea against Pollution signed by the State of Israel (Sviva, 2015). In 2008, the Israel Ministry for Environmental Protection reached a decision to stop disposing sludge at sea in favor of land application or incineration (Tal-Spiro, 2010). In contrast, coal fly ash (FA) is fully utilized in Israel, currently almost exclusively in production of cement and concrete (Keren and Tza'adi-Nativ, 2005; NCAB, 2015a). Having a dominance of these uses for FA, along with minimal storage and disposal capacity for the material, raised concerns by the Israeli National Coal Ash Board (NCAB) about potential disruption or monopoly control over disposition of a material that is an unavoidable by-product of critical national infrastructure (NCAB, 2015b). Concern over these two waste management challenges, resulted in consideration of the use of blended sewage sludge and FA with the addition of lime as an agricultural additive (Logen and Burnham, 1994). The blending of sewage sludge, FA and lime has been patented by the N-Viro International Corporation (Toledo, OH, USA) which also developed agricultural uses for the product (hereafter named NVS). Sewage sludge has the potential to supply nitrogen (N), phosphorous (P), organic carbon and trace elements. Blending FA with sewage sludge improves the physical properties of the sludge and provides additional nutrients (Adriano and Weber, 2001; Shen et al., 2007), but also introduces additional constituents of potential concern (COPCs). The addition of burnt lime to the mixture elevates the pH and temperature, as well as liberating ammonia, all of which together pasteurizes the resulting blended material (Logen and Burnham, 1994; Su and Wong, 2003). Thus, in addition to the fertilizer value, NVS and its constituents have physical and chemical qualities advantageous for improving soil properties (Logen and Harrison, 1995). This is a result of higher calcium (Ca^{2+}) availability and cementation effect of the organic matter that enhances aggregate stability. The FA component acts both as a soil 'thinner' in clay soils to reduce plasticity and cracking, and a 'thickener' in sandy soils which improves water holding properties (Brooks et al., 2011; Kolas et al., 2005; Bar-Tal et al., 2010; Fine et al., 2007). The role of the FA (and alike) is to disperse the moist sludge (often at >80% moisture content) to a texture that

enables intimate contact between the lime and sludge that ensures pasteurization.

The potential benefits from NVS application to agricultural soils are cheap replacement of commercial fertilizers, improved soil structure and disinfection of some infested soils (Fine et al., 2014; Fine, 2015). However, concerns have been raised about the safety of NVS over potential (1) uptake of toxic elements by the plants, (2) salinity and toxic constituents degrading planting bed and groundwater, and (3) long-term damage to soil quality. In order to ensure that NVS is safely applied in Israeli agriculture, the NCAB has supported research of NVS usage for the last 15 years (NCAB, 2015c). The main concern is that the FA incorporated in the NVS may introduce large amounts of trace elements such as As, B, Co, Se, Sr and Cr (Ukwattage et al., 2013; Fine et al., 2014). These elements can potentially leach out at toxic levels and pollute the ground water and other exposed water sources, and become available to plant uptake and to food chain organisms (NCBA, 2015d; Fine et al., 2014). A lot of research has already been conducted by Fine and associates at Volcani Center on the influence of NVS as a fertilizer replacement, soil improvement and soil disinfectant (together with ammonia) (Fine et al., 2004; 2013; 2014; 2015). Yet, various agricultural scenarios and complementary field and laboratory studies are still needed to better assess potential environmental risks. As part of this attempt, a mini-lysimeters (ML) experiment was performed that systematically tested NVS under well-defined environmental conditions, concentrating on quantitative measurement of phyto-available and leachable constituents of three types of materials: FA, raw sewage sludge (RSS) and NVS following their application to two matrices: dune sand and clay soil, that constitute a wide spectrum of chemical, mechanical and mineralogical characteristics.

In addition to the ML study, the materials were examined for total content and pH dependent leachability characteristics. The leachability test was performed for all three additives (i.e., RSS, FA and NVS), both soils (i.e., sand dune and clay soil) and soils-additive mixtures. The test followed US-EPA methods 1313 which is one of four leaching test within the Leaching Environmental Assessment Framework (LEAF) which also includes the LeachXS data management software (US-EPA 2014). Method 1313 is a parallel batch extraction procedure resulting in Liquid-Solid Partitioning (LSP) as a Function of Eluate pH (analogous to PrEN 14429 or PrEN 14997). This test can be used to develop a characteristic leaching profile of the subject material under equilibrium- and mass transfer-controlled release and to provide a comparable basis for the ML behavior.

2. Objectives

In order to determine the safety of NVS in agricultural applications and the ability to provide a credible risk assessment, four major objectives were defined:

1. To determine if NVS is a source of toxic elements to crops.
2. To determine the potential of NVS to pollute soils or groundwater.
3. To examine the influence of soil characteristics on phytoavailability of trace elements contained in the NVS and their transport below the root zone.
4. To define the relative role of the NVS constituents, RSS and FA, in the release of trace elements from NVS.

3. Materials

Three types of materials have been tested: (a) soils (b) additives and (c) plants. All were analyzed for total content of major and trace elements and the two former were analyzed for their leachability characteristics.

Soils:

Two soils that constitute a wide range of chemical, mineralogical and physical properties were tested (Table A1):

- Dune sand, from the Coastal Plains (near Palmachim: 31°56'54"N 34°44'07"E).
- Clay soil, from the Pleshet (at Revadim: 31°46'59"N 34°49'33"E).

The clay soil was slightly crushed and sieved through a 2 mm opening for homogenization.

Additives:

- **Fly Ash (FA)**: The Colombian LA-LOMA FA, which is often used in NVS production, was tested as a worst case scenario as this FA has relatively high content of leachable COPCs among Israeli FAs (Teutsch et al., 2017).
- **SHAFDAN Raw (untreated) Sewage Sludge (RSS)**: Excess activated sludge from the Dan Region (Tel-Aviv) Cities wastewater treatment plant. The RSS is the solid phase produced during the wastewater treatment process. Most sludge is the microbiological mass that is created as a result of the decomposition of organic material in wastewater (Igudan, 2017).
- **N-Viro Soil (NVS)**: The NVS was produced at the DAN-Viro facility located in the SHAFDAN wastewater treatment plant. The NVS used in this study comprised of 57%

RSS, 38% FA and 5% CaO (by weight).

Test plant:

Romaine lettuce (*Lactuca sativa* L.; var. 936), a leafy vegetable common in toxicant uptake experiments (e.g., Brown et al., 1996), was used to test the effects of the above additives on development and metals phytoavailability in the two studied soils.

4. Methods

To detect the influence of NVS on plants and groundwater, two different types of experiments were carried out: (1) greenhouse ML experiment with lettuce as test crop, tested in two typical soils, clay and sand, with addition of NVS and its components, FA and RSS as well as non-amended controls; (2) pH dependence leaching tests according to US-EPA method 1313 of the same materials used for the greenhouse experiment. Total content analyses for all five raw materials were conducted to allow farther characterization and calculate the total elemental content of soil mixtures.

The amount of each additive (RSS, FA and NVS) added to the soil mixtures was based on the nitrogen content of the NVS and the desired load of NVS. Two loading rates were tested: 500 kg N/ha (the maximal annual loading rate permitted in Israel) and 2500 Kg N/ha (five time the permitted load). Consequently, the FA and RSS were applied at the amounts that are contained in the two NVS loads.

4.1. Sample digestion for Total Content Analysis

The solid matter was dissolved using four different procedures (see full protocol in Appendix 1) depending on the desired elements to be quantified. The dissolving methods were:

- a) LiBO_2 fusion for major elements.
- b) Sinter fusion by Na_2O_2 for trace elements.
- c) Concentrated HNO_3 for dissolution of high content organic materials.

Ultimately, two different devices, depending on the compatibility of the measuring device to the specific element were used (both in the Geological Survey of Israel; GSI). To ascertain the accuracy of the analyses, standard and certified reference materials (SRM and CRM) were processed and analyzed together with the samples. Precision was monitored by repeated analysis of the SRMs and the calibration standards. The ICP-OES (Optima 3300, Perkin Elmer) for major elements (up to $\pm 3\%$ error) and ICP-MS (NexIONTM 300D, Perkin Elmer) for trace elements (up to $\pm 5\%$ error).

Loss on ignition (LOI) was conducted for determining the content of organic materials in the samples and commonly include water and CO_2 from carbonates and organic matter (for details see Appendix 1). The detection limits (DL) of twenty elements of interest from the three laboratories in which data were obtained along with the Israeli standards for drinking and irrigation water are given in table 1.

It should be noted that dissolution of RSS for trace element determination by sinter was impossible because of the high content of organic matter. Therefore a triplicate dissolution by concentrated HNO_3 was applied, but this could not fully dissolve the RSS and the residue was further digested by sinter fusion. As the residue amount was small, all three replicates (total weight of 50 mg) were combined into one sample. Hence, the RSS composition is the weighed sum from the two dissolutions (HNO_3 and sinter).

Table 1: Analytical detection limits (DL) and Israeli water quality standards (µg/L) for elements of interest.

Element	Detection limits (DL)			Drinking water ^a (DWI)	Reclaimed irrigation water ^b (IWI)
	GSI ^c	VC ^d	VU ^e		
Constituents of Potential Concern					
Arsenic (As)	0.4	5	0.6	10	100
Cadmium (Cd)	0.1	2	0.2	5	10
Lead (Pb)	0.1	10	0.2	10	200
Chromium (Cr)	1	2	1	50	100
Copper (Cu)	2.5	2	4	1400	200
Nickel (Ni)	4.5	2	1	20	200
Zinc (Zn)	0.008	0.002	-	5000	200
Nutrients					
Boron (B)	-	30	1	1000	400
Iron (Fe)	20	10	2	1000	2000
Manganese (Mn)	10	2	2	200	200
Molybdenum (Mo)	1	5	1	70	10
Radioactive					
Thorium (Th)	1	-		-	-
Uranium (U)	0.1	-	0.3	15	-
Other elements of interest					
Antimony (Sb)	0.1	-	1	60	-
Barium (Ba)	2	1	3	1000	-
Cobalt (Co)	2	-	4	-	50
Selenium (Se)	1	5	0.5	10	200
Silver (Ag)	1	2	-	100	-
Thallium (Tl)	0.1	-	-	2	-
Vanadium (V)	-	-	-	-	100

^aDrinking water quality standards (Israeli Ministry of Health, 2013).

^b Reclaimed irrigation water quality standards (Israeli Ministry of Health, 2010).

^cGSI – Geological Survey of Israel (ICP-OES or ICPMS).

^dVC – Volcani Center (ICP-OES).

^eVU – Vanderbilt University (ICP-OES or ICPMS).

4.2. Method 1313: "liquid-solid partitioning as a function of extracts pH for constituents in solid materials using a parallel batch extraction procedure"

Method 1313 consists of parallel batch extractions of a particle-size reduced solid material at pH values from pH 2 to pH 14 and one extraction at the natural pH of the material (Garrabrants et al., 2012). Extraction is conducted at a liquid:solid (L/S) ratio of 10:1 mL/g dry weight for 24 hours (fine material). Dilute acid or base is added to each extraction vessel according to a pre-test titration in order to achieve the final extract pH values. Natural pH is carried out with water making it equivalent to the European Standard EN 12457-2. Conductivity and pH values of the final extract solution are recorded and leachates are filtered (<0.45 µm) 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.

The resulting shape of the liquid to solid partitioning (LSP) curve is indicative of the speciation of the elements of interest with four characteristic LSP curve shapes (i.e., relative locations of maxima and minima) that are presented schematically in figure 1 (Kosson et al., 2002; Garrabrants et al., 2010).

1. Highly soluble species - The LSP curve is only a weak function of pH.
2. Cationic species - The LSP curve of cationic species typically has a maximum concentration in the acidic pH range that decreases to lower values at alkaline pH.
3. Oxyanionic species - The LSP curve often shows maxima in the neutral to slightly alkaline range.
4. Amphoteric species - The LSP curve tends to be similar in shape to cationic LSP curve with greater concentrations in the acidic pH range. However, the concentrations pass through a minimum in the near neutral to slightly acid pH range only to increase again for alkaline pH values.

Comparison of the general shape of the element of interest with the idealized LSP curves (Fig. 1) can infer the dominant speciation of the element in the solid material.

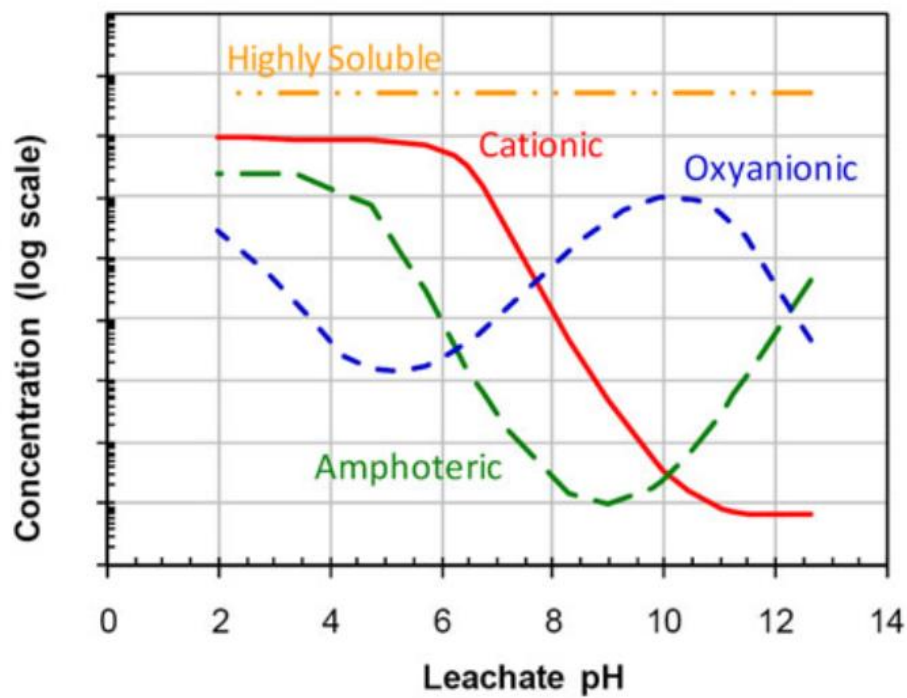


Figure 1: A schematic description of liquid-solid partitioning (LSP) curves representing typical constituent release patterns from solid materials as a function of pH (from Garrabrants et al., 2012).

4.3. Greenhouse mini-lysimeters (ML) experiment

The greenhouse ML experiment designed to characterize plant uptake and leachability potentials of COPCs, nutrients and other elements contained in the NVS product and its constituents under simulated field conditions. Mini-lysimeters constituted from 1.5-L plastic soda bottles were used as pots for growing the lettuces. The soil contained in the ML represented a 0.2-m plough layer, and its entire volume was homogenously mixed with the additives. The load was calculated for total nitrogen of 0.2 g as NVS per 1 kg soil. Assuming a specific density of field soil plow layer of 1.25 kg/L and 10.5 g N/kg NVS, being equivalent to 500 kg N/ha (maximum permitted level). The second higher load of NVS contained five times the maximum permitted value resulting in 2500 kg N/ha. Thus, the amount of NVS applied was according to the total nitrogen content of the NVS, and the corresponding amounts used for FA and RSS were those contained in this NVS load (Table 2).

Table 2: Additives loading.

Additive	Load at 500 kg N/ha		Load at 2500 kg N/ha	
	g/lysimeter	metric tons/ha	g/lysimeter	metric tons/ha
NVS	37	49	179	245
FA	29.5	39	148	195
RSS	6	8	31	40

The experiment was performed in a glasshouse at Volcani Center. The treatments were quadruplicated for the planted ML and in duplicate for the non-planted control counterparts (see table 3). The ML were positioned in 50-L containers filled with sand in groups of four planted ML or five non-planted ML per container. To prevent possible local effects the ML were arranged randomly, yet avoiding replicates within the same container.

Irrigation was computer controlled with fertilizer supplemented tap water using a submersible pump. As fertilizer, Shefer 737 was used at 1/1000 dilution ratio. Chemical composition of the tap water, fertilizer and mean irrigation water values are presented in table A2.

The ML were made from plastic soda bottles that their bottoms were removed and were held upside down. Before packing them, the bottleneck of each (which became the down part) was fitted with a wadding (made of white perlon used for aquaria filters), which prevented soil loss while allowing free through flow of the leachate water (Fig. 2). The bottle outlet was wrapped by a urine Penrose drain, which was connected to an air-tight 2-L urine

plastic bag for drainage collection (Fig. 3B). Since air was also pushed into the bags with the dripping water, a secured side air-outlet was installed to release it (Fig. 3C). The collection bags were placed in dark bags to minimize exposure to light and inhibit algae growth.

Collection bags were sampled every two weeks from irrigation onset. After recording the leachate volume, sub samples were taken in two 50-ml centrifugation tubes. The EC and pH were measured immediately after sampling and then the tubes were centrifuged at 4500 RPM for 10-min and the supernatant from one tube was immediately analyzed for PO_4 , NO_3 , NH_4 using an Autoanalyzer (Gallery Plus, Thermo Scientific). The other tube was acidified with 0.1 ml (1%) HNO_3 and analyzed for Ag, As, Be, Cd, Cr, Mo, Pb, Sb, Se, Th, Tl, U by ICP-MS (at GSI; $\pm 5\%$) and Al, B, Ba, Ca, Co, Cu, Fe, K, Mg, Mn, N, Na, P, S, Si, Ti, V and Zn by ICP-OES (at VC; $\pm 10\%$).

Table 3: Type of mini-lysimeters.

Growth media	Planted	Non-planted	Amendment rate	Total ML*
Clay soil	4	2	-	6
Dune sand	4	2	-	6
Soil+FA	8	4	2	24
Soil+RSS	8	4	2	24
Soil+NVS	8	4	2	24
Sum				84

* Total ML= (Planted+Non-planted) x Amendment rate

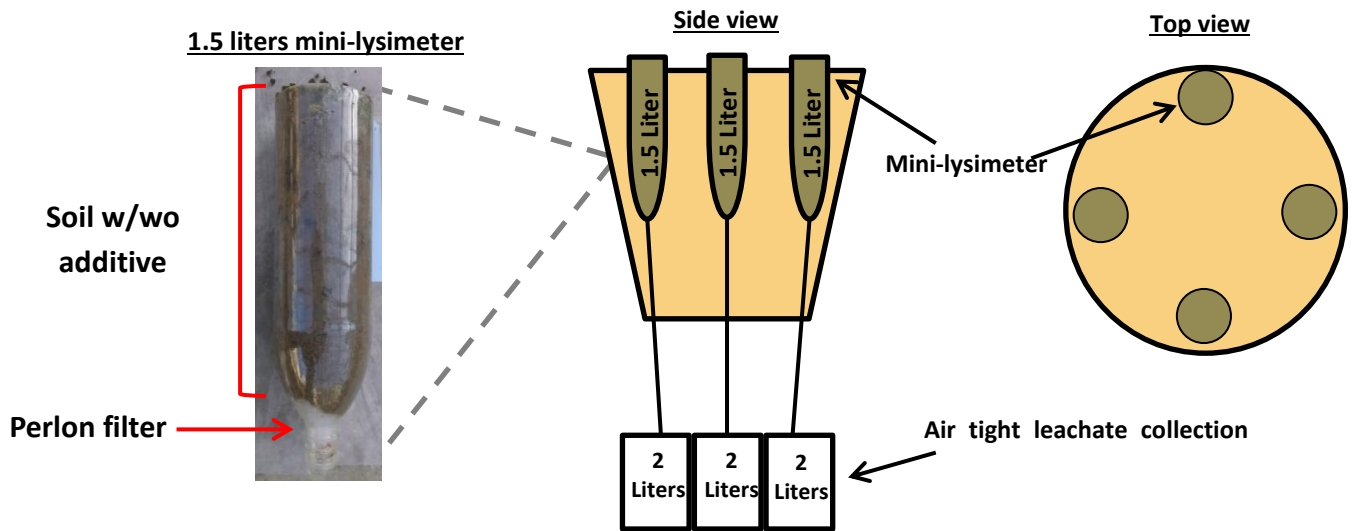


Figure 2: Design and placing of the mini-lysimeters.



Figure 3: (A) overview of the greenhouse lettuce mini-lysimeters experiment; (B) leachate collection bags wrapped in brown paper bags to avoid sun light; (C) the tubes hanging outside the containers are for the release of air entrapped in the plastic bags.

4.4. Data processing

4.4.1. LeachXS data management software

LeachXS Lite™ is a free data management tool that allows to evaluate and characterize the release of material constituents based on comparisons derived from leaching test results for a wide range of materials and waste types (e.g., secondary or recycled materials, stabilized waste and construction materials) (Kosson et al., 2014; Vanderbilt, 2017). The full-featured software in LeachXS Pro allows for advanced modeling and data management capabilities, beyond the features included in LeachXS Lite and was used in this study. For easier data processing, plots production, cumulative release calculations and farther comparisons, all total content, US-EPA method 1313 and ML experiment leachate results were placed in specifically designed templates and uploaded to a software database. Leachate concentrations are presented as a function of liquid to solid ratio (L/S) referring to the collected leachate volume (liter) per mass of soil mixture (kilograms).

4.4.2. Elemental composition balance calculations

The studied elements were analyzed for the various components of the system, including soils, additives, irrigation water, leachate volumes and compositions, and content in plant tops. These were used to calculate and graphically draw the elements of interest redistribution in the system during and at the end of the growing season. The following equations were used for the calculations of total elements released from the substrate based on leachate concentrations, leachate volumes, and content of the elements in the lettuces. The calculated redistribution of an element is between the growing medium, the leachate and the plant canopy. Note that the total content of an element in a single ML is equal to the content in the soil + amount added with an additive + amount added with the irrigation water.

Total element mass – TEM

Total element released - TER

Cumulative - Cum.

Planting bed - PB

Element content - Econt.

Additive contribution – AC

Total element mass released from the planting bed (i.e., soil or soil with additives) (Graphs A₁ and A₂):

Equation (1):

$$TEM_{leachate} (mg) = Cum. release \left(\frac{mg}{kg} \right) * PB weight (kg)$$

Equation (2):

$$Econt. lettuce (mg) = lettuce dry weight (kg) * element concentration \left(\frac{mg}{kg} \right)$$

Equation (3):

$$TER from PB (mg) = Econt. Lettuce (mg) + Econt. Leachate (mg)$$

Element release from any specific additive as % of content (Graphs B₁ and B₂, example for NVS):

Equation (4):

$$TEM_{leachate} from NVS (\%) = \frac{Element leached_{amendment PB} (mg) - Element leached_{non-amendment PB} (mg)}{NVS added TEM (mg)} * 100$$

Equation (5):

$$TEM_{uptake} from NVS (\%) = \frac{Lettuce Econt. amended PB (mg) - Lettuce Econt. non-amended PB (mg)}{NVS added TEM (mg)} * 100$$

The graphic presentation "**Treatment**" of the elements mass balance (section 5.5, graph B₁ and B₂ of each element figure set) represent the results after a deduction of the control value and include an additional black dash line in that separate the control value (as measured) from the rest of the results.

4.4.3. Statistical analysis

Data from the ML experiment were uploaded to JMP statistical analysis software. The software provides Tukey's honest significance (HSD) and variance (ANOVA) tests. The Tukey's HSD clarify which groups among the samples have significant differences and provide a value for the F test with accuracy of 0.05% which are plotted along with the plant uptake (section 5.3.3) and mass balance data (see appendix; Tables A6-A15).

5. Results and discussion

5.1. Total content

Silica (SiO_2) is the main component in both the dune sand and the clay soil (96.6 wt.% and 64 wt.%, respectively; Table 4 and figure 4) and also in the FA (57.1 wt.%), which is very similar to the clay soil as both consist mainly aluminosilicates. Mixing FA with the RSS (6.44 wt.% SiO_2) ended with an NVS content of 42 wt.% silica. Similarly, the Al content in the FA (22.1 wt.%) is the main contributor of the NVS content (15.6 wt.%). All five materials (clay soil, dune sand, FA, RSS and NVS) contain a very small amount of sulfur (less than wt.1%). The content of other major elements including P, Fe, K, Mg, Na and Ti, appear at around 1 wt.% with few exceptions. High content of P in RSS (P_2O_5 8.2 wt.%), and slightly higher content of Fe in clay soils, FA and NVS (Fe_2O_3 of 4.9 wt.%, 6.8 wt.% and 5 wt.%, respectively). As expected from its organic nature, RSS has a very high LOI value (83.1 wt.%), which is the main LOI source of the NVS (22.7 wt.%).

Due to the difficulties in digesting the RSS (see section 4.1), the two stage dissolution procedure for determination of the total major elemental content, the concentrations include larger error which resulted in over 100 % for the total (106.4 wt.%; Table 4).

Table 4: Chemical composition of soils, RSS, FA and NVS (wt.%).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO	Na_2O_2	K_2O	P_2O_5	SO_3	LOI	Total
Clay soil	63.6	9.0	4.9	1.24	7.6	1.7	0.11	0.7	1.1	<0.1	<1	10.4	100.4
Dune Sand	96.6	1.3	0.2	0.03	1.4	0.03	0.004	0.3	0.4	<0.1	<1	1.4	101.8
FA	57.1	22.1	6.8	0.97	3.8	1.5	0.05	1.5	1.3	0.2	<1	2.5	97.7
RSS	6.44	1.42	0.84	0.27	4.05	0.84	0.01	0.5	0.9	8.02	<1	83.1	106.4
NVS	41.9	15.6	5.0	0.72	9.2	1.3	0.04	1.2	1.1	0.8	<1	22.7	98.7

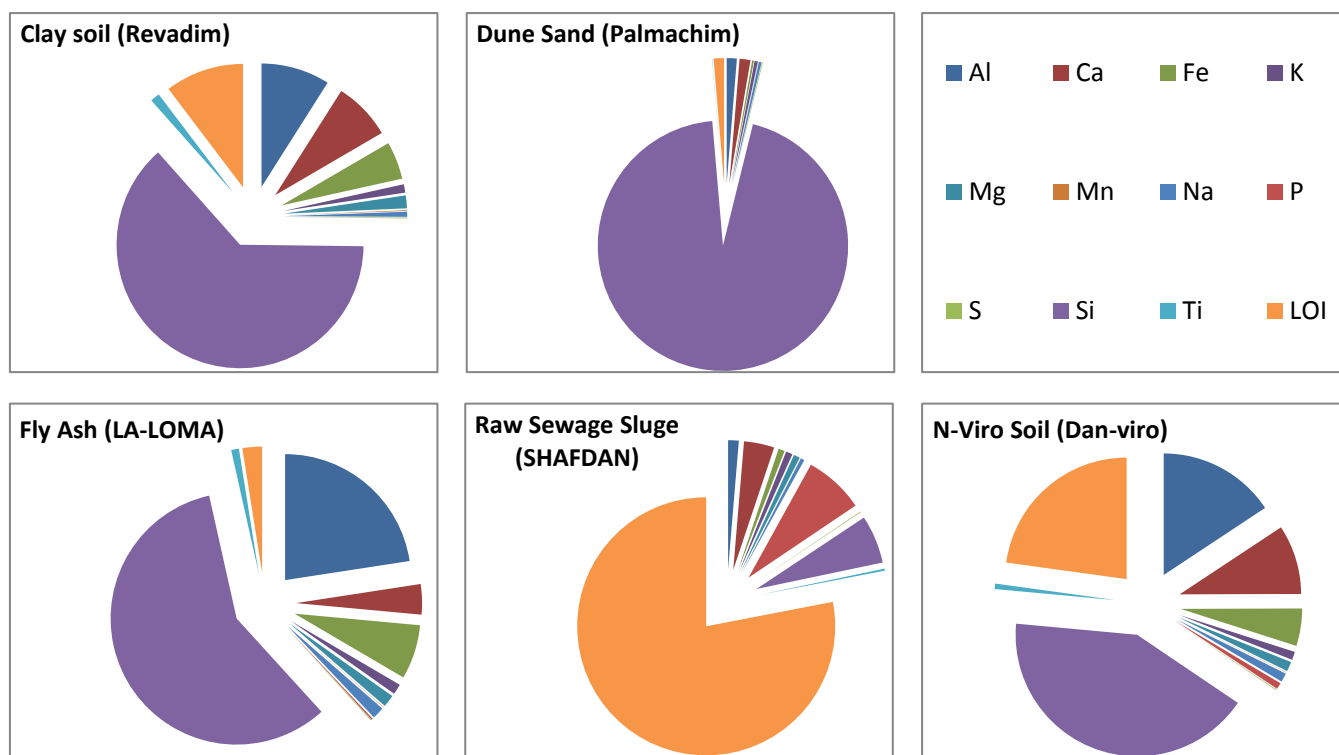


Figure 4: Chemical composition of soils, RSS, FA and NVS (wt.% of oxides).

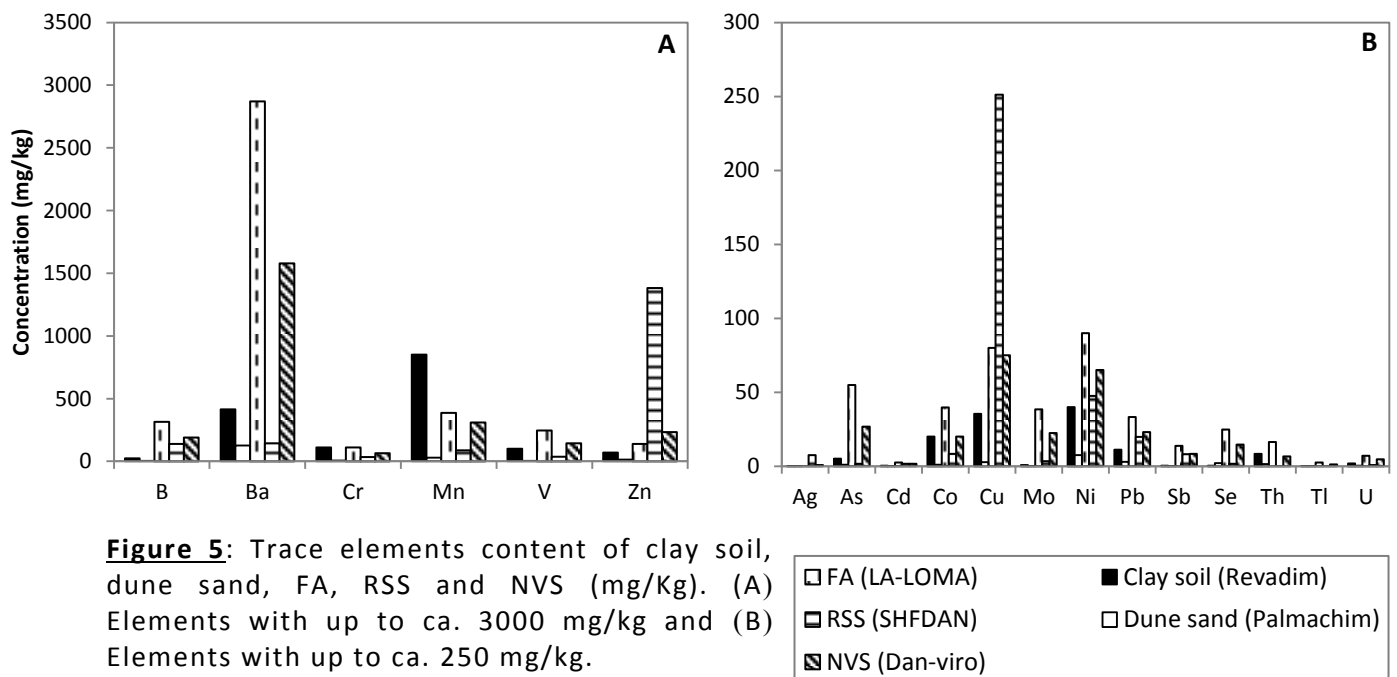
All materials contain various trace elements with higher content of As, B, Ba, Cr, Cu, Mn, Mo, Ni, V and Zn in Clay soil, FA and NVS , and Ag, B, Ba, Cd, Cu, Mo, Ni, Pb, Sb and Zn in RSS (Fig. 5).

The total concentrations of trace elements of clay soil, dune sand and FA were compared to upper continental crust values (UCC; Rudnick and Gao, 2003). The FA total content was also compared to the mean elemental content values of all main FAs used in Israel (Teutsch et al., 2017). Raw sewage sludge content was compared to a range of wastewater sludge values (Fytli and Zabaniotou, 2008).

As expected from the high silica content of dune sand, most elements, including As, B, Cd, Cr and Mo, appear at low contents compared with the UCC. Lead and Se are exceptional with very high contents of up to 5.6 and 22 times the UCC, respectively. Although these values are much higher than the UCC, the content in the dune sand is low (2.89 mg Pb/kg and 1.96 mg Se/kg, Fig. 5). Clay soil being composed of aluminosilicates has a similar composition to the UCC except Cd, Se and Pb with around four times higher values for the two former and 21 times the UCC for the latter. Similar to the sand dune, the content of these elements is low in the clay soil (0.38 mg Cd/kg, 0.34 mg Se/kg and 11.12 mg Pb/kg; Figure 5). Being a residual product from combustion, FA shows the highest total contents by 2-4 orders of

magnitude compared to the UCC, with the maximum value of Se (~280 times UCC; Table A3). Moreover, compared to other main FAs used in Israel, the studied La Loma FA contained high concentrations of As, B, Ba, Cd, Co, Fe, K, Mo, Na, Sb and Tl (Fig. 6 and Table A4) with values above two times more of Cd, Mo, Na and Sb, 1.7 of As and 1.5 of Ba compared to the mean Israeli FAs content. These high total concentrations and the high leachability of trace elements at natural pH (with water) were the reason for choosing this FA as a worst case scenario.

Concentrations of heavy metals in sewage sludge may vary widely, depending on the sludge origins (Fytli and Zabaniotou 2008). The SHAFDAN RSS samples contain relatively low (below the median value) concentrations of all elements of interest compared to reported values (Fytli and Zabaniotou, 2008), with the only exception of high Ti concentration of 5 times the reported values.



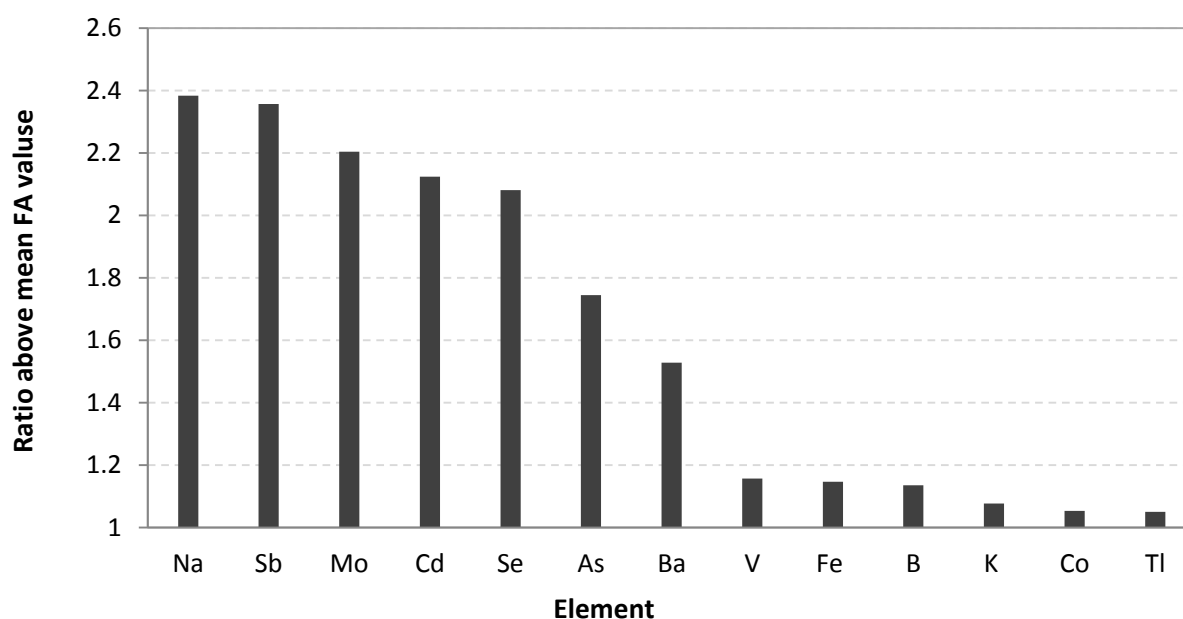


Figure 6: Total content values of the studied FA that are above the mean value of common FAs used in Israel.

5.2. The pH dependent leaching characteristics of constituents of potential concern (COPCs)

Leachability experiments by US-EPA test method 1313 were performed on all five raw materials and mixtures of both soils with FA and NVS used for the ML experiment.

The leachate concentrations are plotted as a function of the solution pH forming a curve that indicates the eluate concentration of the constituent of interest at an L/S of 10 mL/g-dry over a pH range. In addition, the raw materials element fraction leached is plotted together with the leached concentration.

The pH dependent leaching test results (US-EPA test 1313) are presented in figures 7-10 for four COCPs: As, Mo, Se and B. The former three are monitored regularly by the Health or Environmental Protection ministries as As is toxic (Bissen and Frimmel, 2003), while Mo and Se are essential nutrients (Koljonen, 1978; Kirkby, 2012) at low levels but could be toxic at higher levels (Brown, 1982; McGrath, 2010). Although B is also a nutrient (Kirkby, 2012) it can be toxic to plants in relatively low concentrations (Gupta et al., 1985). Solubility of the highly toxic elements Cd and Pb occur only at the acidic pH range (Sandeep et al., 2016), which is neither typical of Israeli soils (pH of 6-8; Singer, 2007) nor relevant for the alkaline

FA and NVS used in this study. Therefore, these elements will not be further discussed and their pH dependent results are presented in the appendix (Figs. A1 and A2).

The leachability characteristics for each element (Figs. 7-10) are presented in a set of four graphs – figures A and B refer to the raw materials (clay soil, dune sand, FA, RSS and NVS) presented as concentration (mg/kg) and fraction released (%), respectively. Figures C and D present pH dependence curves of the soil-amendment mixtures (FA and NVS) and the soil alone for comparison: C for dune sand mixtures and D for clay soil mixtures. In each LSP curve, the natural pH of each material (leaching with deionized water) is marked in a circle. Concentration data that plot on low concentrations horizontal line represents values that are below limit of detection (DL) and are plotted at the DL value. In addition, the Israeli water quality standards for drinking (DWI) and reclaimed water used for agricultural irrigation (IWI; Maximum monthly arithmetic average permitted for agricultural irrigation without restrictions) are marked as horizontal lines in each figure and their values along with the DL values are presented in Table 1. It is clear that drinking water is not the suitable criteria for evaluating the leaching properties of the greenhouse ML experiment and the EPA 133 leaching test. However, currently there are neither international nor local criteria that can be used and hence, drinking and irrigation water standards have been provided as initial references.

5.2.1. Arsenic and selenium

The LSP patterns of As and Se as a function of pH (Figs. 7A and 8A) have similar leachability trends for dune sand, FA, RSS and NVS. These patterns do not display typical oxyanion leaching curves (see figure 1) and there is a rather large variation of leaching patterns. This diversity is probably due to the various associations of As and Se in the different materials. Though very different in nature, there is some similarity of the As LSP between the RSS and the clay soil with RSS containing an order of magnitude higher concentrations than the soil. The As leachability patterns of the two soils present opposite trends. Dune sand shows maximum As leachability of 0.01 mg/L at the lowest pH of 2 that drops under DL at $\text{pH} \geq 7$ as opposed to clay soil As leachability that remain constant throughout the pH range of 2-10 with a value around DWI of 0.01 mg/L, and increases up to a maximum of 0.13 mg/L at pH of 14. Selenium concentrations could only be measured at acidic pH levels, with values exceeding DWI of 0.01 mg/l (0.02 mg/l of dune sand and 0.05 mg/l of clay soil) and drop under DL around pH 7.

The As and Se leachability from FA shows a general trend of increasing concentrations as a function of pH and reaches maximum values of 0.13 mg As/l and 1.8 mg Se/l at the highest pH of 13.5 with concentrations that are above IWI for both elements. This behavior could be explained by the negative charge of the dominant As and Se oxyanion forms in high pH solutions (CaAsO_4^- , AsO_4^{3-} , SeO_3^{2-} and SeO_4^{2-} ; Komonweeraket et al. 2015). The negative charge of the oxyanions prevents adsorption to FA surface and therefore enhances leachability (Komonweeraket et al., 2015; Sandeep et al., 2016).

The maximum leachate concentration of As constitutes only 2% of the total As content in the FA while the majority of As resides in stable phases (Fig. 7B). In contrast, the Se maximum leached concentration constituted 72% of the total Se FA content (Fig. 8B). This difference might be explained by stronger As association with the solid phase that controls the aqueous concentrations of As (Eline et al., 1994), as clay minerals having positive charge edges may adsorb anions (Chang and Sposito, 1996). Hence, it appears that different processes control the partitioning of As and Se during leaching of alkaline FA.

The RSS leachate concentrations curves of As and Se are somewhat similar to an amphoteric pattern (Figs. 7A and 8A), but with only a minor variation with pH. Both elements leached at concentrations around IWI values (0.1 mg As/l and 0.2 mg Se /l). Considering the RSS high LOI and very low As and Se content (1.6 and 1.5 mg/kg, respectively) the calculated fraction

released from RSS (Fig. 7B and 8B) includes a high uncertainty (up to ~50% for Se). Nevertheless, around 100% of both As and Se were released from the RSS at the acidic pH of 4 and at the basic pH ≥ 12 . In the pH range in between, leached concentrations were slightly lower and reached a minimum of 0.06 mg As/l at pH 9 and 0.05 mg Se/l at its natural pH of 6.3.

Interestingly, As and Se pH dependent of NVS shows distinctively different trends from their constituents (FA and RSS). Higher values are typical at the acidic pH range (2.2-7.9 with maximum of 0.7 mg As/l and 1.2 mg Se/l, both at pH 6) and lower concentrations at the basic pH values (7.9-12.5 with a minimum of 0.18 mg As/l at pH 13 and 0.29 mg Se/l at pH 11; Figs. 7A and 8A). The highest fraction released from the NVS of As (24.7%) and Se (76%) is probably affected by the RSS nature.

The high As and Se content in the FA is also reflected in the pH dependent curves of the NVS-soil mixtures (Figs. 7 and 8). The pH curve dependent of the soil-additive mixtures are controlled by the ingredient loads and As and Se content. These show that elevated concentration of both As and Se were leached as the result of their elemental loads in the mixture. This can be clearly seen in the RSS (low rate) addition to soils which is very small (6 gr) and does not affect As and Se leachability at all, while NVS increased according to its additional load in the mixture. In both soils high NVS load leads to higher As and Se leachability than the lower load. The low load of NVS with dune sand (DS-NVS-L) is the only exceptional amendment that released the same As concentrations (above IWI) at the acidic pH range (1.7-5.3) as the high load (DS-NVS-H) with a maximum of 0.25 mg/l at the lowest pH of 1.7 followed by a decrease with increasing pH. This resemblance can happen when the solubility is controlled by specific mineral phases in both cases, which seems likely due to the similar nature of the materials in the mixture, or the same sorptive phases are at play, where sufficient sites are still available for As to sorb, and the increased concentration can easily be accommodated. However, at intermediate pH levels (around pH 7), the higher loads released higher concentration of As.

Except for Se leachability from the high load of FA in the clay soil (CS-NVS-H; 0.24 mg/l, around IWI), all other amendments show lower releases than IWI values throughout the entire pH range, and higher than DWI (0.01 mg/l). Importantly, for both As and Se leached concentrations at natural pH levels which are typical of Israeli soils (pH of 6-8; Singer, 2007)

from all materials (raw and mixtures) are under the Israeli irrigation water safety limits (IWI).

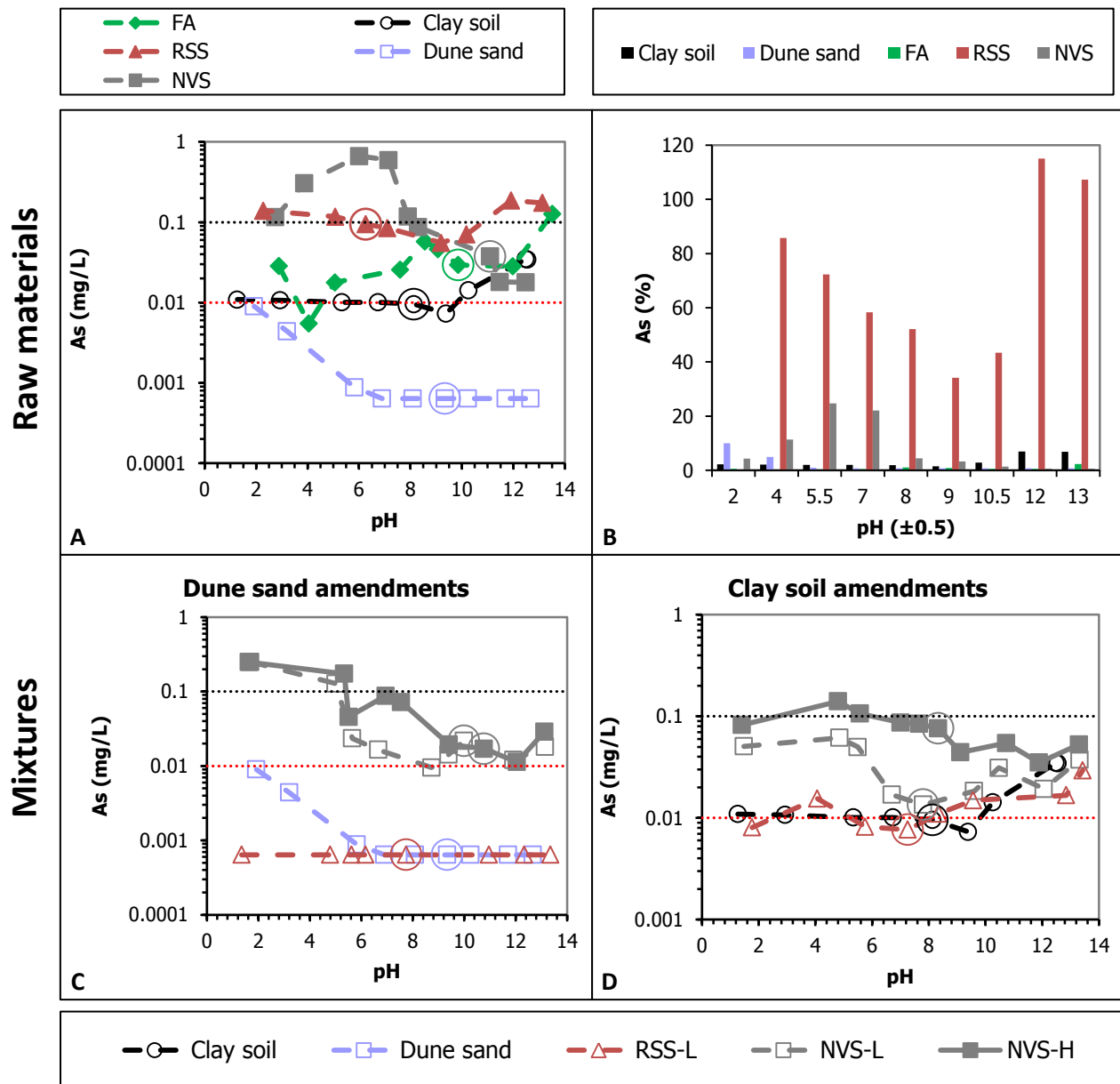


Figure 7: Arsenic pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

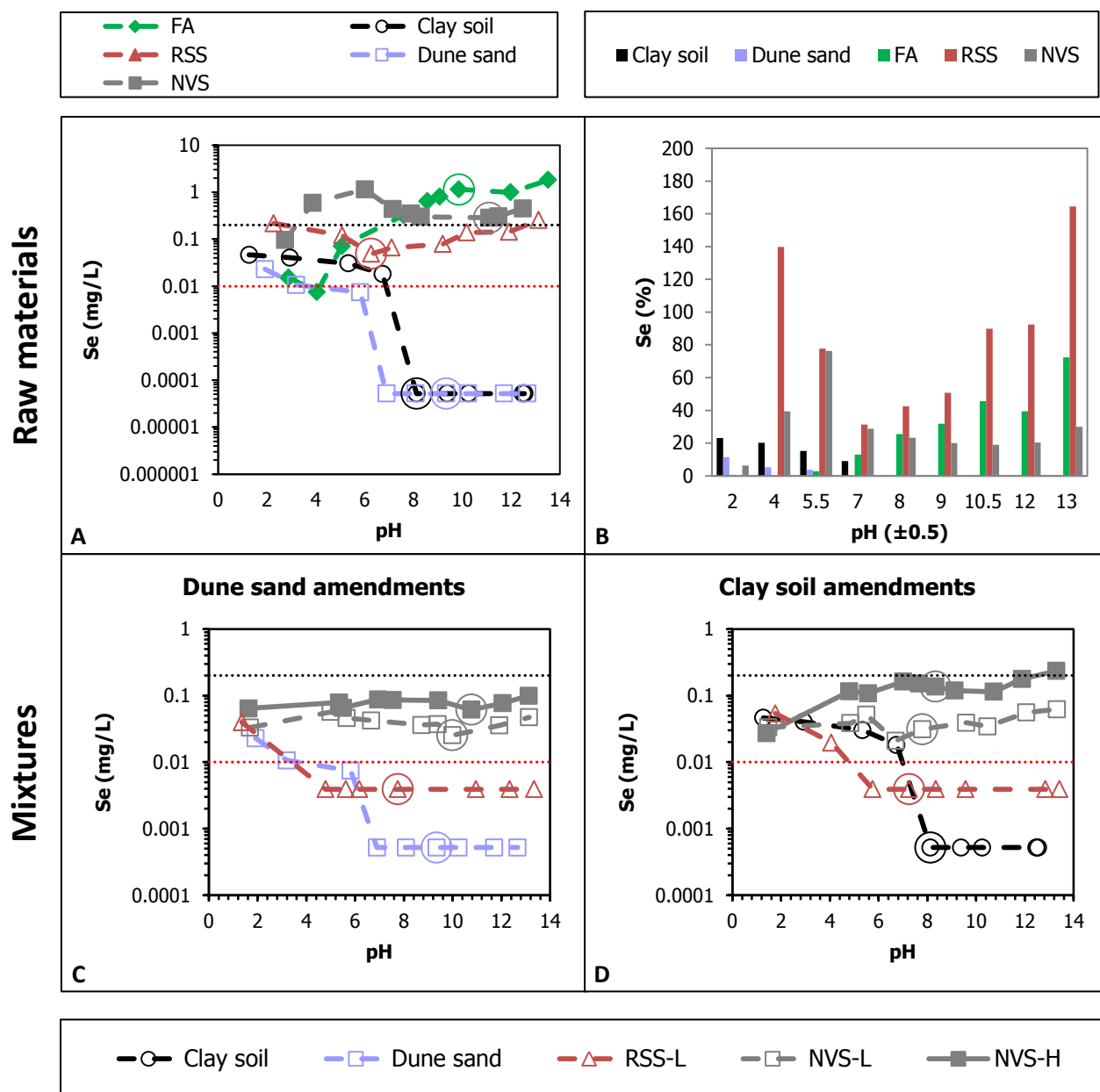


Figure 8: Selenium pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

5.2.2. Boron

Boron pH dependent leaching curve of the raw materials and their mixtures with soil resemble a highly soluble curve with only minor pH effect, although some raw materials leachability is more constant than others.

Leached B concentrations from dune sand are the lowest among the tested materials and in the range of 0.007-0.016 mg/l (up to 3.2%, Fig. 9A). Clay soil and RSS present a similar pattern with some variation as a function of pH with maximum B concentrations at the lowest pH value, drop to a minimum around pH 8 and increase at the basic pH range (Fig. 9A). This pattern possibly relates to B adsorption to organic matter or soil constituents that increases with increasing pH, reaches maximum adsorption around pH 9 and decreases at higher pH (Keren et al., 1981; Keren and Mezuman, 1981; Goldberg et al., 2005; (Komonweeraket et al. 2015).

Fly ash presents the highest B leachability with a concentration range of 10.2-14.5 mg/l (32-45% of its total B content; Figure 9B). Previous studies report that FAs extraction yields high concentrations, typically ranging from 17 to 65% (Cox et al., 1978; James et al., 1982; Sear et al., 2003; Ward et al., 2003). Izquierdo and Querol (2012) underline B as the most mobile trace element in coal ash. The NVS B leachability displays a slight decrease trend as a function of pH, starting at a maximum concentration of 14.9 mg/l at the lowest pH (2.8) and drop to a minimum of 1.7 mg/l at the highest pH (12.5). Moreover, the fraction of B released from NVS changes dramatically from 78% to 9% as the pH increases (Fig. 9B). this trend is probably the result of high available Ca content in the NVS. In Ca rich systems, the diffuse double layer is suppressed; the negative electric field associated with planar surfaces could influence edges, making them more accessible to approaching anions and more negative borate ions could move close enough to interact with the adsorption sites (Keren 1981). Hence, in alkaline environment more intensive B absorption is expected and consequently less B is extracted to the solution.

Boron leachability of soil-additive mixtures resembles the raw material curves. The FA seems to dominate the B LSP of the NVS. Although RSS released relatively high B concentrations (Fig. 9A), its mixture with both soils did not make any impact on the soil and the overall release of the mixture is similar to the non-amended soil (Figs. 9C and 9D). In contrast, the additional NVS raised B leached from the soil mixtures in accordance with its application load (Figs. 9C and 9D) with the high NVS load reaching levels above DWI for the

entire pH range but below the IWI for most pH levels. The results indicate clearly that B content in the FA is the source for the elevated B concentrations leached from the NVS and its soils mixtures.

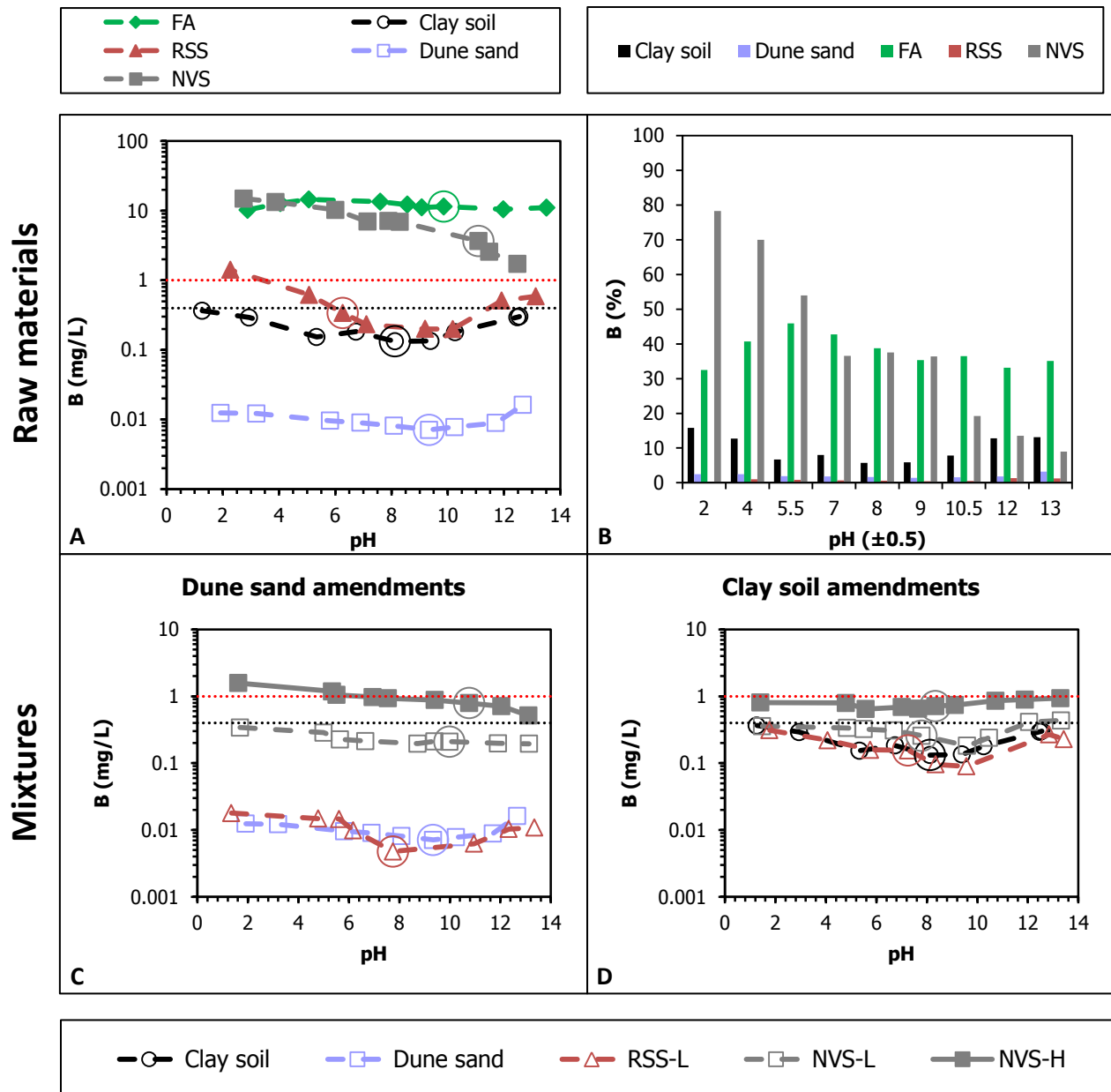


Figure 9: Boron pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

5.2.3. Molybdenum

Leachability of Mo from FA and NVS is lower at the acidic pH range of 2.5-7, and increases up to two orders of magnitude as the pH rises, and at the basic pH range the leachability is constant (Fig. 10A). To a lesser degree of change, the leachability of the clay soil displays a similar pattern. The low leachability at acidic pH range could be explained by lower solubility of Mo below pH 5 (Ward et al., 2009), which is likely caused by increased sorption on Fe and Al oxyhydroxides (Jones, 1995). The LSP of the dune sand, which contains mainly silica, remains stable throughout the entire pH range. The RSS shows a continuous increase with increasing pH. Previous studies by Cumakov (1988) found that the highest proportion of Mo is associated with organic compounds due to the great affinity of Mo to organic matter. In addition, Kabata-Pendias and Pendias, 2001 have noted that solubility of Mo is highly governed by soil pH and at wet alkaline soils Mo is most easily taken up by plants.

In both soils at natural pH level, Mo concentrations released are under IWI of 0.01 mg/l. Molybdenum leachability concentrations of all three additives at basic pH are higher than the DWI of 0.07 mg/l. Leachability above pH 7 of the NVS and the FA is identical, which points to the strong effect of FA on Mo release from NVS.

Molybdenum leached fraction (Fig. 10B) from FA, NVS and RSS are minor below pH of 5.5 (<1%, <4% and <4%, respectively) and much higher at basic pH levels (>40%, 70% and 100%, respectively).

It is very clear that NVS addition to soils strongly affected Mo leachability at the high pH levels while RSS had no affect at all (Figs. 10C and 10D), again pointing to the control of FA on NVS Mo leachability. The high load of NVS added to both soils elevate Mo concentration above DWI (0.17 mg/l in dune sand and 0.25 mg/l in clay soil) and the lower load of NVS resulted in lower concentrations between IWI and DWI.

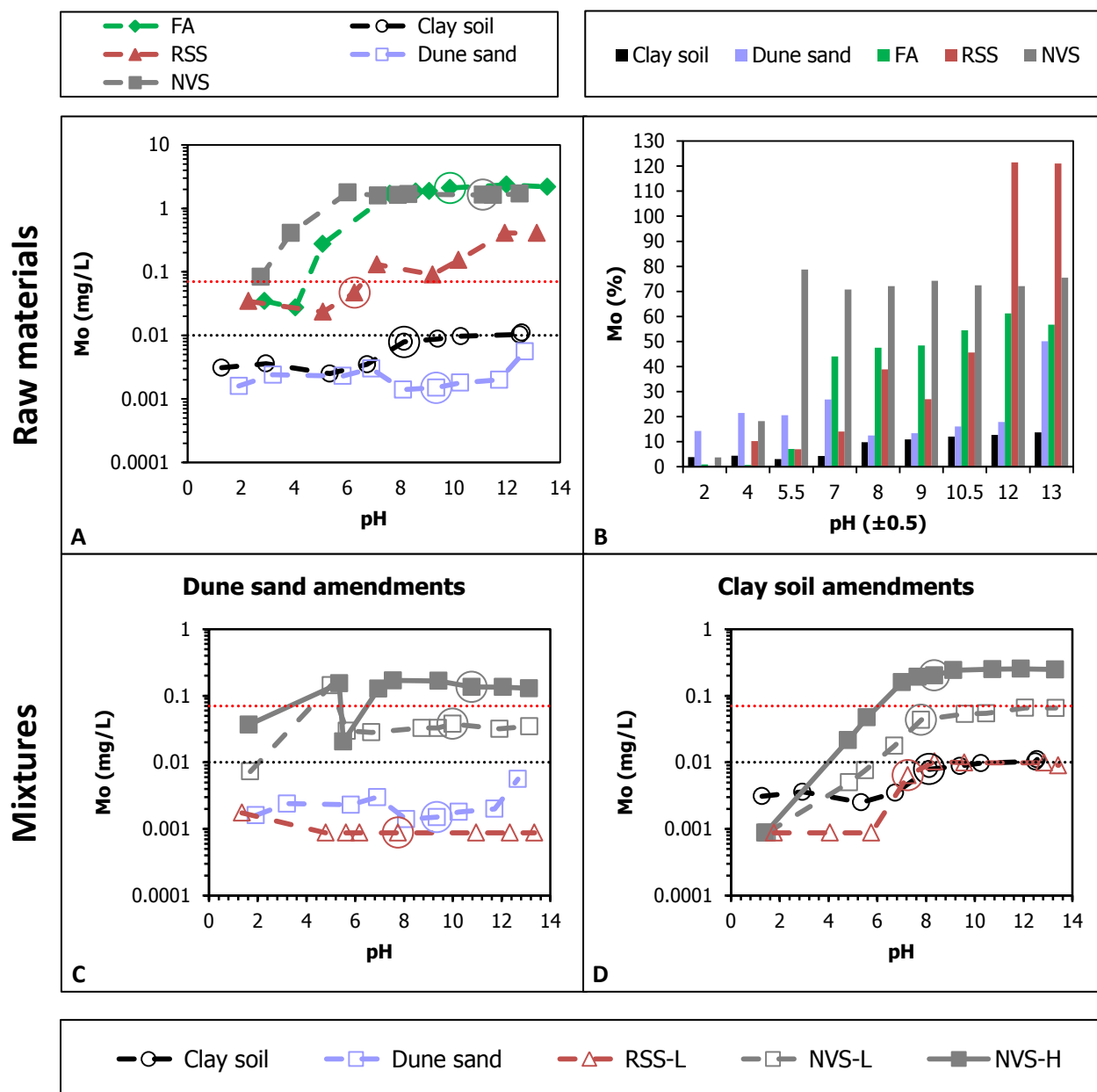


Figure 10: Molybdenum pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

5.3. Mini-lysimeters results

Groundwater pollution is dependent on a wide range of parameters such as soil type and chemistry, water table level, NVS application load, L/S ratio and irrigation time period, and crop type. As mentioned above, the purpose of the ML experiment was to simulate and understand the environmental consequence of NVS applications to soil under field conditions and to monitor plant response to regular and excessive loadings. Therefore, the experiment was conducted under extreme conditions of constant irrigation and leaching with the application layer directly exposed to leaching (i.e., with no soil barrier underneath). The leachate samples were analyzed for 30 elements, of which four elements of interest (As, B, Mo and Se), which are known to appear at high concentrations in FA and have high environmental and/or health significance are presented and discussed. In addition, lettuce yields are presented for evaluations of the additives effect on biomass production.

It should be noted that usually the field application of NVS is followed by an irrigation period before plantation in order to reduce pH and elemental concentration in the planted soil. Such a procedure was not done in this experiment and the data represent the initial leachate of the application layer. Hence, ML leachates (e.g. element concentration, pH and EC) are expected to be higher than at actual field conditions.

5.3.1. Leachate pH and EC

Leachate pH

More noticeable pH changes were observed at non-planted ML compared to the planted ones (Fig. 11). The RSS and NVS additions to both soils led to increasing pH as a function of L/S, while in the controls and FA low load additions the pH stayed stable. The largest change occurred in the non-planted dune sand ML amended with high load of RSS (DS-RSS-H; Fig. 11A; pH 7.54-10.86; see Table 5 for abbreviations). This pH increase is probably the result of ammonia release due to microbial activity in the RSS and NVS. Interestingly, the FA high load additions reacted differently in each soil where pH decreased in dune sand and increased in clay soil. The clay soil with higher organic matter content caused higher ammonia formation in the collection bag causing increase in pH compared to the dune sand. In addition, the pH elevation could be a result of a loss of carbonation layer from the clay soil with FA.

The expected opposite trend occurred in the DS-FA-H treatment with high initial pH that decreased as irrigation advanced (pH=10 at L/S=0.25 to pH=6.9 at L/S=4). The pH in the

leachates from the control and DS-FA-L treatment remained stable at close to neutrality. The pH of the leachate from all the non-planted ML with the clay soil (Fig. 11B) increased with ensuing irrigation up to 10.2 for CS-RSS-L at L/S=2, CS-NVS-L at L/S=6.4 and CS-FA-H at L/S=3.6. The non-planted ML were irrigated for a longer period than planted ML, resulting in higher L/S values.

The pH range of the leachates from the planted ML was 7.7-8.8 for both soils throughout the entire growing period, similar to Israeli soil pH range (Singer, 2007). The pH values of the non-amended planted dune sand control (DS) and the planted FA amended dune sand (DS-FA) treatments were slightly lower (7.2-7.9; Fig. 11C). The RSS and NVS leachate (in both loading rates) peaked at pH > 8 at L/S 0.5 (the second sampling following one month of irrigation) and decreased thereafter. Similar pH values and trends were observed for most of the clay soil amended ML (Fig. 11D), with the exception of CS-NVS-H that released little leachate and had the lowest pH value (ca. 7.6).

Table 5: Amendments natural pH.

Amendment	Soil	Additive	Rate	Natural pH
CS	Clay soil	-	-	8.13
CS-FA-L	Clay soil	Fly ash	Low	
CS-FA-H	Clay soil	Fly ash	High	
CS-RSS-L	Clay soil	Raw sewage sludge	Low	7.26
CS-RSS-H	Clay soil	Raw sewage sludge	High	
CS-NVS-L	Clay soil	N-Viro soil	Low	7.8
CS-NVS-H	Clay soil	N-Viro soil	High	8.34
DS	Dune sand	-	-	9.34
DS-FA-L	Dune sand	Fly ash	Low	
DS-FA-H	Dune sand	Fly ash	High	
DS-RSS-L	Dune sand	Raw sewage sludge	Low	7.75
DS-RSS-H	Dune sand	Raw sewage sludge	High	
DS-NVS-L	Dune sand	N-Viro soil	Low	9.99
DS-NVS-H	Dune sand	N-Viro soil	High	10.77

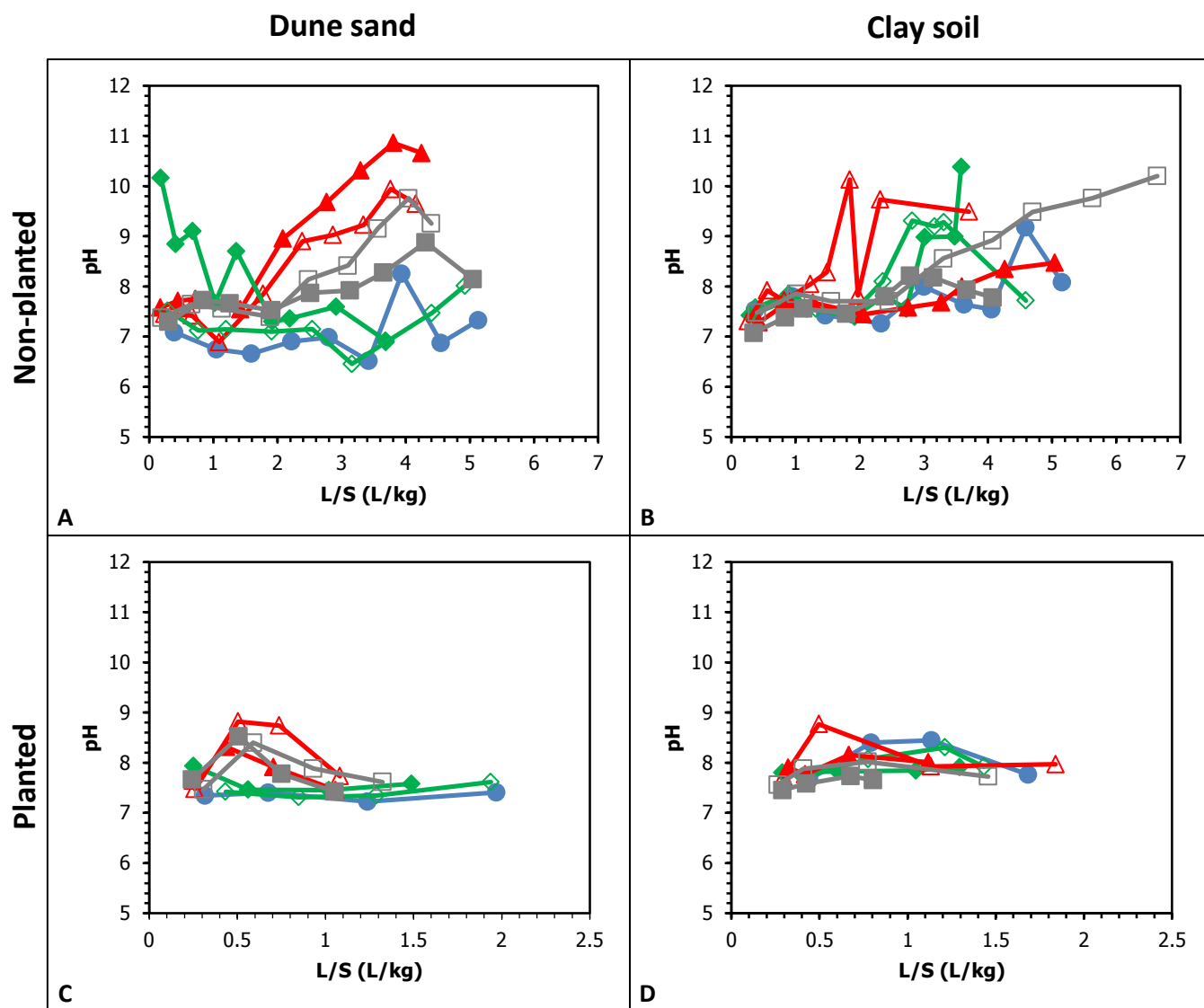
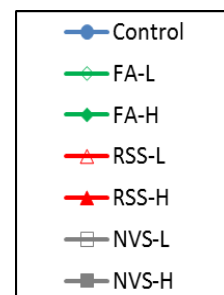


Figure 11: The pHs of the leachates from the mini-lysimeters as function of soil type, presence of a lettuce plant and cumulative irrigation (expressed as L/S ratio of the leachate). Irrigation of the planted mini-lysimeters ceased upon harvest however the not-planted counterparts were irrigated further.



Leachate EC

All amendments present identical EC trends (Fig. 12), given a decrease of EC values as a function of L/S. Two leaching behaviors have been previously identified for soil-FA mixtures (Sauer et al. 2012): (a) “first-flush” leaching, characterized by high initial concentrations followed by monotonically decreasing concentrations with increasing pore volumes of flow, and (b) lagged-response, characterized by increasing concentration that reaches a peak and then decreases. The EC trends observed in this study reflect first flush leaching. In addition, the EC of the clay soil and its mixtures are higher than those of the dune sand and as expected, the high load treatments resulted in higher EC values than the low loads. This is due to higher element content in the solid phase and therefore higher leachability that increased various ions concentrations.

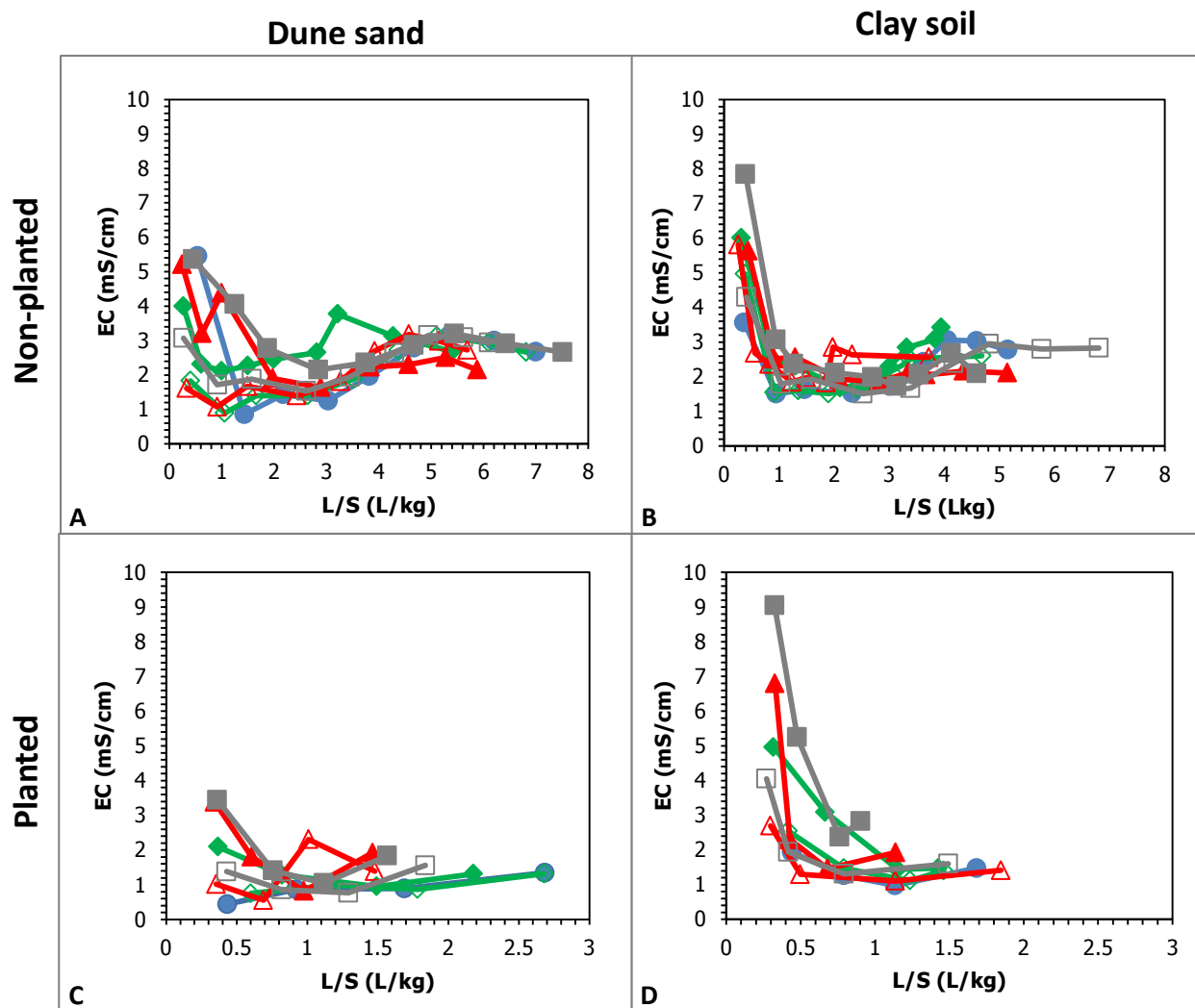


Figure 12: mini-lysimeters leachate EC (mS/cm) as function of L/S along the lettuce growth period (in case of planted mini-lysimeters) and farther time scale for the not planted controls.

5.3.2. Lettuce yield

Amending the soils with RSS and NVS increased plant weight (Fig. 13). It is apparent there is a slight increase in most treatments, yet statistically insignificant, to the clay soil compared with the dune sand. This trend occurred although all ML received a balanced fertilizer solution. The clay soil treatments, either amended or non-amended, do not differ significantly from each other, with the exception of the high RSS load (CS-RSS-H) that produced a significantly higher yield compared to both FA loads and NVS-L treatments (Fig. 13). The NVS treatments do not differ significantly from their RSS counterparts. The FA treatments of both soils do not differ significantly from the untreated controls, inasmuch as the lettuces from the FA treatments produced lower yields and the development was somewhat retarded. Although not statistically significant, the reduction was 8-10% in the dune sand and 15-22% in the clay soil. These yield results are probably due to the macro element nutrition conditions of the various mixtures.

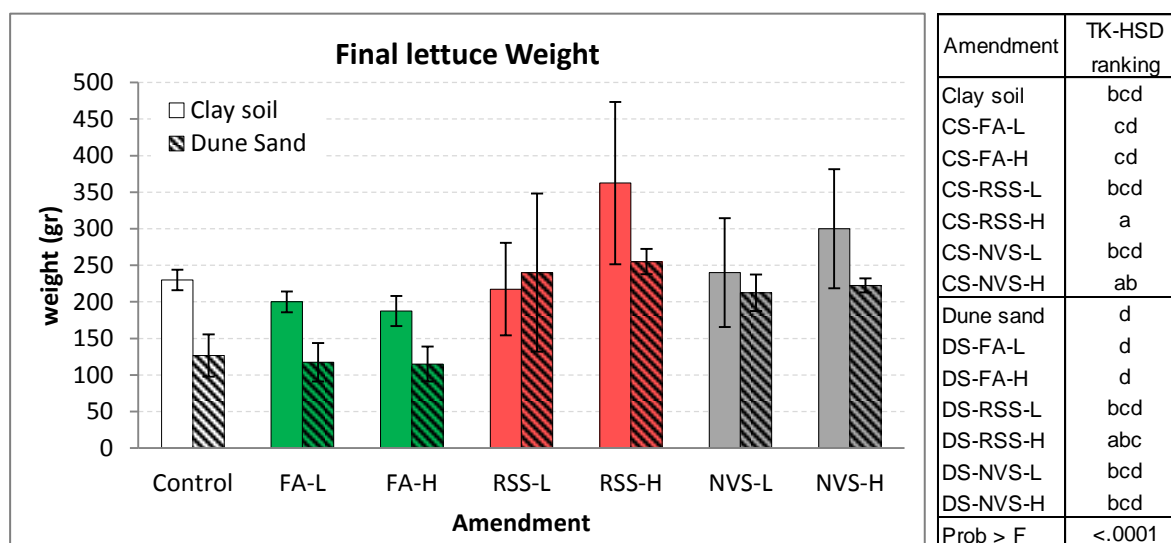


Figure 13: Lettuces average weight (oven dry).

Although no statistical significance exists between the lettuces final weights, except for the high load of RSS in both soils, a clear increase in plant development were observed for RSS and NVS additions (see figs. A5-A7). Perhaps four replicates were not enough to provide a credible statistical rank.

5.3.3. Plant uptake

Plant uptake results are presented for the four studied COPCs (As, B, Mo and Se), which are highly leachable from FA and have significance in plant or human health. The plant uptake results for Cd and Pb are also presented as these toxic elements have published food standard limits for leafy vegetables (Israeli Ministry of Health, 2017). In addition, Cr and P plant uptake data are presented in figures A8 and A9.

5.3.3.1. Arsenic uptake

It has been previously reported that As tends to accumulate in roots and old leaves (Thoresby and Thornton, 1979), but plants developed at low As content showed that higher accumulation took place in the leaves (Tlustos et al., 1998). Hence, lettuce crops are more likely to accumulate higher As amounts as a function of its content in the growth media. Normal As concentrations in lettuce have been reported to be in the range 0.02-0.25 mg/kg (Kabata-Pendias and Pendias, 2001). This value is much lower than the upper As food standard in leafy vegetables of 5 mg/kg (dry weight basis; Table A5; Israeli Ministry of Health, 2017).

Arsenic concentrations in the lettuce canopies are presented in figure 14. Inasmuch as the application of FA and NVS at both soils increased, As in the canopies contained 6-7 times more compared to the non-amended controls and the RSS treatments. Nevertheless, the concentrations in the plants never exceeded one-tenth of the ceiling value, and at low load additions (i.e., permitted values) resulted within the reported range of As concentrations in lettuce (Kabata-Pendias and Pendias, 2001; Imura, 1981, Kosta et al 1974; Lag and Steinnes, 1978; Laul et al., 1980; Porter and Peterson, 1975; Shacklette et al., 1980). The RSS treatments had no increase of As concentrations compared to the not amended controls (5 and 0.9 mg/kg in the clay soil and dune sand, respectively).

Arsenic uptake under FA addition was lower in the clay soil treatments than in the sand treatments probably due to adsorption on the clays. This trend was also observed in the As leachates concentrations (see following section 5.3.4.1.).

5.3.3.2. Boron uptake

Boron uptake is proportional to its concentration in the growth media and the water flow (Jin et al., 1987; Szabo, 1988). In addition, FA is known to be a source for B uptake by plants (Kabata-Pendias and Pendias, 2001). Therefore, with the exception of crops from untreated controls that show an almost identical uptake from both soils, all B concentrations presented in figure 15 were higher in crops developed in clay soil amendments with higher values related to FA containing treatments (CS-FA-H, 95 mg/kg and CS-NVS-L 100 mg/kg). In contrary, in the dune sand, the highest concentration of 78 mg/kg was found in lettuces developed in non-treated controls. The difference between the two amended soils is due to physical properties. The ability of the clay soil to keep higher water capacity than the dune sand and therefore to provide the plant with more soluble nutrients. Nevertheless, within the variance of the replicates of the treatments, no statistical significance was observed between the controls and the treated ML. It is important to emphasize that B was introduced into the soils through several paths including the irrigation water, fertilizer and FA. Although there are no safety limits for B in leafy crops, the concentrations measured were compared to previously reported lettuce leaves and all were higher than the mean of 1.3 mg/kg (Kabata-Pendias and Pendias, 2001; Shacklette et al., 1978). However, the B concentrations measured in the lettuces were in the range of normal concentrations for mature leaf tissues of various species (10-100 mg/kg; Kabata-Pendias and Pendias, 2001). On a farther note, some plant distress observed in several crops was possibly related to B sensitivity (see figure A10).

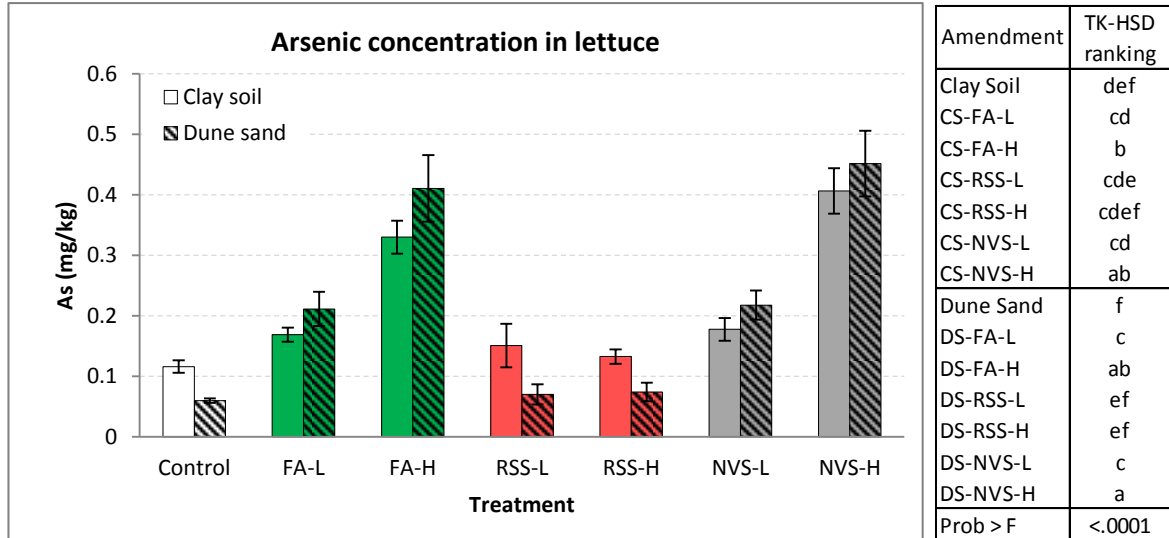


Figure 14: Arsenic concentration (mg/kg) in lettuce.

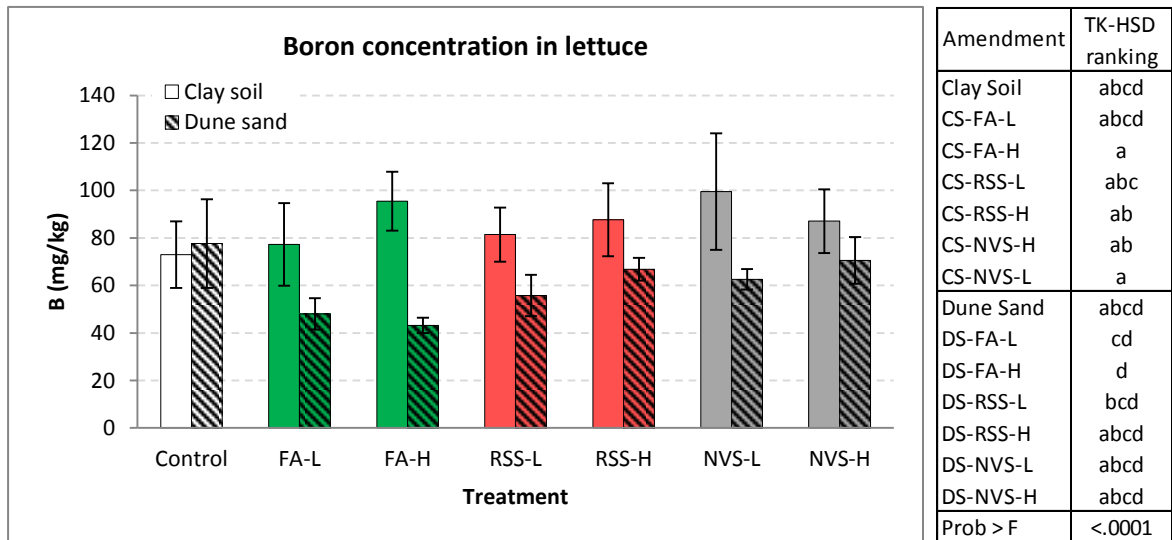


Figure 15: Boron concentration (mg/kg) in lettuce.

5.3.3.3. Molybdenum uptake

Molybdenum uptake by plants usually correlates with soil pH, and high soluble concentrations are observed at high pH (Doyle et al., 1973). Therefore, FA addition to soils is expected to cause higher Mo accumulation in lettuce crops due to the pH elevation. However, in the results presented in figure 16, Mo concentrations in non-amended controls were almost identical in both soil types (0.8 mg/kg in dune sand and 0.7 mg/kg in clay soil). Compared to the controls, additive-soil mixtures show higher concentrations of Mo in clay amendments than dune sand. With the exception of CS-RSS-L amendment, all other RSS-soil mixtures show no difference compared with the control crops Mo uptake. Nevertheless, despite CS-RSS-L high mean value of 1.5 mg/kg there is no statistical significance that additional RSS increased Mo concentration in lettuce. The FA and NVS treatments increased Mo concentrations in the high loads crops. The highest Mo concentration of 3.1 mg/kg that was measured in lettuces developed with the high load of FA in clay soil (CS-FA-H) is 4.5 times higher than the control. Similarly, the high NVS addition to both soils were found to be much higher than the controls (2.6 mg/kg in CS-NVS-H which is 3.5 times than the control and 2.8 mg/kg in DS-NVS-H, which is 3.8 times than the control). Compared to reported Mo content in lettuce leaves of 0.074 mg/kg (Kabata-Pendias and Pendias 2001), all Mo concentrations in lettuces produced in this experiment were 1-2 order of magnitude higher. These high values, even of the control lettuces, may have been caused by the Mo concentration of 9 mg/l in the irrigation water that contained a fertilizer. Nevertheless, the Mo concentrations found in the lettuces are in the range of published mature leaf tissues (0.2-5 mg/kg; Kabata-Pendias and Pendias, 2001).

5.3.3.4. Selenium uptake

The most significant factor affecting Se accumulation in plants is Se concentration in the soil (Adriano, 1986; Alloway, 1968; Mikkelsen, et al., 1989). Among other factors (e.g., pH, soil mineralogical composition and plant species), soil texture had also proven to have major influence on Se uptake (Alloway, 1995). Plants grown on sandy soils have been found to contain significantly more Se compared to those grown on silt-loam-clay and organically amended soils (Jonsson, 1991; Cary et al., 1967).

As opposed to previous findings, in this experiment, soil texture did not show any significant influence on Se uptake by the lettuces (Fig. 17), as mean lettuce concentration grown on clay soil of 0.35 mg/kg is slightly higher than dune sand (0.27 mg/kg) without any statistical significance. However, the results indicate that Se uptake increased dramatically due to FA addition to soils, while RSS had no effect on Se concentration in lettuce compared to the untreated controls (all around 0.3 mg/kg). At high application loads, FA and NVS increased Se concentration by an order of magnitude with higher uptake from FA amendments (2.7 mg/kg in DS-FA-H, and 3 mg/kg in CS-FA-H) which were 8.5 times than the controls compared to NVS (1.9 mg/kg in DS-NVS-H, and 1.7 mg/kg in CS-NVS-H) which are 5-6 times more than the control. Also the low FA and NVS loadings increased Se concentrations in lettuce compared to the controls (CS-FA-L, CS-NVS-L and DS-NVS-L by 2.5 times and DS-FA-L by 4.2).

The higher Se accumulation in lettuces grown in FA and NVS amendments can be explained by the pH of the growth substance. Fly ash and lime are responsible to the pH elevation of the soil-additive mixture (Table 5). As previously mentioned, Se leachability increases at higher pH values. Therefore, in the naturel pH values of the mixtures (Table 5), FA and NVS amendments are more likely to release Se to soil solution and make it available to plant uptake.

With the exception of FA, all amendments resulted with Se concentration within the range of mature leaf tissues (0.1-2 mg/kg; Kabata-Pendias and Pendias, 2001). However, compared to reported Se content of lettuce crops from the USA (0.06 mg/kg; Oakes et al., 1977; Shacklette., 1980), all lettuces produced in the ML experiment were higher.

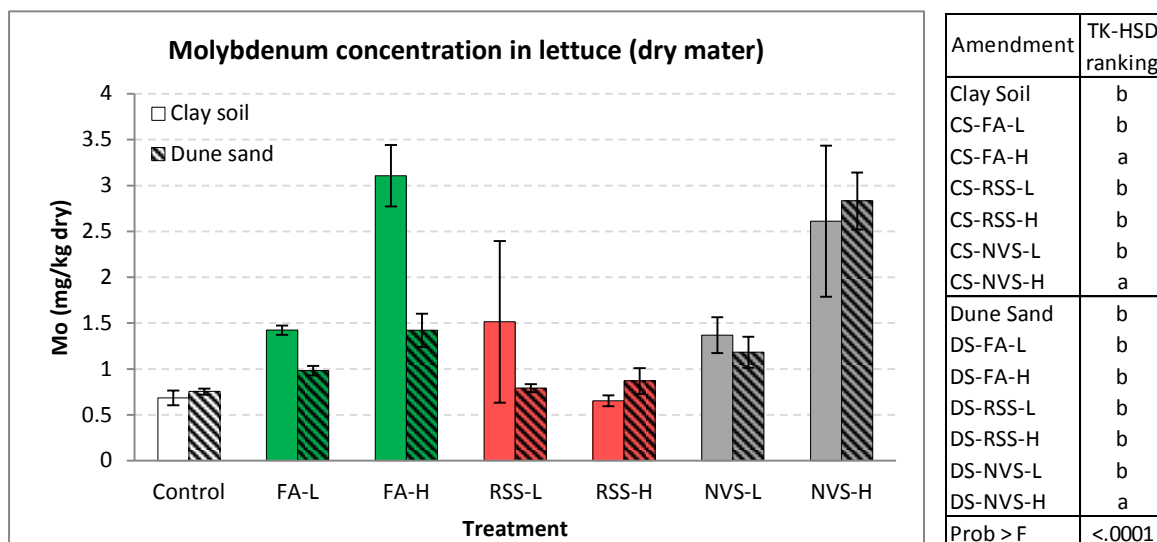


Figure 16: Molybdenum concentration (mg/kg) in lettuce.

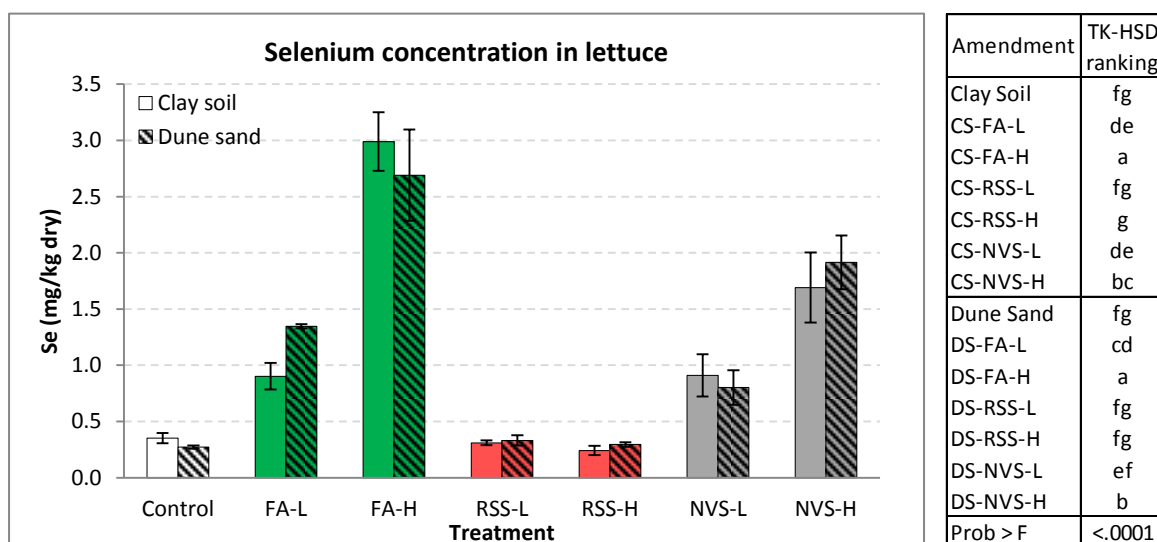


Figure 17: Selenium concentration (mg/kg) in lettuce.

5.3.3.5. Cadmium uptake

Cadmium uptake by plants is affected by various parameters (e.g., plant type, soil salinity, pH, clay fraction, organic matter and phosphorus content) although, in most cases, linear relationships between Cd in plants to Cd in growth medium have been found (Jones et al, 1987; Kabata-Pendias and Wiacek, 1985; Christensen et al, 1991). In addition, Cd is easily absorbed by plants and tends to accumulate spatially in roots and leaves (Bini et al, 1995; Kabata-Pendias and Wiacek, 1985).

The ML study resulted in higher Cd concentrations in lettuces developed in FA and NVS soil mixtures compared to the controls and RSS treatments (Fig. 18). The elevated concentrations were up to four times more in the case of clay soil control and nine times more in the case of dune sand. It should be noted that even the highest concentrations did not reach the food safety limit for leafy crops of 1 mg/kg.

Compared to the controls, the RSS increased Cd concentration in the lettuce but with no statistical significant. Bolton and Thorose (1997) has noted that high organic matter content in soil leads to decreasing in Cd availability while others claim that Cd availability to crops on a sewage sludge amended soil does not indicate immobilization of Cd under influence of increased organic matter content (Tichý et al., 1997). However, Henning et al. (2001) relate the higher extent of Cd availability in sludge treatments to mineralization of Cd from organic complexes to inorganic forms unobtainable for plant uptake.

Fly ash and NVS additions led to major elevation in Cd concentrations with a direct connection to their loading extent. The high FA load treatments led to high Cd lettuce accumulation (0.49 mg/kg in clay soil and 0.53 in dune sand (compared with 0.04 and 0.1 mg/kg of the controls, respectively). Very similar results were noted also for the high NVS load treatments (0.48 mg/kg in clay soil and 0.55 mg/kg in dune sand). Interestingly, comparing, Cd concentrations between the two soils of any additional material at any load do not show any major difference and all results are within standard deviations.

Cadmium uptake by lettuce plants was mainly affected by the Cd added from the FA rather than soil properties such as pH, organic matter and clay content.

5.3.3.6. Lead uptake

Previous studies reported that Pb content in plants is highly correlated with its soil content (Warren, 1978; Kovalevskiy, 1979). In addition, Wilson and Cline (1966) reported that only a very small fraction (0.003-0.005 %) of the total soil Pb may be taken up by plants and the final accumulated concentration in the plant depends on Pb species and amounts in the soil. Lead concentrations in lettuces are diverse with large standard deviations (Fig. 19). Nevertheless, results that have acceptable standard deviations show that the additives did not increase Pb concentrations in the lettuces but slightly reduces it (0.4 mg/kg in DS-FA-L and CS-FA-H and 0.44 mg/kg in CS-RSS-L) compared to the controls (0.5 mg/kg for both soils).

Zimdahl (1975) and Hughes et al. (1980) have noted that the mode of Pb uptake by roots is passive and that the rate of uptake is reduced by liming. Moreover, in soils where Pb-organic complexes are formed, Ca does not significantly limit the availability of Pb. This can explain the high load of NVS elevated Pb concentrations in the lettuces (0.8 and 0.9 mg/kg in CS-NVS-H and DS-NVS-H, respectively) despite the NVS high Ca concentration.

All lettuces produced in this study resulted in lower concentration than the upper mean Pb content (3.6 mg/kg; Warren et al., 1970) reported for lettuces (Kabata-Pendias and Pendias, 2001). In addition, despite the high standard deviations and with the exception of CS-RSS-H (1.1 ± 0.6 mg/kg), all the lettuce Pb concentrations produced in this study are lower than the safety limit of 1.5 mg/kg (Israeli Ministry of Health, 2017).

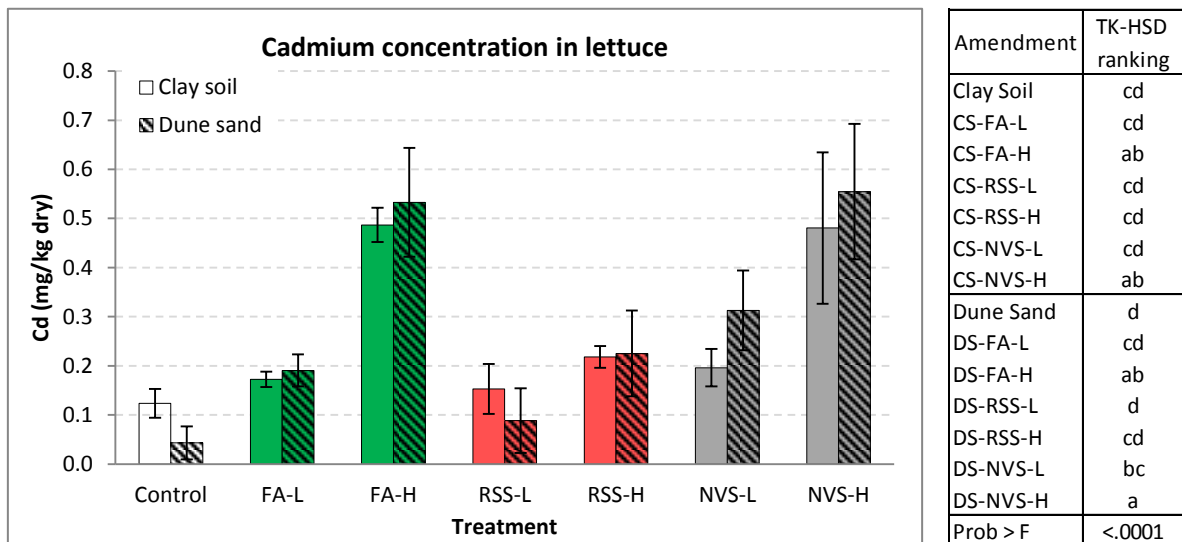


Figure 18: Cadmium concentration (mg/kg) in lettuce.

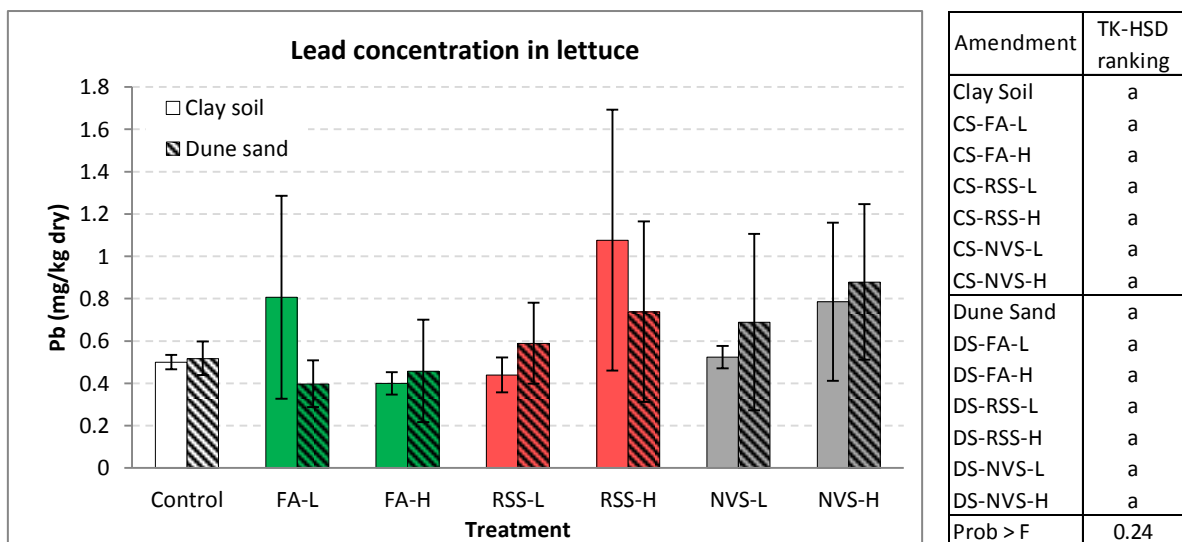


Figure 19: Lead concentration (mg/kg) in lettuce

5.3.4. Mini-lysimeters leachate concentrations

Elemental concentrations in ML leachates from both amended and non-amended soils of planted and reference materials are presented in figures 20-23. The Israeli standards for drinking water and long-term irrigation are displayed for evaluation. The leachates represent concentrations prevailing at the bottom of the soil and soil mixture layer and by no mean imply concentrations that might be encountered in the unsaturated zone, and hence could not be taken as values for groundwater contamination (Keren, 2013). Note that L/S ratios could differ between treatments despite the equal irrigation provided as plant growth extent ensuing water consumption varied. In addition, irrigation of the non-planted ML continued after harvesting the lettuces, resulting in higher L/S ratios (Tables, 6 and 7).

Table 6: Planted mini-lysimeters cumulative L/S.

Amendment	Sampling number			Total L/S
	1	2	3	
P-CS	0.44	0.79	1.14	1.68
P-CS-FA-L	0.41	0.78	1.21	1.43
P-CS-FA-H	0.29	0.61	1.05	1.30
P-CS-RSS-L	0.30	0.50	1.13	1.84
P-CS-RSS-H	0.24	0.34	0.59	1.04
P-CS-NVS-L	0.26	0.41	0.77	1.46
P-CS-NVS-H	0.29	0.42	0.68	0.80
P-DS	0.32	0.68	1.24	1.97
P-DS-FA-L	0.43	0.85	1.29	1.94
P-DS-FA-H	0.25	0.56	1.02	1.49
P-DS-RSS-H	0.26	0.50	0.74	1.08
P-DS-RSS-L	0.25	0.44	0.71	1.06
P-DS-NVS-L	0.31	0.59	0.93	1.32
P-DS-NVS-H	0.24	0.51	0.75	1.05

Table 7: Non-planted control mini-lysimeters cumulative L/S.

Amendment	Sample number								Total L/S
	1	2	3	4	5	6	7	8	
CS	0.37	0.95	1.46	2.33	3.00	3.63	4.05	4.59	5.15
CS-FA-H	0.37	0.90	1.32	1.86	2.36	2.82	3.17	3.31	4.59
CS-FA-L	0.29	0.80	1.18	1.92	2.38	2.73	3.01	3.48	3.58
CS-RSS-L	0.26	0.56	0.82	1.23	1.49	1.84	1.97	2.32	3.70
CS-RSS-H	0.43	0.90	1.27	2.05	2.75	3.27	3.59	4.26	5.04
CS-NVS-L	0.40	1.01	1.55	2.46	3.30	4.07	4.69	5.63	6.64
CS-NVS-H	0.35	0.84	1.12	1.79	2.39	2.78	3.14	3.67	4.07
DS	0.39	1.05	1.59	2.22	2.80	3.42	3.93	4.55	5.13
DS-FA-L	0.29	0.77	1.20	1.91	2.54	3.16	3.69	4.41	4.92
DS-FA-H	0.18	0.42	0.68	1.02	1.36	1.92	2.20	2.92	3.69
DS-RSS-L	0.24	0.67	1.09	1.78	2.39	2.87	3.34	3.76	4.16
DS-RSS-H	0.18	0.45	0.72	1.43	2.09	2.77	3.30	3.81	4.25
DS-NVS-L	0.19	0.66	1.13	1.88	2.48	3.10	3.56	4.04	4.40
DS-NVS-H	0.30	0.84	1.26	1.91	2.51	3.13	3.65	4.31	5.05

Leachability of Cd, Cr and Pb were found to be minor and not related to FA addition to soils.

Therefore, data of these three elements are presented in the appendix figures A11-A13.

5.3.4.1. Leachability of arsenic

Arsenic concentrations in the leachates from the non-planted and planted clay soil treatments were all in the same order of magnitude (0.003-0.06; Figs. 20A and 20B), and as the L/S increased the concentration gradually decreased. The dune sand treatments showed the same trend except for the FA treatments where As concentrations tended to increase at increasing L/S (Fig. 20A). A possible explanation is related to reduction of Fe (III) to Fe (II) that would result in loss of As sorption to Fe (III) and concurrent increasing elution of As with Fe. In percolation column on similar materials, this trend has been observed (unpublished data).

This general decreasing trend as a function of L/S is well known (e.g., Weibel et al. 2017). Moreover, other studies that used ML to monitor trace elements leachability described reduction of As concentrations as a function of L/S, time and soil depth (Hjelmar 1990).

In each planted ML, leachate As concentrations were consistently higher in the high load than in the low load counterpart treatments (Fig. 20C and 20D). Inasmuch as the non-amended clay soil released more As to the leachate than the non-amended dune sand, As concentration from all amended clay soil treatments were lower than those from the dune sand counterparts. At the same load, NVS treatments leachable concentrations were the highest. While all As concentrations in the leachate from the clay soil treatments were below the DWI (0.1 mg/l), most concentrations from the sand treatments were above it, yet usually (leachates at L/S < 0.5) were below the IWI (1 mg/l). Almost all As concentrations decreased to some extent with increasing L/S. In contrary, in the non-amended dune sand, an increase was observed (from 1.2 to 7 µg/l; Fig. 20C), which may be a result of the fertigation.

Although As concentration leached of NVS-soil mixtures presents a moderate decreasing trend, As leachability can be described as “first-flush” leaching as all initial concentrations measured were at maximum value. However, FA-soil mixtures did not follow the “first-flush” leaching characteristic as most As concentration stayed stable throughout the experiment and in the FA-dune sand mixtures (non-planted ML), it even increased. This trend correlates well with the sample pH as the As concentration increased as the pH raised.

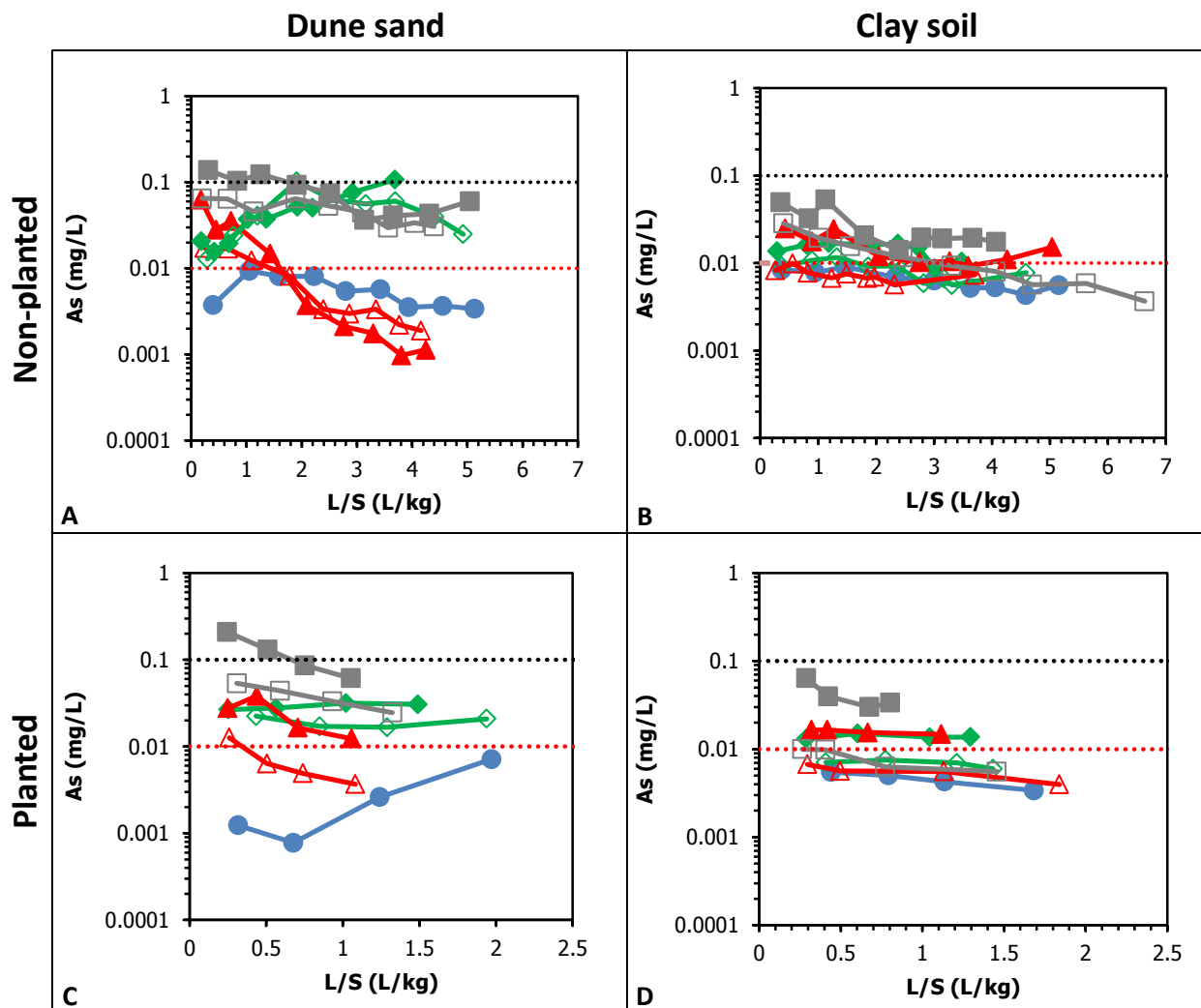


Figure 20: Arsenic leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).

5.3.4.2. Leachability of boron, molybdenum and selenium

These three elements show similar trends. Clearly, the FA addition to the two soils affected the leachability of B, Mo and Se, as higher concentrations were leached from the FA and NVS amendments, especially in the high load applications. The RSS addition had no or only minor effect compared to the non-amended controls (Figs. 21-23). In addition, all FA containing amendments present a “first flush” leaching trend that is clearer in the dune sand amendments compared to clay soil due to less interaction with the sand surfaces and minimum adsorption.

Both planted and non-planted FA and NVS dune sand amendments at both loading rates show the same leachability trend for both B and Mo (Figs. 21 and 22), with concentrations decrease as a function of L/S. In contrary, B and Mo concentrations leached from the FA and NVS clay soil amendment stay stable. The Se leachability trends of FA and NVS soils amendments are similar with a decreasing pattern for both soils (Fig. 23), similar to the B and Mo dune sand patterns.

For all three elements, other than the initial leachate collection of dune sand amendments that had slightly higher concentration values than the clay soil mixtures, no major differences were noted in leachability that related to the soil type, implying the elements source is from the FA only.

High B concentrations (around IWI value) were measured for all non-amended controls and RSS-soil mixtures at both planted and non-planted ML leachate. It should be noted that B and Mo safety standard for irrigation water (IWI, 0.4 mg B/l and 0.01 mg Mo/l) are lower than the drinking water criteria (DWI, 1 mg B/l and 0.07 mg Mo/l) due to high plant sensitivity. As previously mentioned, high concentrations of B are found in most ingredients added to the soils in the ML experiment (i.e., irrigation water, fertilizer and FA) that lead to elevated background concentrations. Nevertheless, the results still emphasize the FA and NVS relative contribution to B leachability.

The RSS addition to soils had only minor effect on Mo leachability, especially at planted ML. Planted DS-RSS-LandH and planted CS-RSS-H Mo leachate concentrations increased above IWI value. In addition, RSS slightly increased leachability of Se compared to the non-amended control and this effect was stronger in the clay soil than in the dune sand.

As opposed to all RSS-soil mixture and non-amended controls, FA and NVS addition to both soils lead to major elevated B, Mo and Se concentrations, above DWI and IWI safety standards. Because of the increased leachability in general and of COPCs in particular and for reducing pH and EC, the field is irrigated post NVS implementation and before plantation. The changes in leachate concentrations of FA and NVS amendments as a function of L/S are described in figure A14.

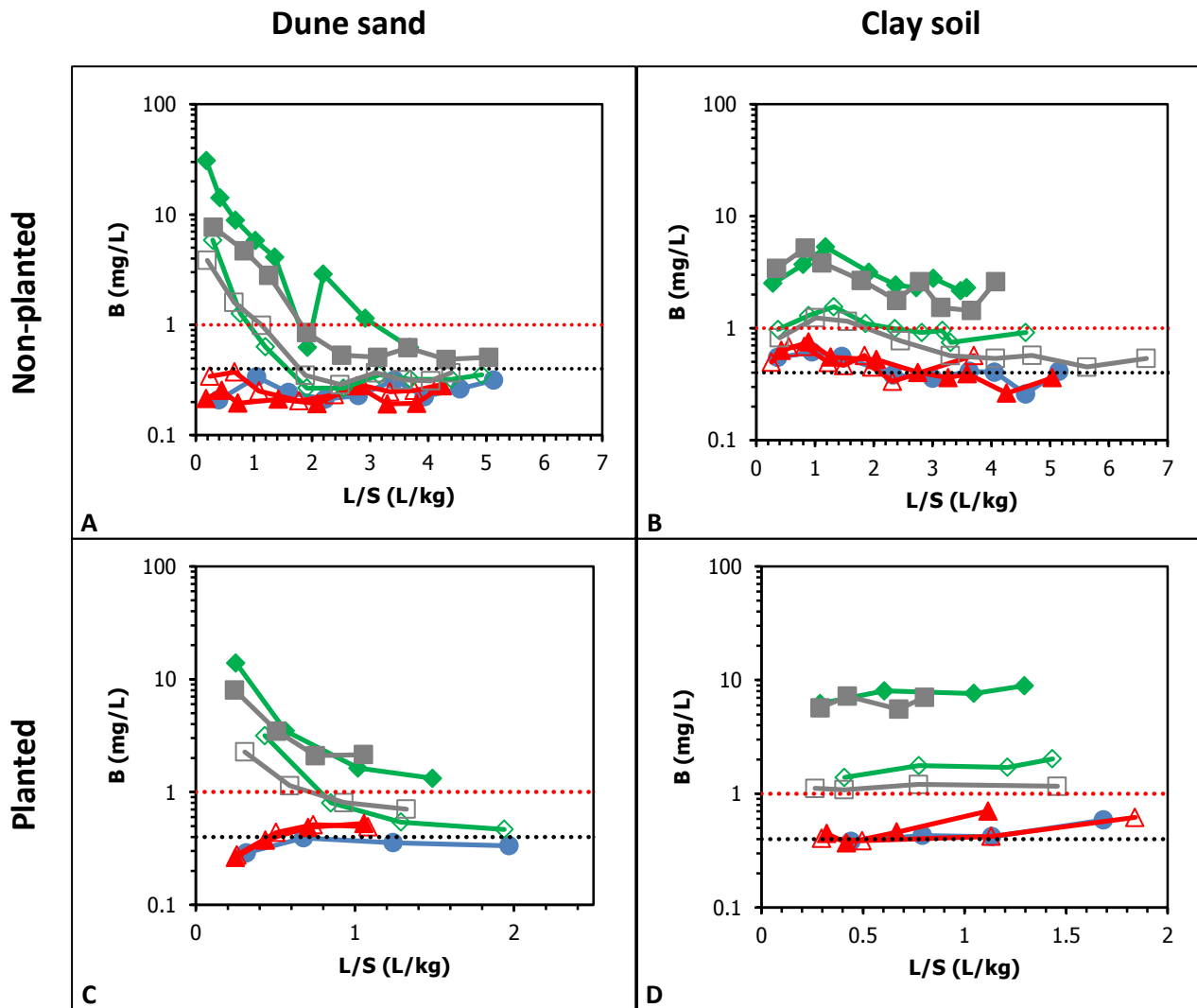
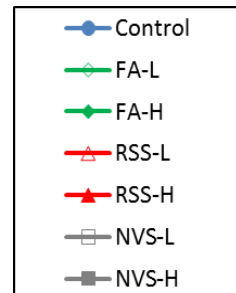


Figure 21: Boron leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).



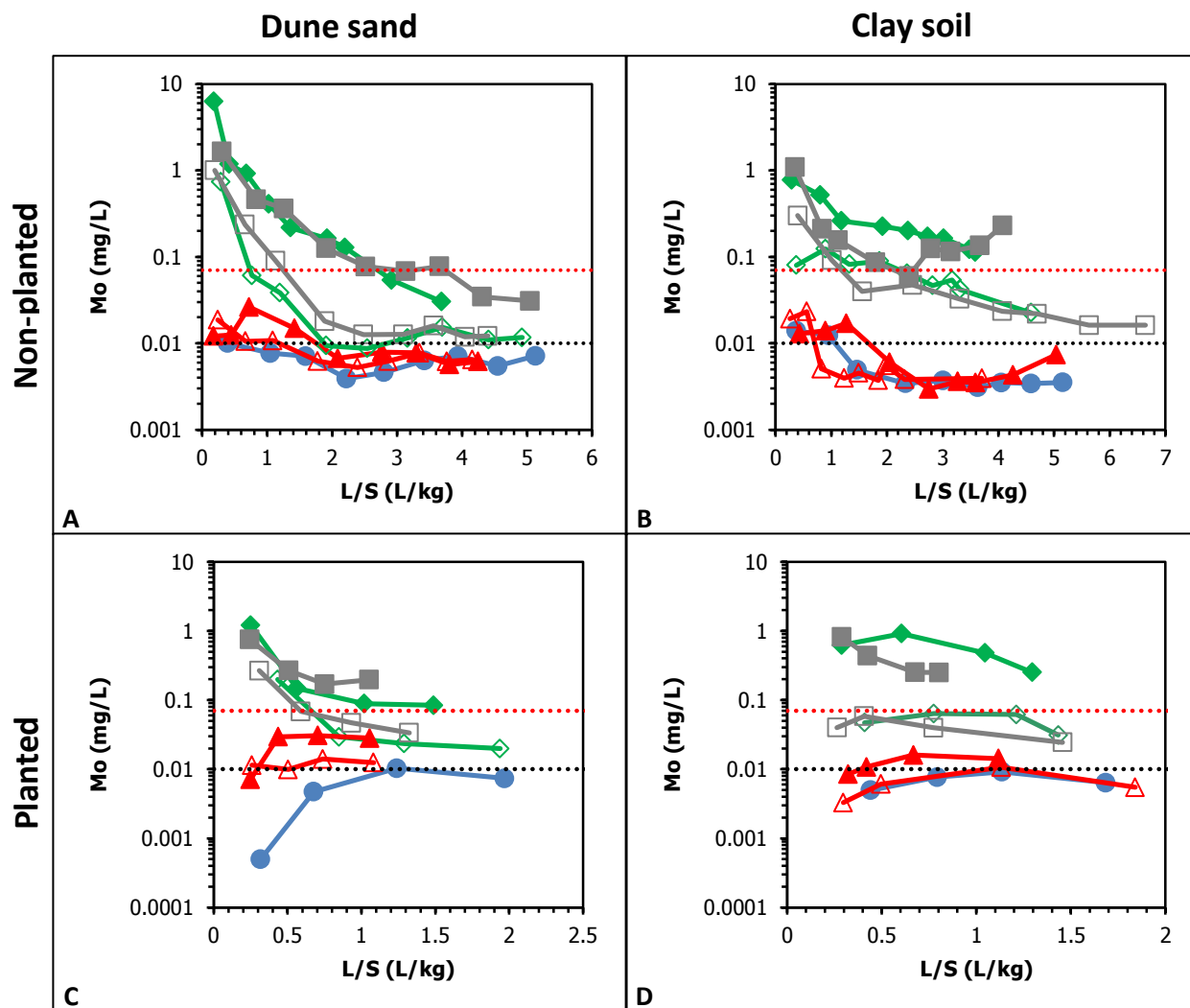


Figure 22: Molybdenum leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).

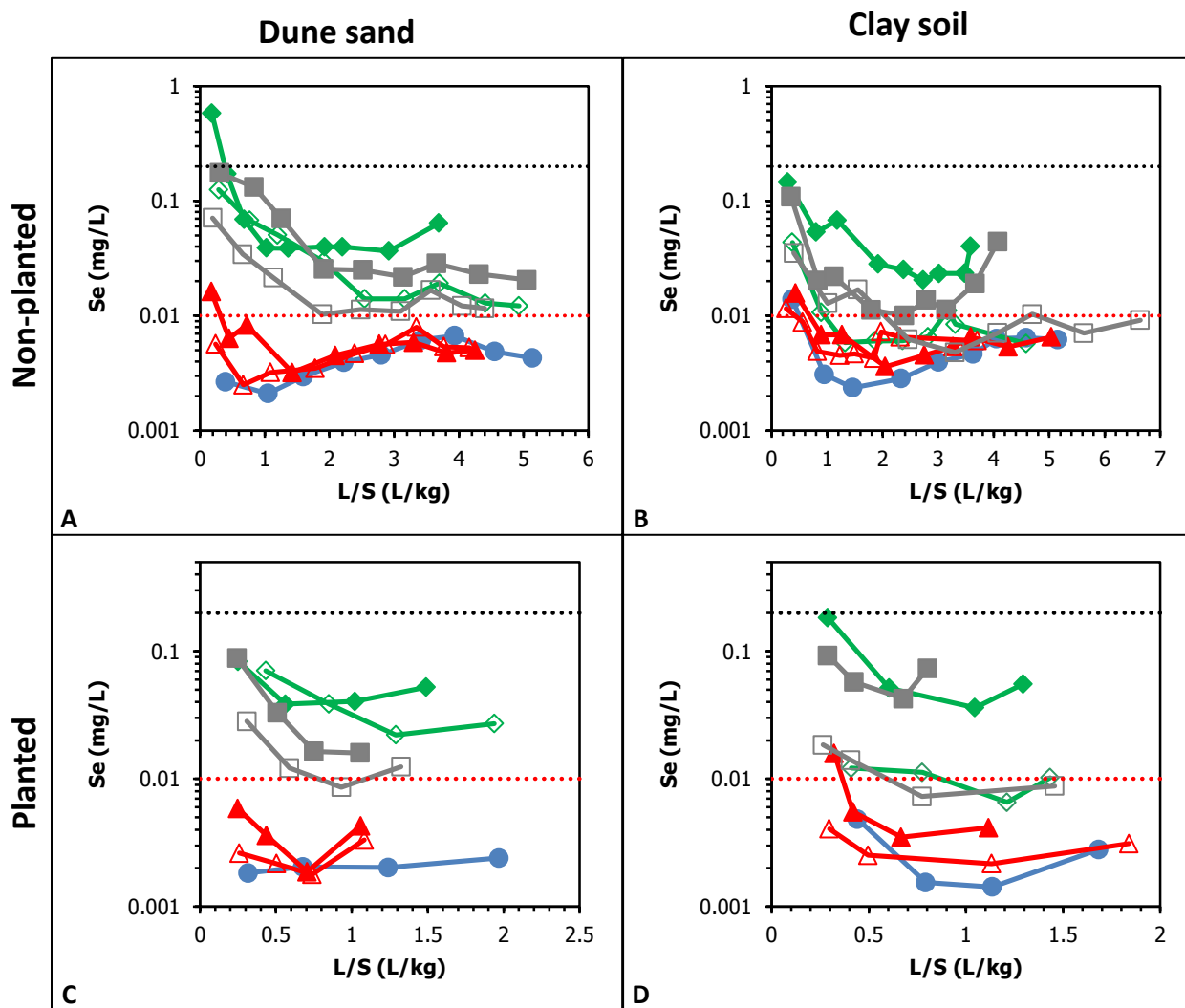


Figure 23: Selenium leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).

5.4. Elements leachability comparison of mini-lysimeters with 1313

Leached concentrations of As, Mo and Se from the soils and their NVS mixtures from the two experiments (i.e., ML and 1313) were compared in order to (1) test the lab-field correlation, (2) to evaluate the option of forecasting elemental leachability by laboratory test (instead of a plantation experiment) and (3) to check if some parameters (e.g, pH, L/S) have dominant effect on trace element leachability. The results are presented in figures 24-26 and each figure includes the concentration of each element (mg/kg) in the pH range 5-9 and additional three horizontal lines: (1) cumulative concentration value of the ML irrigation water (i.e., fertigation) as a red dashed line, (2) the available leachability concentration which is the maximum value leached during the 1313 pH dependent test as green dash-dotted line, and (3) the cumulative leached concentration of each ML marked as a black arrowed line along the leachate pH range. Unfortunately, B concentrations were not comparable due to its high concentration in the fertigation.

Fertigation is expected to have a strong influence on the leached concentrations, and is different for each element depending mainly on the soils properties (e.g., Huddleston, 1994). In this study, the fertigation contained high concentrations of As, Mo and Se, which caused high background levels (Red line in figures 24-26). Moreover, the final sampling of the ML leachate did not exceed an L/S of 7 (at the maximum), which is lower than the ratio used for the 1313 test at L/S of 10. This implies that leached concentrations by the ML with “first flush” characteristics are expected to be higher and lead to higher leachability at low L/S taking place at initial irrigation. With L/S increase, the leachate solution is diluted resulting in lower leached concentrations. Another important difference between the two experiments is the washing intensity applied to the studied soils and soil-mixtures. The contact intensity of the solution during 1313 batch experiment is more aggressive compared to an ML irrigation treatment and therefore, more likely to extract higher trace elements concentrations. In addition, all cumulative concentrations leached from the ML were either similar or lower than the given fertigation. Nevertheless, positive correlations between the two experiments have been observed.

The dune sand contains very low As amounts (0.9 mg/kg; Fig. 5B) with limited leachability that occurs only at acidic pH (< 6; Fig. 7A), therefore the only source for elevated As concentrations in the non-amended dune sand ML leachate is fertigation (Fig. 24A₁).

Generally, As leaching from dune sand amendments was constantly higher in ML than in the counterpart 1313 leachate due to minor ability of dune sand to absorb the additional As added by fertigation. In the clay soil comparison, better correlation was found with increasing NVS loadings ($CS < CS-NVS-L < CS-NVS-H$). A very good correlation exists between the two experiments in the pH range appropriate for the Israeli soil environment (7-8.5) for the CS-NVS-H (Fig. 24B₂). This may be explained by As and organic matter loadings in the NVS-soil mixtures. The content of soil organic carbon may reduce the adsorption of As possibly due to the coverage of binding sites on mineral surfaces (Kaiser et al., 1997). Therefore, at the high addition loading of NVS to clay soil, there is probably a reduction in the capacity of adsorption sites due to the high content of organic matter in both ML and 1313 experiments and therefore the remaining As leached concentrations are similar. Moreover, the interaction between natural organic matter (NOM) and As may facilitate the mobility of As from soils and sediments, resulting in increased As concentrations in groundwater (Redman et al., 2002).

The Mo pH dependent data shows a clear trend of increasing concentration as a function of pH, which does not match the ML results. The concentrations leached from both dune sand and clay soil ML are surprisingly similar, an unexpected phenomenon due to Mo tendency to form complexes with organic matter that is higher in the clay soil. Soil Mo is strongly influenced by soil conditions and additional fertilizer, which have a direct effect on Mo geochemistry (Alloway, 1995). Moreover, the maximum available content leached at pH 6 (Fig. 10A) is lower than the cumulative Mo concentration in fertigation. This indicates that Mo leached from the ML is dominated mainly by fertigation and is less influenced by Mo total content in the growth media and the leachate pH. This observation is supported by the work of Liu et al. (2009) who had noticed a synergetic effect that increased Mo availability to plants and raised grain yield and quality while incorporating Mo and P fertilizers. Nevertheless, other than the untreated control dune sand, Mo concentrations leached from clay soil and all NVS-soil mixtures at both loading rates present better correlation with 1313 at pH>7. Other than undetectable leached concentrations by 1313 test (Figs. 26A₁ and 26A₂), strong Se correlation was observed between the two experiments. All measured concentrations show a great resemblance, especially for the clay soil amendments. This correlation probably relates to Se total load, soil properties and pH. Like As and Mo, the Se results of the non-amended soils emphasize that the main source in the leached ML was

from fertigation, which is higher than the cumulative concentrations of the ML leachate and the maximum available content released by the 1313 test. The high correlation between the ML and 1313 experiments for all NVS treated soils, especially at pH >6 are probably due to Se ability to interact with metal oxides at high pH values (Hingston, 1981). It has been established that metal oxides and aluminosilicates provide surface sites for sorption of heavy metals (McBride, 1989). Therefore, regardless of the high fertigation concentrations, Se leachability was limited probably due to absorption related to solution pH rather than other parameters. To conclude, comparison of the pH dependent and ML results can provide information about the dominant parameters influencing element leachability from the growth media. This comparison yields that As, Mo and Se concentration released in the ML leachate were strongly affected by fertigation background concentrations, mainly in the dune sand amendments. The stronger effect in the dune sand than in the clay soil is due to fewer interactions with soil surfaces and organic matter.

Additional NVS to the soils, especially at high loads applications (NVS-H), increased element leachability up to a point that overshadows the fertigation effect. At these high concentrations, it is possible to notice that element leachability is mainly controlled by the solution pH rather than the L/S ratio, as high correlation between the two experiments was observed although the ML L/S is lower than the 1313 leaching test.

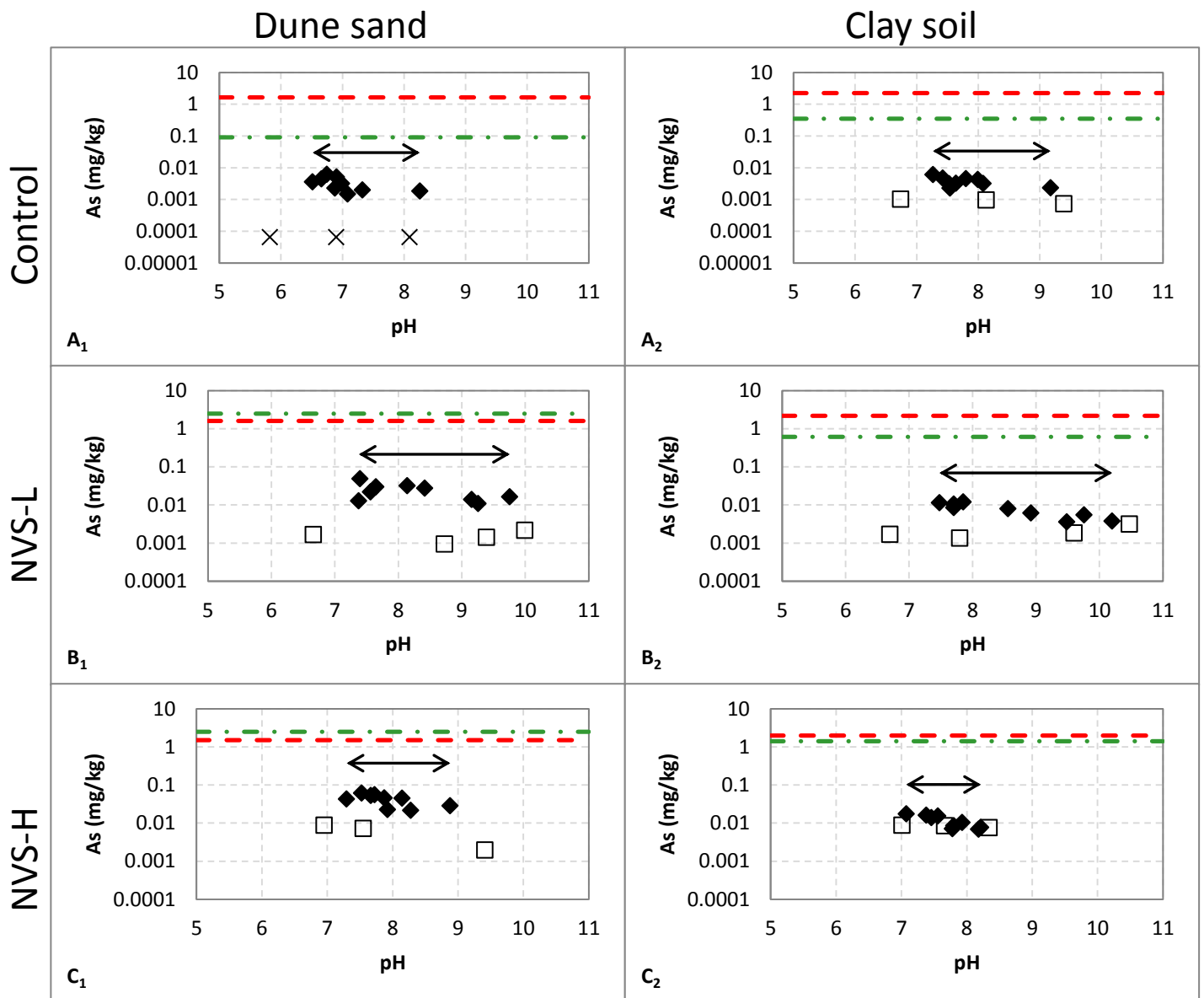
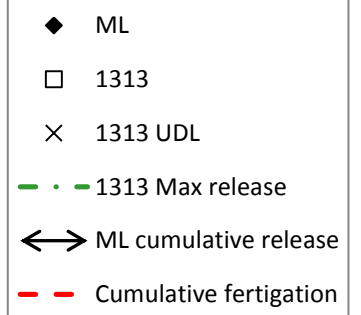


Figure 24: Comparison of As leachability from the non-planted ML and the pH dependent (EPA 1313 method) of non-amended controls and NVS-soil mixtures. The dune sand figures are plotted on the left side and the clay soil on the right. Each ML data point is marked by a diamond and the cumulative concentration of each ML is plotted as an arrow along the pH measured range. The 1313 data below detection limit (UDL) is marked by an X. Arsenic cumulative concentration of the fertigation is marked by a red dashed line and the 1313 maximum release by a dotted-dashed green line.



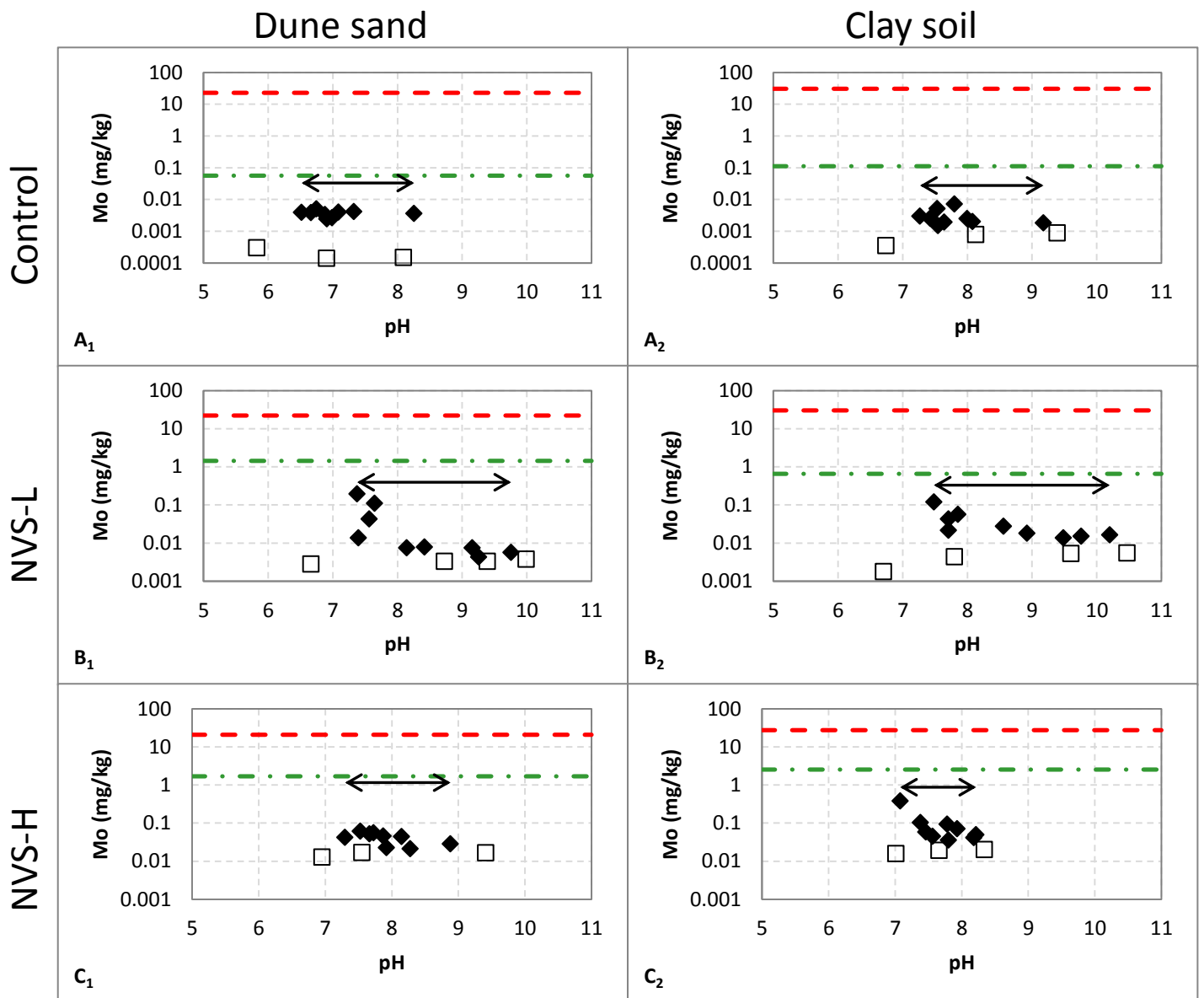
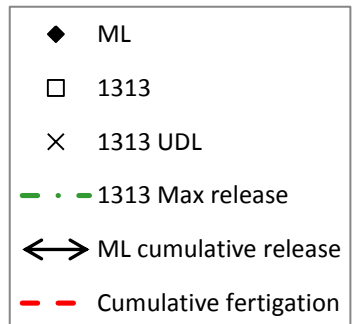


Figure 25: Comparison of Mo leachability from the non-planted ML and the pH dependent (EPA 1313 method) of non-amended controls and NVS-soil mixtures. The dune sand figures are plotted on the left side and the clay soil on the right. Each ML data point is marked by a diamond and the cumulative concentration of each ML is plotted as an arrow along the pH measured range. The 1313 data below detection limit (UDL) is marked by an X. Arsenic cumulative concentration of the fertigation is marked by a red dashed line and the 1313 maximum release by a dotted-dashed green line.



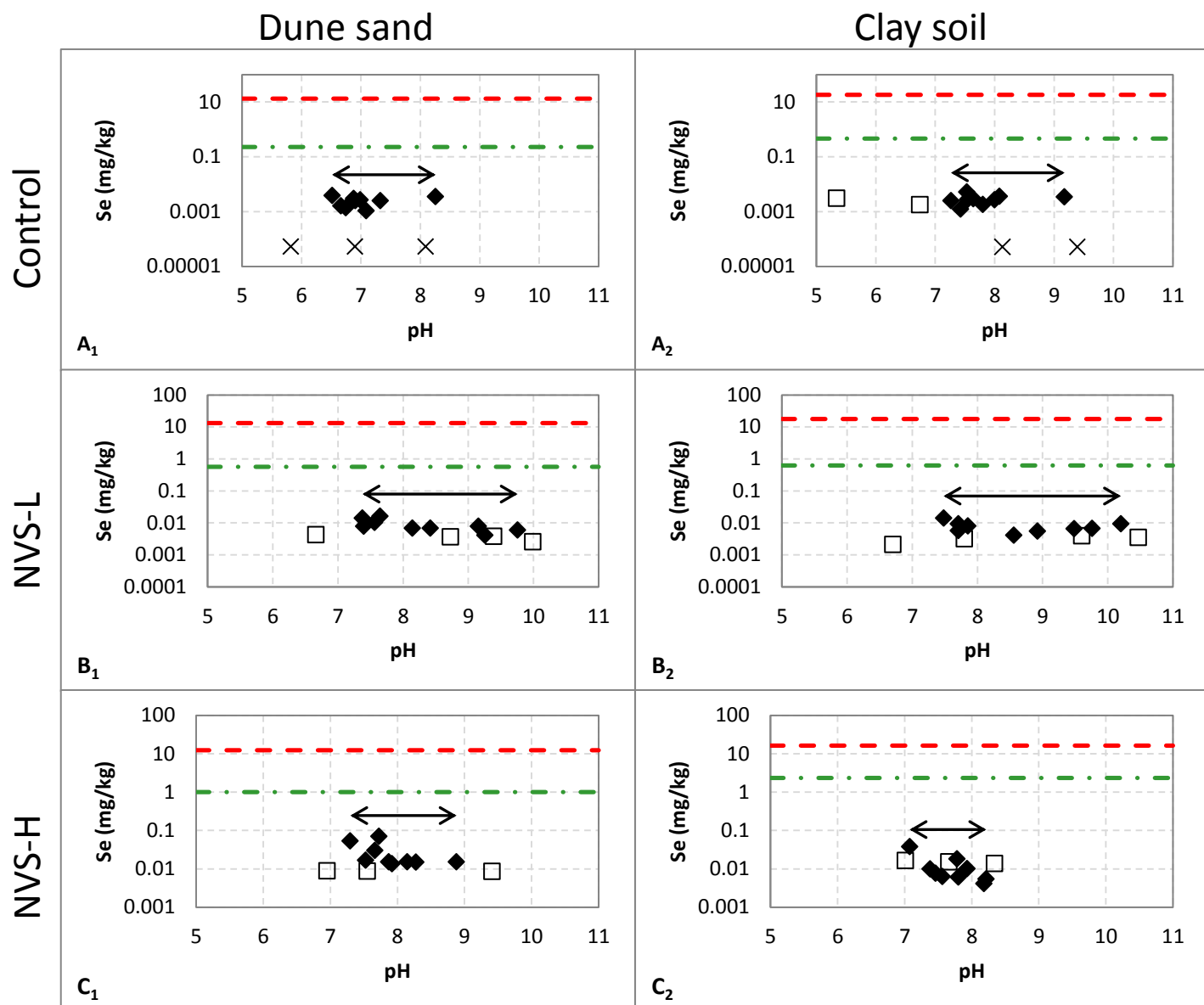
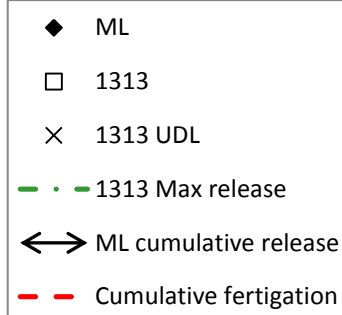


Figure 26: Comparison of Se leachability from the non-planted ML and the pH dependent (EPA 1313 method) of non-amended controls and NVS-soil mixtures. The dune sand figures are plotted on the left side and the clay soil on the right. Each ML data point is marked by a diamond and the cumulative concentration of each ML is plotted as an arrow along the pH measured range. The 1313 data below detection limit (UDL) is marked by an X. Arsenic cumulative concentration of the fertigation is marked by a red dashed line and the 1313 maximum release by a dotted-dashed green line.



5.5. Elements mass balance - amendments leachable fraction and their contribution to plant uptake

Elemental mass balance was calculated in order to estimate the fraction of the element released from the amendments, and its partitioning between leachate and plant uptake. Elements sources include the soil, the additives and the irrigation water (Table 8). Calculations were done for eight constituents of interest comprising both essential and toxic elements.

Table 8: Trace elements contents (mg) of the source materials in the mini-lysimeters.

Element (mg)	Clay	Sand	FA		RSS		NVS		Fertigation	
			Low	High	Low	High	Low	High	Planted L/S≈2	Control L/S≈2
As	7.3	1.8	1.6	8	0.01	0.1	1	5	0.04	0.7
B	34	0.004	9.5	46	0.6	2.8	7	34	1.5	1.3
Cd	0.5	0.1	0.1	0.4	0.01	0.1	0.1	0.3	UDL*	UDL*
Cr	160	12	3	16	0.2	1	2	12	UDL	UDL*
Mo	1.2	0.2	1	5.7	0.02	0.1	0.8	4	0.06	11
P	660	900	50	245	220	1090	240	1190	50	48
Pb	16.2	5.8	1	4.9	0.1	0.6	0.8	4	UDL*	UDL*
Se	0.5	3.9	0.7	3.7	0.01	0.05	0.5	2.5	0.05	8
U	2.6	0.55	0.2	1.05	0.005	0.03	0.2	0.8	0.01	0.01

*UDL – under detection limit

Element release is defined here as the sum of elemental content in the leachate and in the plant canopies (in the planted treatments). Solubilized elements that may have resided in the soil column have not been accounted for. Each pair of columns in figures 27-30 represents planted and non-planted treatments. In each set of figures, A₁ and A₂ represent the elemental release from the control soils (i.e., non-amended sand and clay soil) are denoted by the two columns to the left of the vertical dash line. These values represent the release from the soils themselves and the irrigation water. The net release of each element from the additives is presented in figures B₁ and B₂ as percent of the amount that was (i) present in the soil and added by fertigation in the case of the non-amended soils (defined as control); or (ii) the amount within the additive. The net released amounts from the non-amended ML (control) are depicted by the columns to the right of the vertical broken line. These values are defined as the sum of leached and canopies (in the planted counterparts) contents minus the amounts released from the appropriate control soil at the same final L/S

for planted and non-planted ML (ca. L/S of 2). The As mass balance calculations of the sand dune mixture with low RSS (DS-RSS-L) is described here as an example.

Arsenic mass balance calculations presented in figure 27 were based on the equations provided in chapter 4.4.2 (element composition balance calculation).

The average As amount leached from the ML planted DS-RSS-L (0.0146 mg; Fig. 27A₁) was calculated from the cumulative As leachate concentration (0.007 mg/kg) multiplied by the soil+RSS amendment weight (1.99 kg). The same calculation was applied to the control non-planted DS-RSS-L ML (0.03 mg: cumulative release of 0.017 mg/kg multiplied by the total amendment weight of 1.99 kg). The As amount taken by lettuce plants (0.0005 mg) is calculated as the As concentration in the lettuce (0.07 mg/kg; dry matter) multiplied by the lettuce weight (0.007 kg).

The contribution of RSS to the As release of the planted DS-RSS-L is calculated by reduction of the control dune sand (0.0144 mg) from the planted DS-RSS-L ML (0.0146 mg). This value is presented as percentage of the total As RSS content (0.01 mg). Same calculations were applied to non-planted DS-RSS-L ML (0.034 mg minus the non-amended, non-planted control As leached of 0.033 mg divided by RSS As content of 0.01 mg). In this case, the non-planted RSS contribution is lower than the control value and therefore the percent value in Fig. 27B₁ is negative. The RSS percent contribution to plant uptake were calculated as the As amount in lettuce growth from DS-RSS-L mini-lysimeter (0.0005 mg) minus the As content in lettuce from non-amended control (0.0002 mg) divided by the total As content in the RSS (0.01 mg).

5.5.1. Arsenic mass balance

Evidently, leaching was larger in the sand than in the clay treatments, however, plant uptake was smaller in the sand treatments. In non-planted treatments, the largest As release (0.21 mg As/ML) was for one of the FA and NVS treatments (DS-FA-L and DS-NVS-H). Most of the As released was to leaching, yet a larger proportion was released from the dune sand mixtures (Fig. 27A₁) than the clay soil mixtures (Fig. 27A₂). Thus leaching can be viewed as a mechanism to escape uptake. As leaching was less intense in the clay soil treatments compared with the dune sand ones, elevated As concentrations in the soil solution allowed for more efficient uptake by the lettuces. Still, it was shown that As concentrations in the paired treatments, clay soil and dune sand, were never statistically significantly different. Evidently, the net release of As content was no more than a few percent of the As contained in the additives, except for the RSS, which released up to 65%. The maximum FA and NVS As releases (up to 4%) were from the lower application rate.

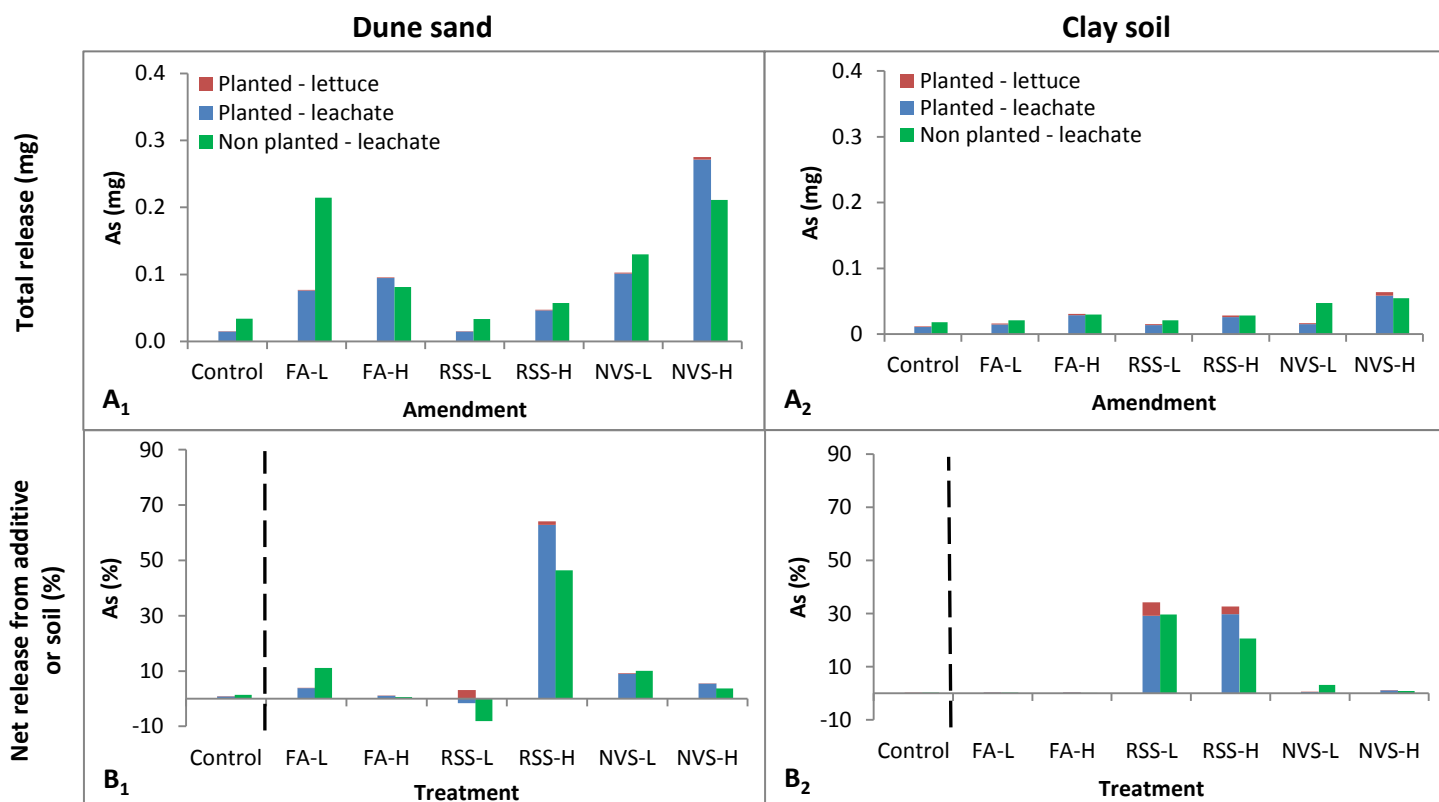


Figure 27: Arsenic mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁ and A₂ show the overall amount released and B₁ and B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A6.

5.5.2. Boron mass balance

As previously mentioned, elevated B quantities reached the growth media through FA and irrigation water with additional fertilizer, resulting in high B releases. The results indicate that FA addition to soil increased B releases to leachate in both planted and non-planted ML (Figs. 28A₁ and 28A₂) although B quantities in the plants were the lowest on those grown on FA amendments in both soils due to smaller plant size.

Boron leachability follows the sequence FA>NVS>RSS. Releases of B from RSS were less than 1mg for all cases and 1.3 mg from CS-RSS-L. With the exception of DS-FA-H and DS-RSS-L, B releases to planted ML leachate from amended dune sand were higher than amended clay soil, with a major release of DS-FA-H of 31.3 mg (see figure 28A₁).

Plant uptake of B was higher at all clay soil ML (untreated control and amendments) compared to the equivalent sand dune ML. Interestingly, the highest B uptake was noticed at CS-RSS-H (1.5 mg) and the second highest at CS-NVS-H (of 1.2; Fig. 28A₂), although it appears that a considerable part of it comes from the irrigation water.

The dune sand B content is negligible (Table 8) and the release from dune sand control is around 100% (Figs. 28B₁). This indicates that B from fertigation and the additional RSS B are taken up by the plant. Similar trend is also observed for the clay soil amendments as most of the RSS releases were taken up by the plant (Fig. 28B₂).

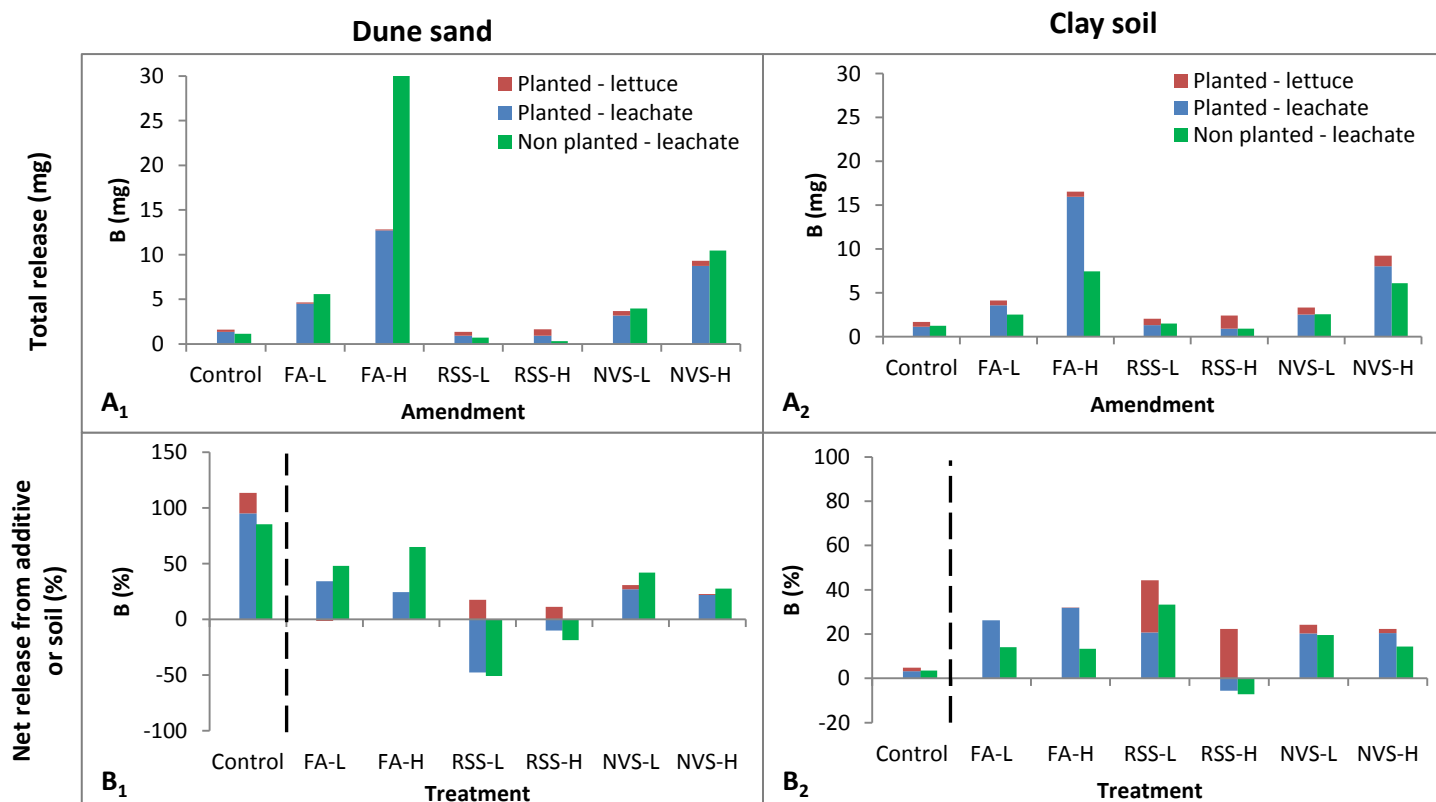


Figure 28: Boron mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁ and A₂ show the overall amount released and B₁ and B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A7.

5.5.3. Molybdenum mass balance

Leachate quantities of Mo from the control soils, did not differ between planted and non-planted ML (0.03 mg from dune sand and 0.02 mg from clay soil). Amendments of FA and NVS (at all applications) increased the leachable amount of Mo. However, RSS addition had no contribution to the Mo content of leachate and even reduced Mo leached amounts when added to clay soil (at both loadings) and to the dune sand low loading (DS-RSS-L).

Greater Mo release to ML leachate occurred at the non-planted dune sand amendments (Fig. 29A₁ and 29A₂), especially those containing FA. The highest release of Mo was from DS-FA-H (4 mg; Fig. 29A₁), more than four times the CS-FA-H releases (0.9 mg). This difference is probably due to higher hydraulic conductivity and lower water capacity of the dune sand, resulting in higher L/S applied and a more intensive wash that leached out a larger portion of soluble Mo from FA in the soils.

Molybdenum plant uptake by the clay soil ML (0.005 mg; Fig. 29A₂) were twice as much the dune sand ones (0.0025 mg; Fig. 29A₁). This trend is reflected in all amended ML in which clay soil-additive mixtures released less Mo to leachate than the associated dune sand amendments. Fly ash addition to dune sand increased Mo leachability, especially at the high loading rate. This is opposed to the plant uptake where almost no effect of the type of treatment was observed. The RSS amendments did not release any Mo to the leachate but contributed to its accumulation in plants (Fig. 29A₁ and 29A₂) with higher values from clay soil amendments (0.015 and 0.009 mg at low and high loads, respectively) than from dune sand (0.003 and 0.007 at low and high loads, respectively). This is probably related to the ability of organic matter to absorb Mo and to provide a slow release from the organic bond forms (Kabata-Pendias and Pendias 2001). Moreover, by comparing the FA and RSS effects on Mo leachability and plant uptake, it appears that RSS enhanced Mo uptake by the plants while FA increased the leachability.

Molybdenum uptake by NVS addition elevated plant content by one order of magnitude compared to the controls. The lettuce uptake was similar for both soils at the low load (0.01 mg for DS-NVS-L and CS-NVS-L) and higher for the high load of clays soil (0.04 mg; CS-NVS-H) compared with the dune sand (0.02 mg; DS-NVS-H). This trend is not surprising considering larger crop production on the clay soil ML than with the dune sand ML (Fig. 13) although with the same Mo concentration of 1.2-1.4 mg/kg at low NVS additions and 2.6-2.8 mg/kg at high NVS additions (Fig. 16).

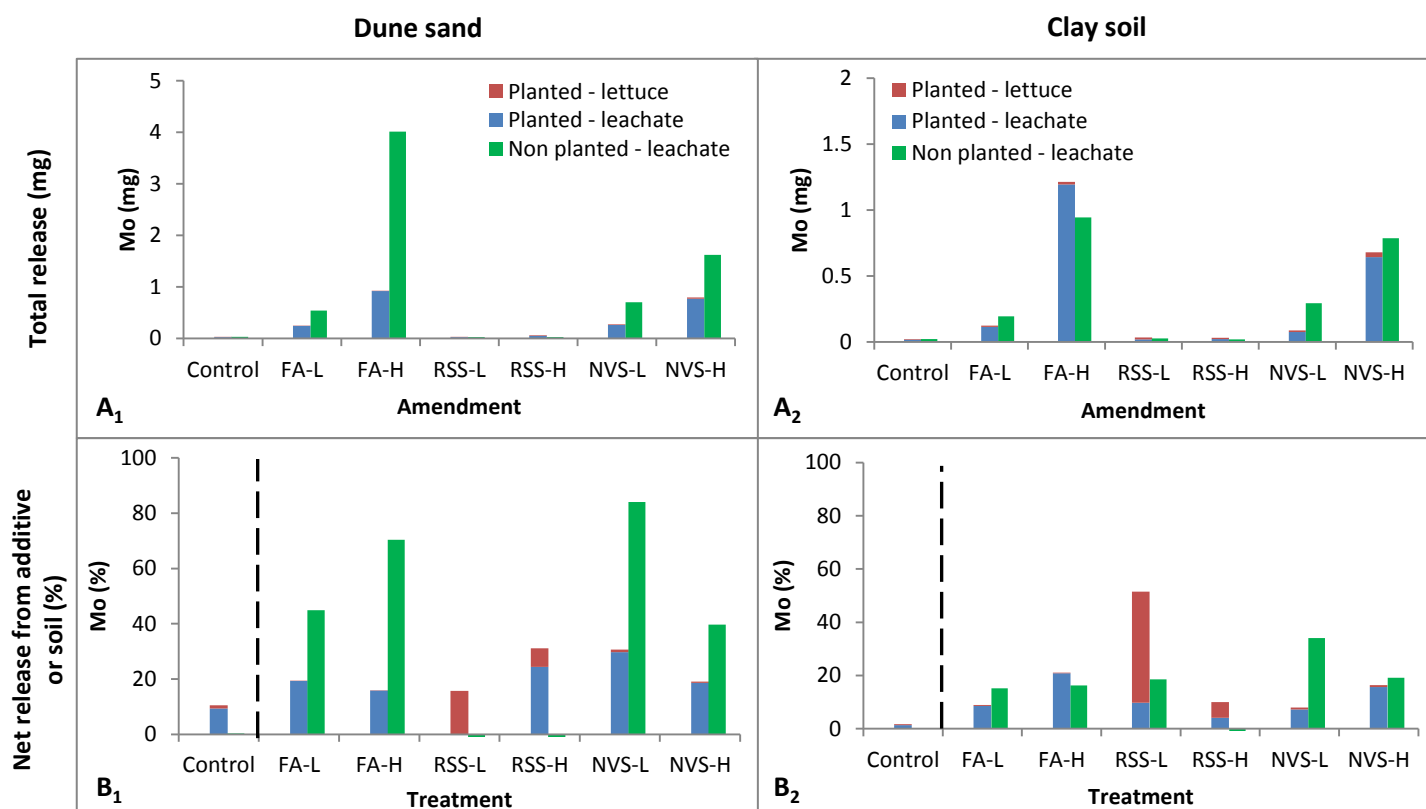


Figure 29: Molybdenum mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁ and A₂ show the overall amount released and B₁ and B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A8.

5.5.4. Selenium mass balance

Similar to the other examined elements, Se releases are higher from the dune sand amendments, and are significantly elevated by FA addition (Figs. 30A₁ and 30A₂). Similar leachability of the non-planted control ML was observed (0.012 mg and 0.013 mg in dune sand and clay soil, respectively). Interestingly, in planted ML, Se releases to leachate were almost identical (0.007 mg and 0.008 mg in both dune sand and clay soil controls, respectively) and somewhat different in the Se lettuce contents (0.003 mg and 0.001 mg, respectively).

In the dune sand amendments, the higher releases occurred by the non-planted ML with a maximum release from DS-FA-H (0.4 mg). Selenium releases to leachate from clay soil amendments were very similar for both planted and non-planted ML. However, the lettuce uptakes of the FA amendments were doubled for clay soil ones compared with the dune sand amendments.

The RSS did not contribute to Se leachability as the high load amendment (DS-RSS-H) released identical quantities as the control and even reduced it when added to dune sand at low load (DS-RSS-L; Fig. 30A₁).

Selenium releases from both NVS-soils mixtures reflects the FA and RSS contents in the ML. Although leached Se amounts were higher from the dune sand NVS amendment, the Se uptake by lettuce was the same in both soil mixtures (0.01 mg and 0.002 mg, in the low and high loads, respectively). As reported in the literature, there is a positive linear correlation between Se in plant tissues and Se content in soils (Kabata-Pendias and Pendias 2001). In addition, total soil Se may provide a better measure of plant response than its soluble fraction (Sippola, 1979; Combs and Combs 1986). However, Alloway (1995) emphasized Se speciation in soils as the marked effect on its plant uptake. Therefore, it appears that Se fractions released by the additives and taken up by plants (Figs. 30B₁ and 30B₂) are related to organic Se forms in the growth media.

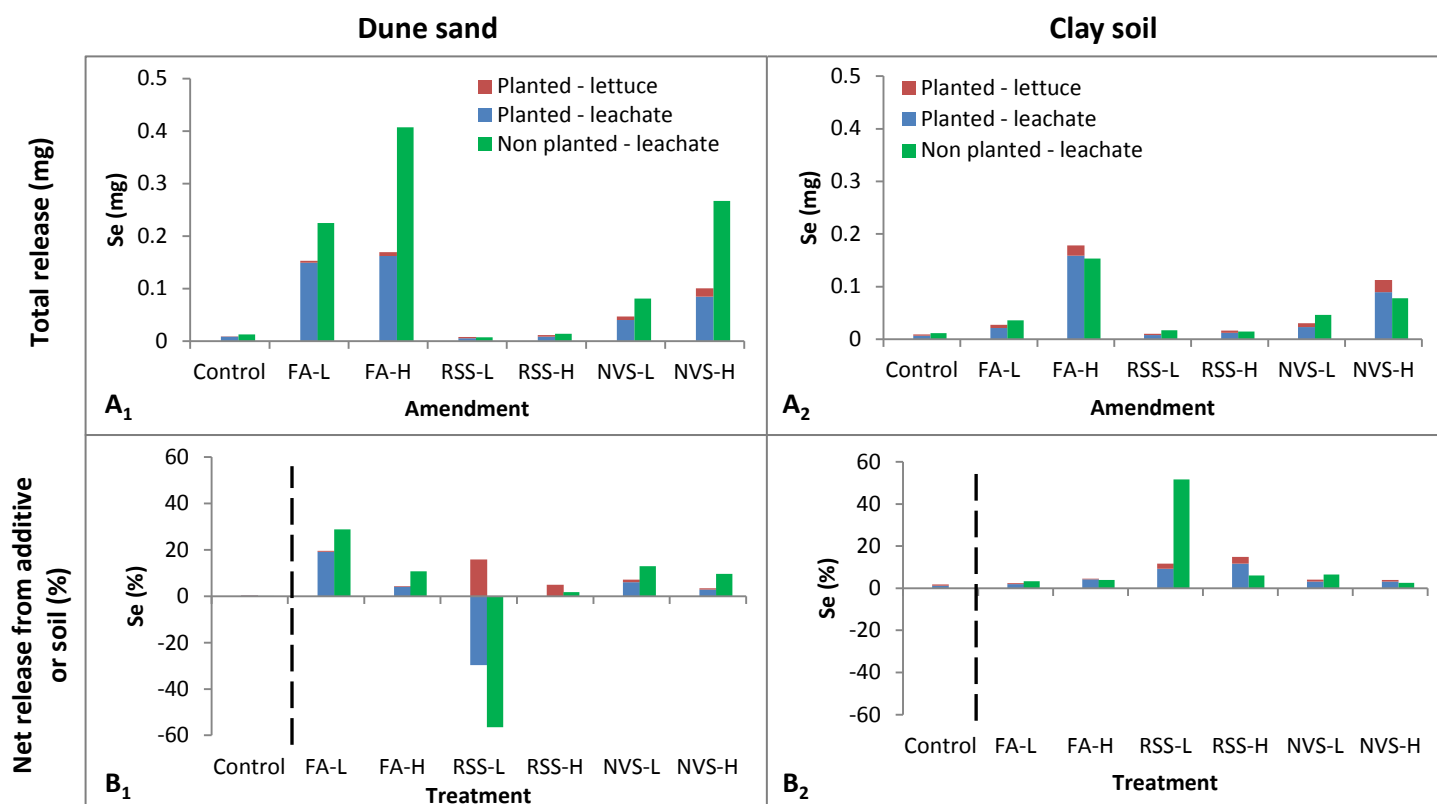


Figure 30: Selenium mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁ and A₂ show the overall amount released and B₁ and B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A9.

6. Summary and conclusions

The main goal of this study was to understand the influences of NVS as an agricultural fertilizer on microelements leachability, benefits for plantation and potential of environmental pollution or toxicity. The approach was to examine NVS and its components, FA and RSS, mixed together with two typical agricultural soils, clay soil and dune sand. Two types of experiments were conducted as part of this attempt, pH dependent leaching test (US-EPA method 1313), and greenhouse mini-lysimeters study. In addition, total content analyses were performed for all raw materials used in these two experiments (i.e., two soils, FA, RSS and NVS).

As NVS is a mixture of 57% RSS (83% organic matter), 38% FA (mostly alumomoisilicats) and 5% lime (CaO), it contains intermediate amounts of its components with 22.7% organic matter, 42% silica and 15.6% Alumina. The FA high amounts of trace elements (e.g., As, B, Ba, Cr, Cu, Mn, Mo, Ni, V and Zn) is reflected in the NVS chemical composition. The raw materials pH dependent curves show high leachability of As, B, Cr, Mo and Se from FA and NVS at a wide pH range. Compared to Israeli standards for both drinking and irrigation water (DWI and IWI, respectively), FA and NVS trace element leachability at natural pH values (i.e., leached with dionized water) was high. Arsenic is the only element that leached at lower than IWI concentration and above DWI while B, Cr, Mo and Se leached at higher concentration than both IWI and DWI standards. The NVS-Soil mixtures were strongly affected by the FA component, as trace elements leached concentrations were higher compared to the non-amended controls, and were well correlated with NVS loading to the mixture (higher addition elevated leachability). At natural pH values, NVS-soil mixtures leached B concentrations were above both irrigation and drinking water standards at all cases while Cr concentrations were under IWI and DWI standards, As and Se concentrations were safe only for irrigation, and Mo concentrations resulted safe for irrigation only at low NVS loadings.

The average lettuce weight (four replicates per treatment) increased with addition of RSS and NVS and slightly decreased by FA addition compared to the control crops, but there is no statistical significance that the treatments actually improve plant size. This insignificance raises questions regarding the design and technicality of the experiment: (a) are four replicates enough to create a credible scale for comparison? (b) were the plantation

conditions (e.g., temperature, sun exposure and space) sufficient to simulate real field conditions?

Elemental concentrations measured in the lettuces (Figs. 14-19) induce that FA and NVS additions to the planting beds increase As, Mo and Se uptake contributed by the FA. Nevertheless, viewing the entire dataset, the lettuce dry weight and elemental mass balance enables to understand the elevated elements concentrations taken by the lettuce. The As and Se uptake by lettuce grown on dune sand was higher due to smaller plant size compared with the clay amendments. In contrary, B and Mo uptake was higher in lettuces developed on clay amendments. These greater accumulations might be explained by higher water capacity the clay soil and its ability to keep the root zone exposed to the soil solution that in this case included high B concentration, and therefore high availability to plant uptake. As for Mo, accumulation was also affected by the exposure of the roots zone to high amounts of water and its high tendency to accumulate in plant tissues (Kabata-Pendias and Pendias 2001), together resulting in high concentrations in more developed crops. Most of the elements examined during this research leached of the ML at low concentrations, some even under detection limit. Arsenic is the only element leached at levels that may raise concern. Fly ash and NVS additions to soil lead also to elevated concentrations of B, Mo and Se in ML leachate compared to non-amended controls. These three elements present a “first flush” behavior with high initial concentrations that decrease as a function of L/S. Moreover, both FA and NVS additions to soils at both loadings increased Mo leachability above IWI although it presents a sharp decreasing trend as the L/S increases. Perhaps a longer experiment with higher L/S ratios is required to determine the behavior of Mo in the system and its safety in agricultural use. In general, higher leachability occurred from amended dune sand ML than from clay soil ones. These relative high concentrations are probably the result of physical characteristics of the sand such as high hydraulic conductivity, low water holding capacity and smaller surface area that limited absorption. Sandy growth media is exposed to more intensive wash, which results in higher L/S than the clay soil ML ($L/S=2$ and $L/S=1.7$, respectively) that may have extracted more leachable elements. Another factor is the soil retention ability of soluble elements. Clay soil can hold more water than dune sand and therefore to contain more soluble elements within the growth media that do not leach out and reach the leachate collection bag. Supporting this observation is the amount of As, B, Se and Mo taking by the plant. In the clay ML As uptake

was significantly higher assuring the elements extraction although instead of washing out the elements remains as soluble in the growth media available for plant uptake.

In order to evaluate the influences of soil pH and L/S ratios and to create a basis for evaluating field to lab conditions, the ML experiment and 1313 pH-dependent results were compared. The comparison yielded that the leached concentration of As, Mo and Se from the ML was strongly affected by fertigation that created high background concentrations. The NVS addition to both soils increased As, Mo and Se leachability to concentrations that overshadowed background concentrations. In this case, making it possible to notice that there is a strong pH effect on leachate concentrations and high correlation between the two experiments regardless the different conditions of the two procedures could be clearly recognized. Hence, in the future, the US-EPA 1313 pH dependence test could serve as a screening tool for testing new growth materials.

Mass balance results presented in figures 27-30 show that trace elements releases from RSS do not differ much than the non-amended controls and have a minor contribution on the total element release. In some cases, RSS addition even led to a reduction in elemental releases resulting in lower amounts in ML leachate and/or plant tissues. This might be explained by adsorption to organic matter or microorganism trace elements consumption.

Highlighted by the mass balance is the low amounts of several trace elements that leached out during the growth period in contrast to the relatively high lettuce uptake (Cd, Cr, Fe, Pb and U; see figures A15-A20). This implies different chemical conditions in the rhizosphere area compared with the entire ML such that the plant can cause microelements dissolution in its immediate roots vicinity. This phenomenon takes place irrespective of the experiment conditions such as pH and L/S ratio.

To conclude, from examining NVS and its main components, fly ash and raw sewage sludge, applied at maximum permitted load and five times the permitted load in agricultural soils, and by using lettuce as a test plant, it is possible to determine that:

- i. Leachability of As and Se from NVS-soils mixtures (at both loading rates) at natural pH are safe whereas B and Mo are leached at safe concentrations (below irrigation criteria) only at low load applications.
- ii. Fly ash B, Mo and Se leachability is characterized by high initial concentration that decreases as a function of L/S (i.e., “first slush leachability”).
- iii. Addition of FA to soils lead to higher As, B, Mo, and Se concentrations in ML leachate. However, the concentration decreases as a function of L/S to a point that As and Se are safe for agricultural use by the Israeli safety standard for irrigation (IWI) while B and Mo remain above the safety standard.
- iv. Despite the different conditions, good correlation has been found between ML leachate and 1313 pH-dependent for constituents of potential concern (As, Mo and Se). Hence, trace elements leachability is mainly affected by the soil pH and not by the L/S ratio.
- v. Both RSS and NVS additions to soils increased lettuce yield. However, it should be noted that the RSS in its studied form cannot be applied in the field while the NVS can be directly applied.
- vi. All lettuce produced in this study, even those grown on high load NVS and FA, were safe for human consumption. Concentrations of all three major toxic metals, Cd, Pb and As, were lower than the ceiling concentrations for leafy vegetables.

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Appendix 1 - Sample preparation procedures and total content analysis

Sample dissolution

The solid matter was dissolved using three different procedures depending on the desired elements to be quantified. For all digestions, the samples were first dried at 105 °C.

a) LiBO_2 fusion for major element analysis :

- Well mixed 0.25 g dry material with 1.25 g LiBO_2 in a platinum crucible is heated to 1000°C to create a flux for 20 minutes.
- After cooling, the flux is dissolved in a solution of 150 mL of distilled water and 8 mL of 65% Nitric Acid (HNO_3).
- The solution is transferred to a 500 mL bottle with addition of the internal standard Sc such that the final concentration of Sc in the tested solution is 5 mg/L.
- The solution volume is completed to 500 mL with distilled water to a final sample dilution of 2000 for major element analysis.
- o The SRM/CRM used for major element analysis: BCR-32, JB-1, BHVO-1, SO-3, SCO-1 and NBS-1633a.

b) Sinter fusion by Na_2O_2 for trace elements analysis :

- Well mixed 0.5 g dry material with 2 g Na_2O_2 in a zirconium crucible is heated for 1.5 hours at 550°C to create a fusion.
- While hot, the crucible is placed in a plastic beaker which has a small amount of distilled water in it to avoid sticking of the crucible
- 25 mL of distilled water is added to the crucible (placed within the plastic beaker).
- The crucible content is poured into the beaker.
- A full crucible of 1:3 HNO_3 is added to the solution (in the plastic beaker).
- Solution is stirred until it is clear.
- The solution is transferred to a bottle of 100 mL and completed to this volume with distilled water.
- Final dilution for trace metal analysis (1:1000) is reached by further 1:5 dilution with addition of Rh and Re as internal standards with a final concentration of 10 µg/L.

- The SRM/CRM used for trace element analysis: JB-1, BHVO-1, SO-3 and NBS-1633a.
- c) High content organic materials such as RSS and fully grown lettuce produced during the mini-lysimeter experiment were digested by HNO_3 .
- 0.5 gr of the dried matter is placed in a glass test tube.
 - 4 mL of concentrated HNO_3 (65%) are added to the sample.
 - The test tube is placed in a metal hot block at 150°C .
 - When full dissolution is reached, Millipore water is added up to a final volume of 10 mL.

Loss on ignition

Loss on ignition (LOI) is conducted for determining the volatile materials of the samples, which commonly include water and CO_2 from carbonates and organic matter. One gram of dry sample is weighed in an alumina crucible and heated for four hours in a 1050°C furnace. The weight loss is presented as weight %, and together with the sum of major elements should add to 100 % ($\pm 1\%$). Typically, many FAs amount to a few percent lower than 100.

Total Content Analysis

Elemental concentrations of the total digests were measured at the Geological Survey of Israel (GSI) by two different devices depending on the compatibility of the measuring device to the specific element:

- ICP-OES (Optima 3300, Perkin Elmer) - Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si and Ti.
- ICP-MS (NexION, Perkin Elmer)- Ag, As, B, Ba, Be, Cd, Co, Cu, Cr, Mn, Mo, N, Pb, Sb, Se, Th, Tl, U, Zn and V.

Table A1: Soil properties¹

Soil type	pH	composition wt. %			texture	Clay minerals	CEC ²
		Sand	silt	clay			
Revadim	8.1	47.5	22.5	30	Silty clay	Montmorillonite	30
Palmachim	9.3	98.5	1.2	0.3	Sand	none	1

¹Chemical compositions of the two soils are presented in Table 4.

²Cation Exchange Capacity (meq/100 g)

Table A2: Chemical composition of water and fertilizer used for irrigation (mg/l).

Element	Tap water	Fertilizer (Shefer 737)	Irrigation water (mean)
Ag	UDL*	UDL*	UDL*
Al	UDL*	UDL*	UDL*
As	0.01	0.001	0.003
B	UDL	3	0.3
Ba	0.04	0.2	0.03
Be	0.01	UDL*	0.003
Ca	65	80	60
Cd	0.001	0.0004	0.0005
Co	UDL*	0.1	UDL*
Cr	0.005	0.01	0.003
Cu	0.004	13	0.01
Fe	0.02	326	0.2
K	4	49050	50
Li	0.01	UDL*	0.01
Mg	22	44	18
Mn	UDL*	157	0.1
Mo	0.002	0.15	0.01
Na	85	1240	75
Ni	UDL*	0.2	UDL*
P	0.06	13470	9
Pb	0.002	0.003	0.001
S	15	110	16
Sb	UDL*	UDL*	UDL*
Se	0.02	UDL*	0.01
Si	4	12	3.5
Sn	UDL*	0.4	UDL*
Sr	0.7	0.8	0.6
Th	UDL*	UDL*	UDL*
Ti	UDL*	0.07	UDL*
Tl	0.001	UDL*	0.0004
U	0.002	0.0008	0.001
V	UDL*	0.2	UDL*
Zn	0.05	79	0.1

*UDL – under detection limit.

Table A3: Clay soil, dune sand and FA comparison to upper continental crust (UCC; Rudnick and Gao, 2003) mean values (mg/kg for all except the major elements that are in wt.%).

Element (mg/kg)	GSI			UCC
	Clay soil	Dune sand	FA	
Al, wt.%	9	1.3	22	15.5
Ag	0.01	0.01	0.2	55
As	5	0.9	55	5
B	23	0.002	315	17
Ba	415	125	2870	624
Be	1	0.2	7.3	2
Ca, wt.%	7.6	1.4	4	3.6
Cd	0.4	0.04	2.6	0.09
Co	20	1	40	17
Cr	110	6.5	110	92
Cu	35	3	80	28
Fe, wt.%	5	1.2	7	5.05
K, wt.%	1.1	0.4	1.3	2.8
Mg, wt.%	1.7	0.03	2	2.5
Mn, wt.%	0.1	0.004	0.05	0.1
Mo	0.8	0.1	38	1
Na, wt.%	0.7	0.3	1.5	3.3
Ni	40	7.5	90	47
P, wt.%	<0.1	<0.1	0.2	0.15
Pb	11	3	33	0.5
Sb	0.4	0.1	14	0.4
Se	0.3	2	25	0.09
Si, wt.%	63	97	57	67
Th	8	1.4	16	10.5
Ti, wt.%	1.2	0.03	1	0.65
Tl	0.2	0.05	2.5	0.9
U	2	0.3	7	2.7
V	100	4	245	100
Zn	70	13	140	70

Table A4: Fly ash (LA-LOMA) total content comparison with average content of main FAs used in Israel.

Element (mg/kg)	FA (LA-LOMA)	FAs 2004-2013			Ratio LA-LOMA/Israeli FAs
		Min	Max	Average	
Al, wt.%	22	0.2	34	24	0.9
Sb	14	1	23	6	2.4
As	55	5	129	32	1.7
Ba	2870	436	5000	1878	1.5
Be	7	3	24	8	0.9
B	315	40	1650	277	1.1
Cd	3	0.2	4.7	1	2.1
Ca,, wt.%	4	UDL	16	5	0.8
Cr	110	75	260	128	0.9
Co	40	20	76	38	1.1
Cu	80	50	229	79	1
Fe, wt.%	7	UDL	16.2	6	1.1
Pb	33	14	102	44	0.8
Mg, wt.%	2	UDL	5.6	2	0.9
Mn, wt.%	0.05	UDL	0.16	0	0.9
Mo	38	5	75	17	2.2
Ni	90	50	183	88	1
P, wt.%	0.2	UDL	2.5	1	0.2
K, wt.%	1.3	UDL	2.3	1	1.1
Se	25	2	40	12	2.1
Si, wt.%	57	UDL	62	51	1.1
Ag	0.2	1	6.3	1	0.1
Na, wt.%	1.5	UDL	3	1	2.4
S, wt.%	UDL	UDL	1.3	1	-
Tl	2	1	6	2	1.1
Th	16	6	189	29	0.6
Ti, wt.%	1	UDL	1.8	1	0.8
U	7	4	31	10	0.7
V	245	115	364	212	1.2
Zn	139	60	330	157	0.9
LOI, wt.%	2	12	95	41	0.1

Table A5: Upper limit concentrations of trace elements permitted in sewage sludge and dry leafy vegetables (mg/kg).

Element	RSS		Lettuce
	Israel ^a	US-EPA ^b	Israel ^c
Arsenic (As)	-	75	5
Cadmium (Cd)	20	85	1
Lead (Pb)	300	840	1.5
Chromium (Cr)	400	3000	-
Copper (Cu)	600	4300	-
Nickel (Ni)	90	420	-
Zinc (Zn)	2500	7500	-
Selenium (Se)	-	100	-

^aWater regulation and sludge use (Ministry of Environmental Protection, 2004).

^bImplementation guidance (United States Environmental Protection Agency, 1995).

^cFood control published guide lines (Israeli Ministry of Health, 2017).

Table A6: Statistical significance of As mass balance results (Figs. 28A₁ & 28A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	e	e	c
CS-FA-L	e	e	c
CS-FA-H	e	de	bc
CS-RSS-L	e	e	c
CS-RSS-H	e	de	bc
CS-NVS-L	de	e	c
CS-NVS-H	de	bcde	a
Dune Sand	e	e	c
DS-FA-L	b	bcd	c
DS-FA-H	cd	bc	c
DS-RSS-L	e	e	c
DS-RSS-H	de	cde	c
DS-NVS-L	c	b	bc
DS-NVS-H	a	a	b
Prob > F	<0.0001	<0.0001	<0.0001

Table A7: Statistical significance of B mass balance results (Figs. 29A₁ & 29A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	fg	d	c
CS-FA-L	efg	d	c
CS-FA-H	c	a	bc
CS-RSS-L	fg	d	bc
CS-RSS-H	g	d	a
CS-NVS-L	eg	d	bc
CS-NVS-H	cd	c	ab
Dune Sand	fg	d	c
DS-FA-L	cde	d	c
DS-FA-H	a	b	c
DS-RSS-L	g	d	c
DS-RSS-H	g	d	bc
DS-NVS-L	def	d	c
DS-NVS-H	b	c	bc
Prob > F	<.0001	<.0001	<.0001

Table A8: Statistical significance of Mo mass balance results (Figs. 30A₁ & 30A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	c	c	d
CS-FA-L	c	c	cd
CS-FA-H	bc	a	bc
CS-RSS-L	c	c	bcd
CS-RSS-H	c	c	cd
CS-NVS-L	c	c	cd
CS-NVS-H	c	b	a
Dune Sand	c	c	d
DS-FA-L	c	c	d
DS-FA-H	a	ab	d
DS-RSS-L	c	c	d
DS-RSS-H	c	c	cd
DS-NVS-L	c	c	cd
DS-NVS-H	b	b	ab
Prob > F	<0.0001	<0.0001	<0.0001

Table A9: Statistical significance of Se mass balance results (Figs. 31A₁ & 30A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	e	c	c
CS-FA-L	e	c	c
CS-FA-H	cd	a	a
CS-RSS-L	e	c	c
CS-RSS-H	e	c	c
CS-NVS-L	e	c	c
CS-NVS-H	de	b	a
Dune Sand	e	c	c
DS-FA-L	bc	a	c
DS-FA-H	a	a	bc
DS-RSS-L	e	c	c
DS-RSS-H	e	c	c
DS-NVS-L	de	bc	c
DS-NVS-H	ab	b	ab
Prob > F	<0.0001	<0.0001	<0.0001

Table A10: Statistical significance of Cd mass balance results (Figs. A12A₁ & A12A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	b	d	de
CS-FA-L	b	d	de
CS-FA-H	b	cd	bcd
CS-SRR-L	b	cd	cde
CS-SRR-H	b	cd	bc
CS-NVS-L	b	cd	cde
CS-NVS-H	b	cd	a
Dune sand	b	d	e
DS-FA-L	ab	b	e
DS-FA-H	a	a	cde
DS-RSS-L	b	d	de
DS-RSS-H	b	d	bcde
DS-NVS-L	b	c	bcde
DS-NVS-H	b	d	ab
Prob > F	0.002	<0.0001	<0.0001

Table A11: Statistical significance of Cr mass balance results (Figs. A13A₁ & A13A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	cd	b	bc
CS-FA-L	cd	b	bc
CS-FA-H	cd	b	bc
CS-RSS-L	d	b	bc
CS-RSS-H	d	b	a
CS-NVS-L	cd	b	bc
CS-NVS-H	cd	b	ab
Dune Sand	d	b	c
DS-FA-L	b	b	c
DS-FA-H	a	a	c
DS-RSS-L	d	b	bc
DS-RSS-H	cd	b	bc
DS-NVS-L	cd	b	bc
DS-NVS-H	bc	b	bc
Prob > F	<.0001	<.0001	<.0001

Table A12: Statistical significance of Fe mass balance results (Figs. A14A₁ & A14A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	b	d	cde
CS-FA-L	b	d	cde
CS-FA-H	b	d	cde
CS-RSS-L	b	cd	bcde
CS-RSS-H	b	cd	a
CS-NVS-L	b	cd	bcd
CS-NVS-H	b	d	ab
Dune Sand	b	bc	de
DS-FA-L	b	bc	de
DS-FA-H	ab	cd	e
DS-RSS-L	b	cd	bcde
DS-RSS-H	ab	a	bc
DS-NVS-L	b	bcd	bcde
DS-NVS-H	a	ab	bcde
Prob > F	0.0023	<.0001	<.0001

Table A13: Statistical significance of Pb mass balance results (Figs. A15A₁ & A15A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	b	abcd	b
CS-FA-L	bc	cde	b
CS-FA-H	bc	de	b
CS-SRR-L	bc	a	b
CS-SRR-H	bc	ab	a
CS-NVS-L	bc	abc	b
CS-NVS-H	b	de	ab
Dune sand	bc	de	b
DS-FA-L	bc	e	b
DS-FA-H	c	e	b
DS-RSS-L	bc	bcde	b
DS-RSS-H	a	bcde	ab
DS-NVS-L	bc	de	b
DS-NVS-H	bc	de	b
Prob > F	<.0001	<.0001	<.0001

Table A14: Statistical significance of U mass balance results (Figs. A16A₁ & A16A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	cde	cd	cd
CS-FA-L	a	a	cd
CS-FA-H	abc	bc	cd
CS-RSS-L	bc	b	a
CS-RSS-H	ab	bc	bcd
CS-NVS-L	cde	de	ab
CS-NVS-H	bcd	de	cd
Dune Sand	ef	b	cd
DS-FA-L	de	b	cd
DS-FA-H	bcd	bc	cd
DS-RSS-L	def	bcd	cd
DS-RSS-H	f	e	abc
DS-NVS-L	f	e	cd
DS-NVS-H	f	e	d
Prob > F	<.0001	<.0001	<.0001

Table A15: Statistical significance of P mass balance results (Figs. A17A₁ & A17A₂).

Amendment	Leachate		Lettuce uptake
	Control	Planted	
Clay soil	d	b	bcd
CS-FA-L	d	b	bcd
CS-FA-H	d	b	bcd
CS-RSS-L	d	b	b
CS-RSS-H	bcd	b	a
CS-NVS-L	d	b	bcd
CS-NVS-H	bcd	b	ab
Dune Sand	bcd	b	d
DS-FA-L	d	b	cd
DS-FA-H	d	b	cd
DS-RSS-L	b	b	bcd
DS-RSS-H	a	a	b
DS-NVS-L	cd	b	bcd
DS-NVS-H	bc	b	bc
Prob > F	<.0001	<.0001	<.0001

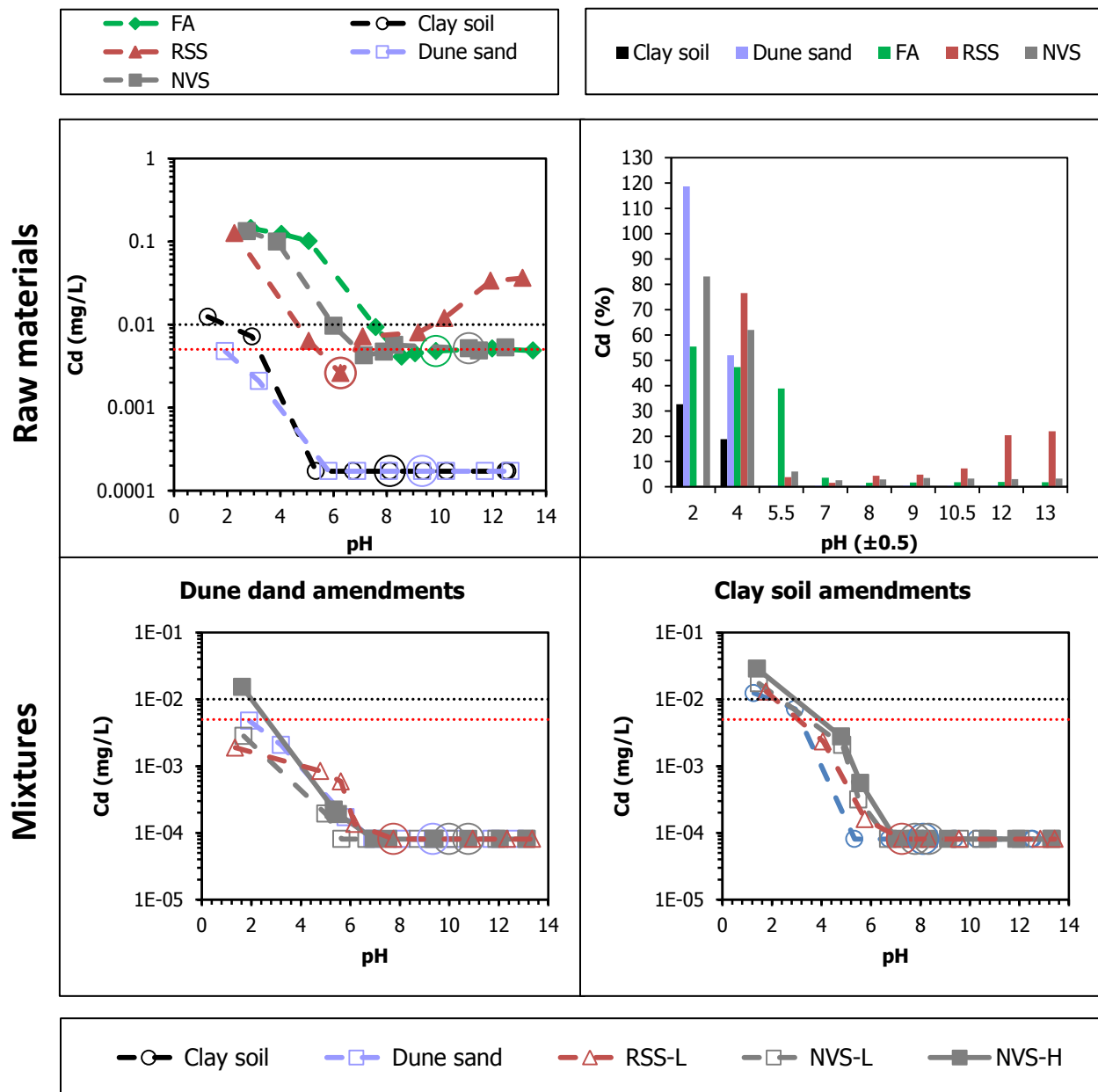


Figure A1: Cadmium pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

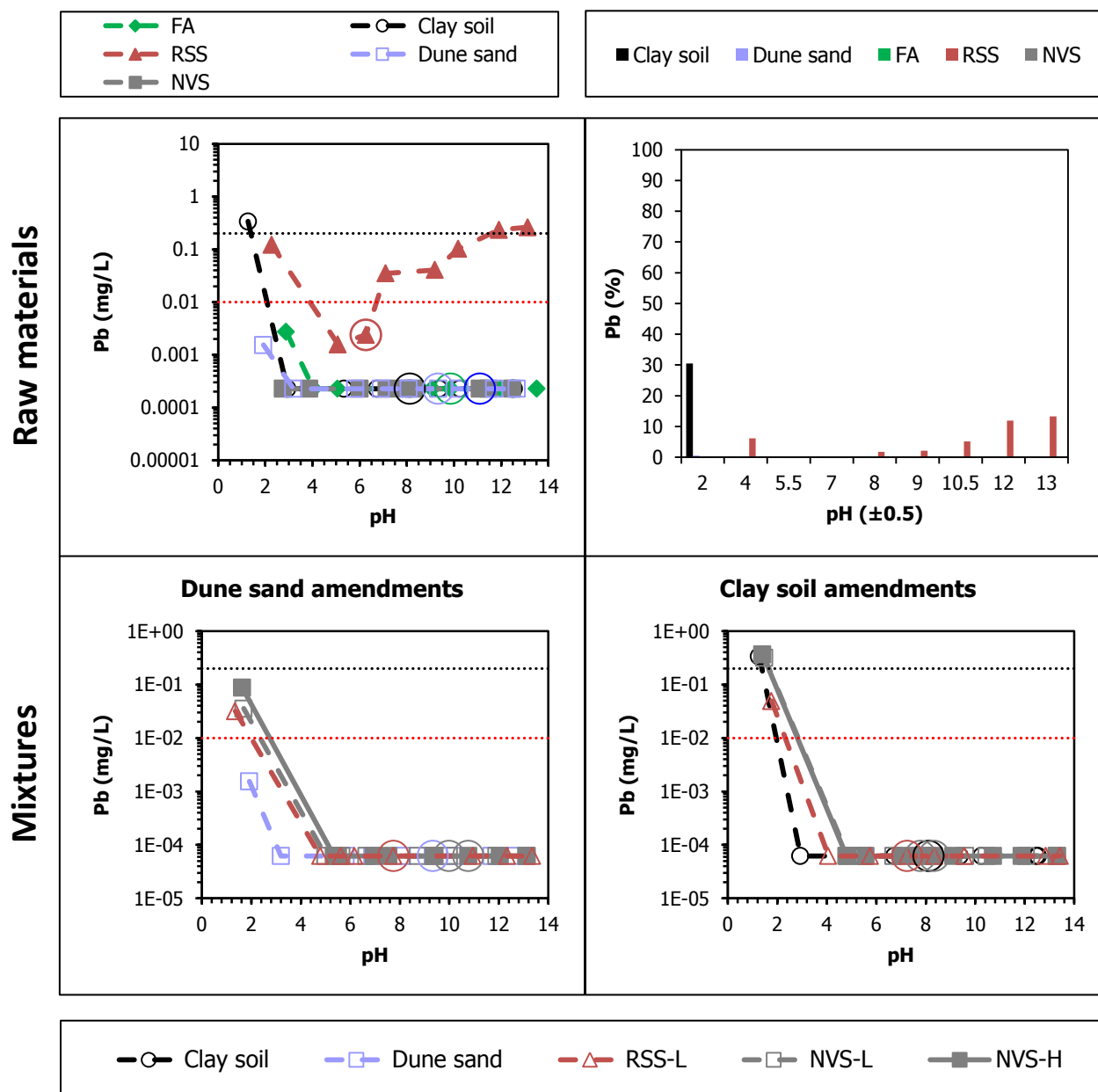


Figure A2: Lead pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

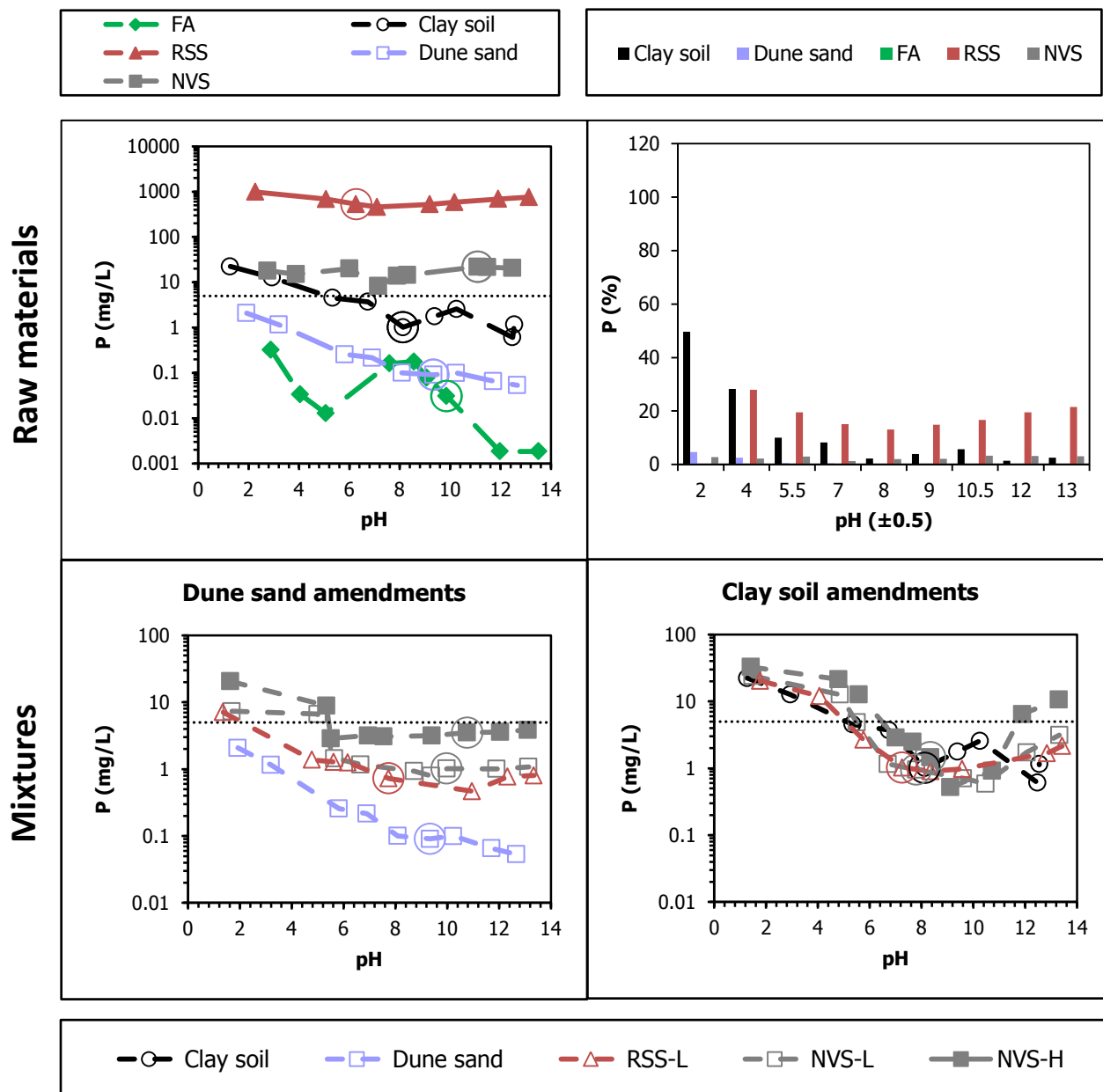


Figure A3: Phosphorus pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The dotted lines represent Israeli water standards; drinking water quality standard (DWI) in red and the long-term irrigation (IWI) in black. Horizontal data line of low concentration represents values below limit of detection.

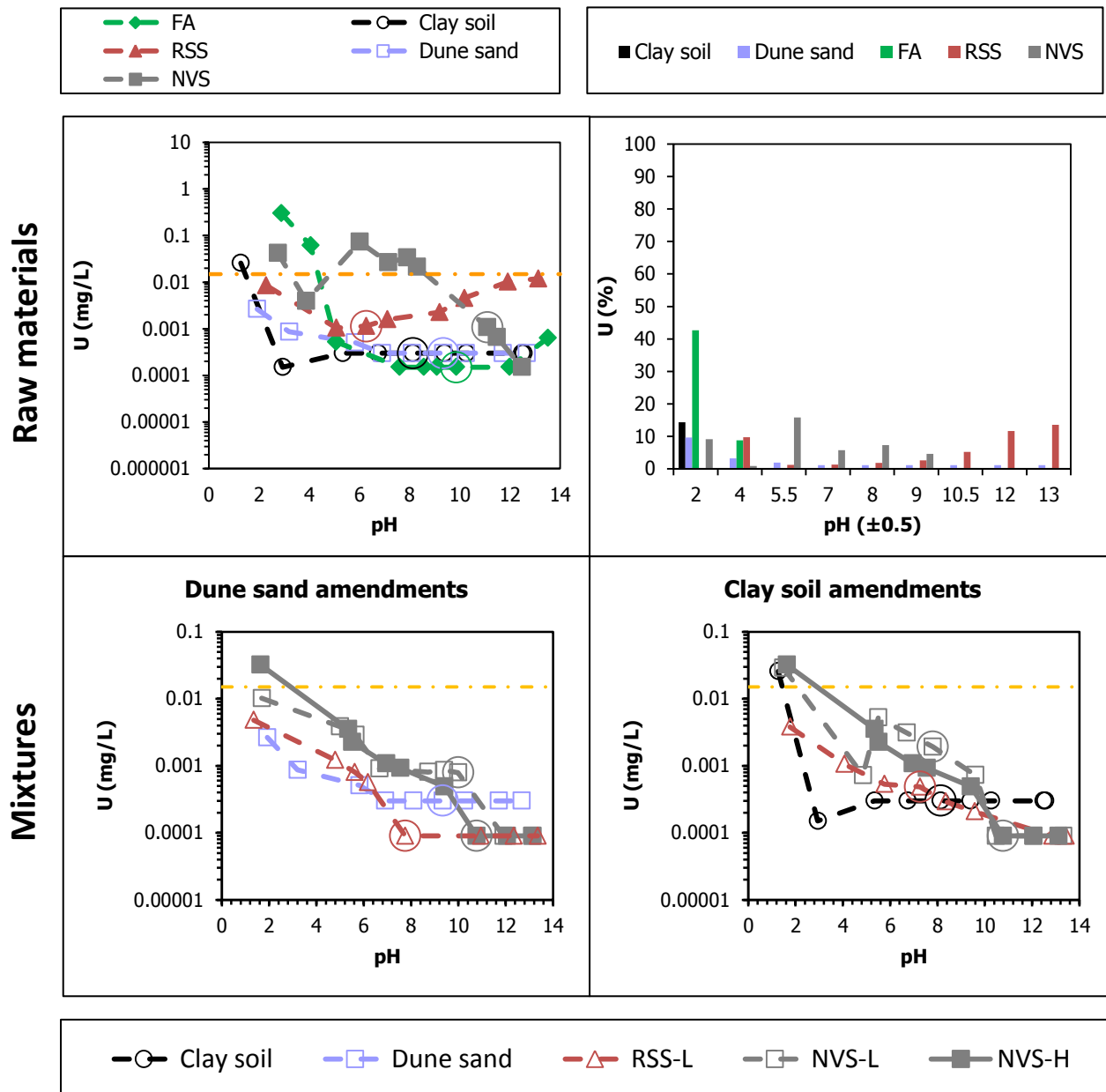
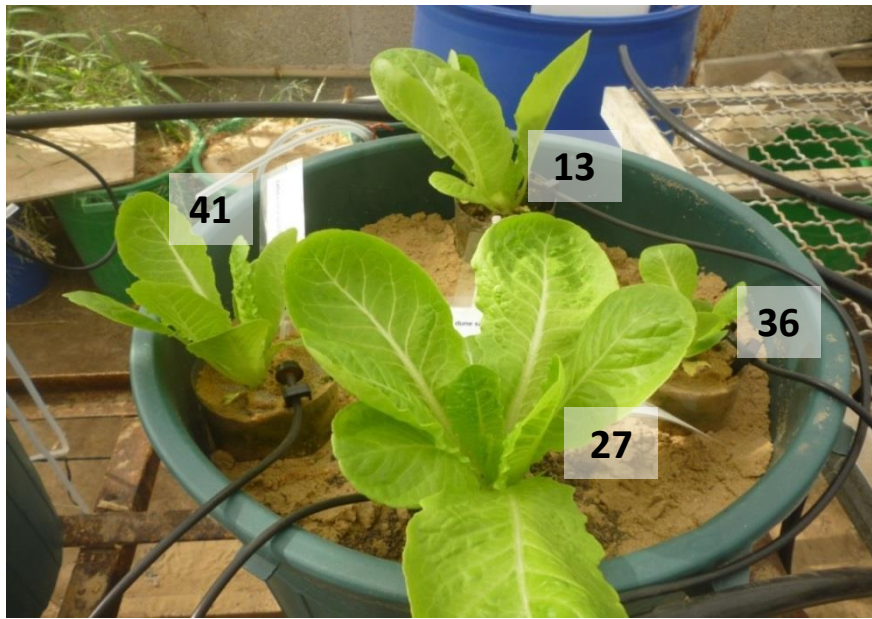


Figure A4: Uranium pH dependent characteristics. (A) Concentrations (mg/L) leached from the five studied raw materials. (B) The leachate fraction as percentage of the total content. Dune sand (C) and clay soil (D) mixed with amendments. The soil is presented in all four figures for comparison with the other raw materials and with the mixtures. The orange dash/dotted lines represent both Israeli water standards; drinking water quality standard (DWI) in and the long-term irrigation (IWI).



- 13. Lettuce CS-RSS-L
- 27. Lettuce CS-NVS-H
- 36. Lettuce DS-FA-L
- 41. Lettuce DS-RSS-L

Figure A5: Lettuce development during the growth

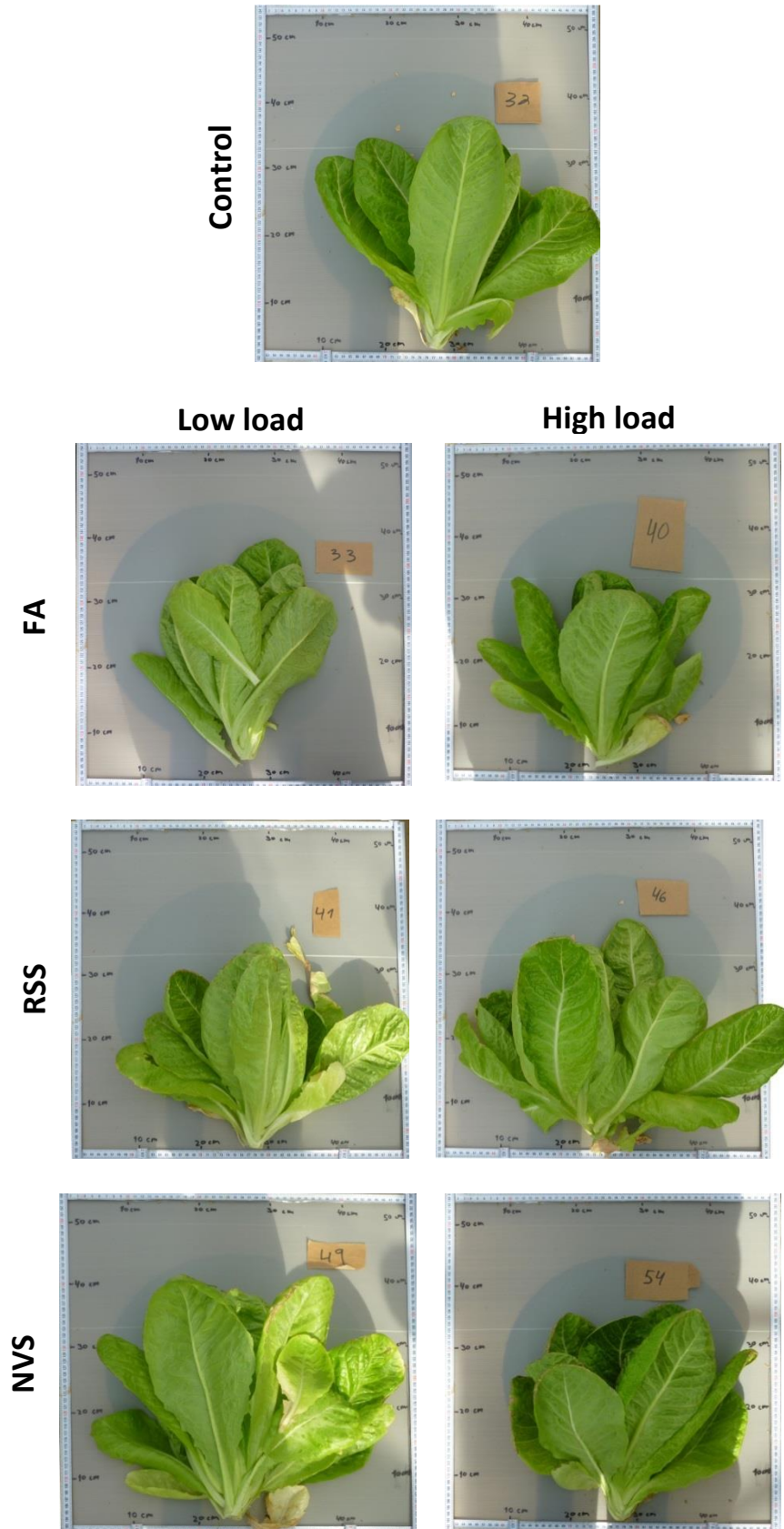


Figure A6: Dune sand and additive-dune sand mixtures largest lettuce production.

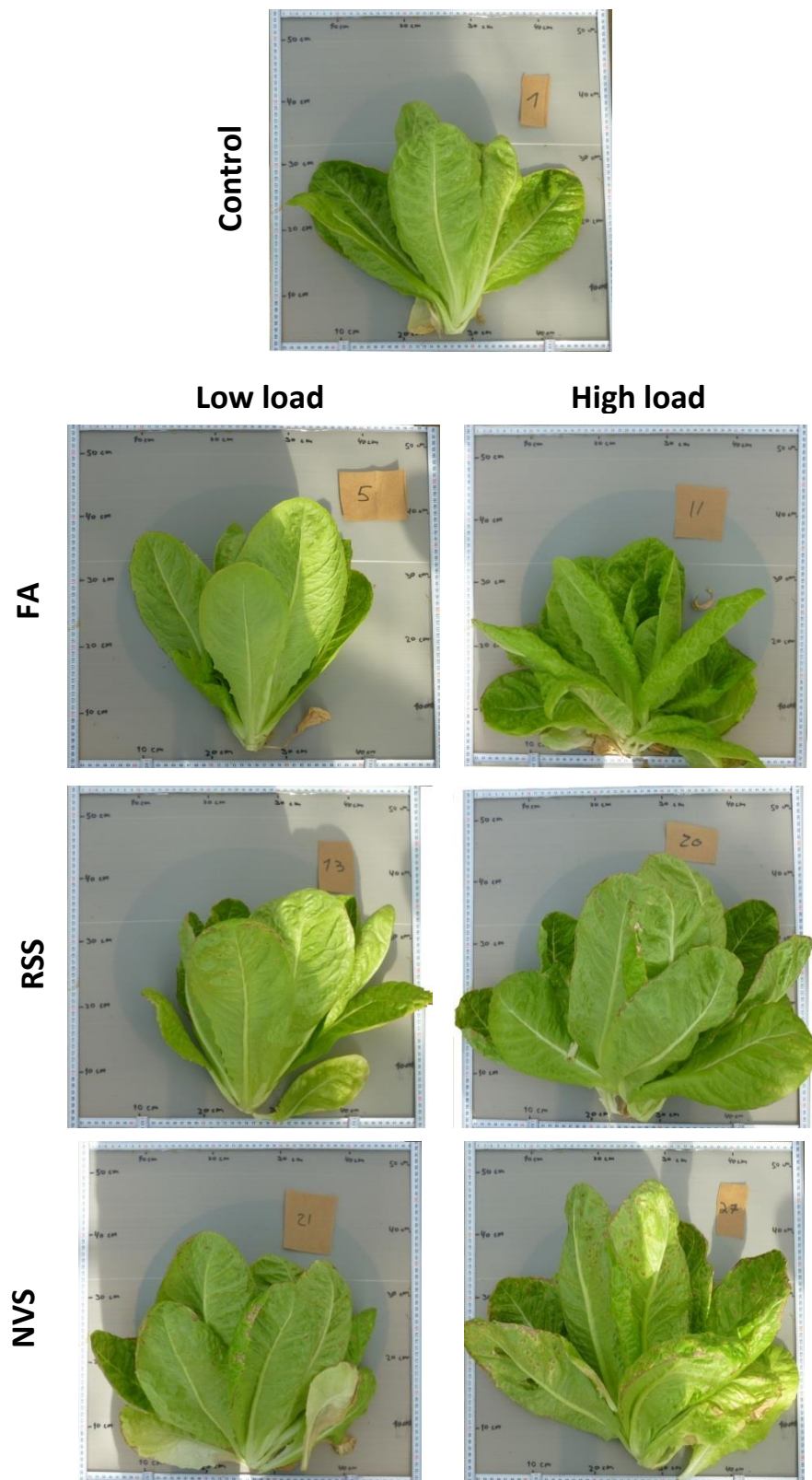


Figure A7: Clay soil and additive-clay soil mixtures largest lettuce production.

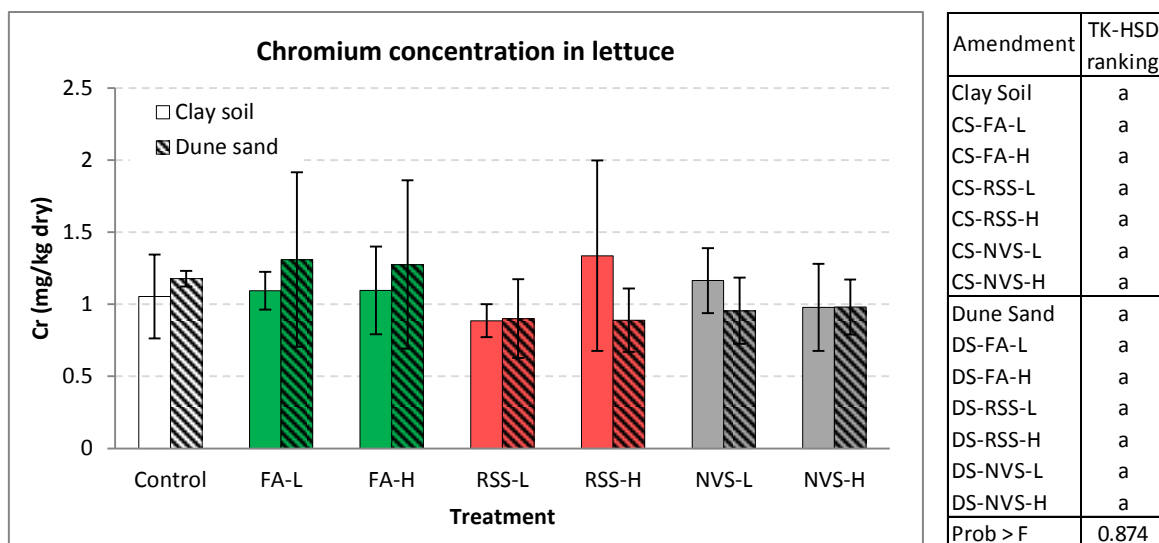


Figure A8: Chromium concentration (mg/kg) in lettuce.

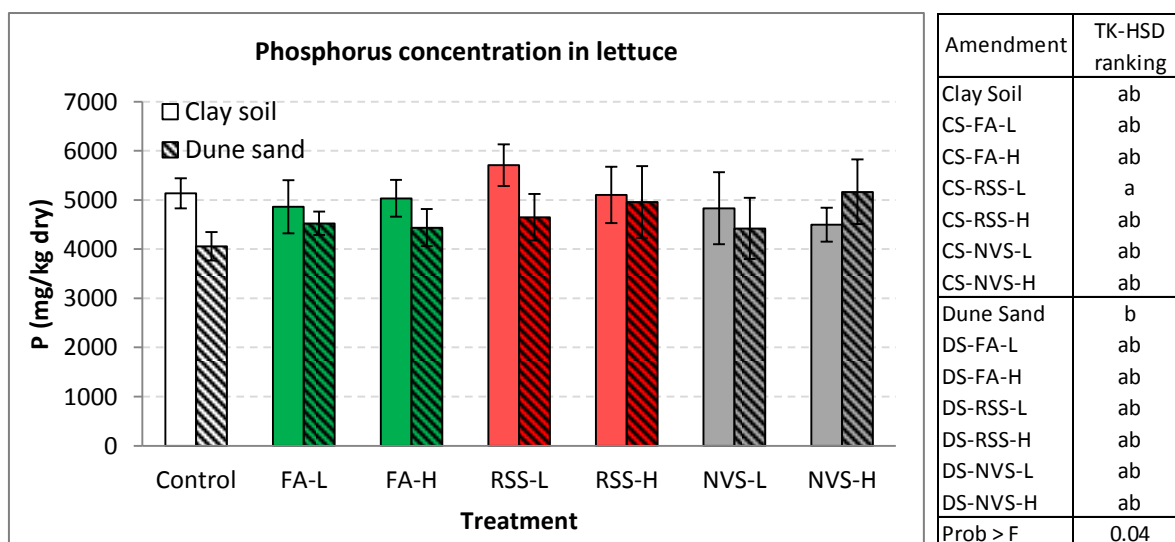


Figure A9: Phosphorus concentration (mg/kg) in lettuce

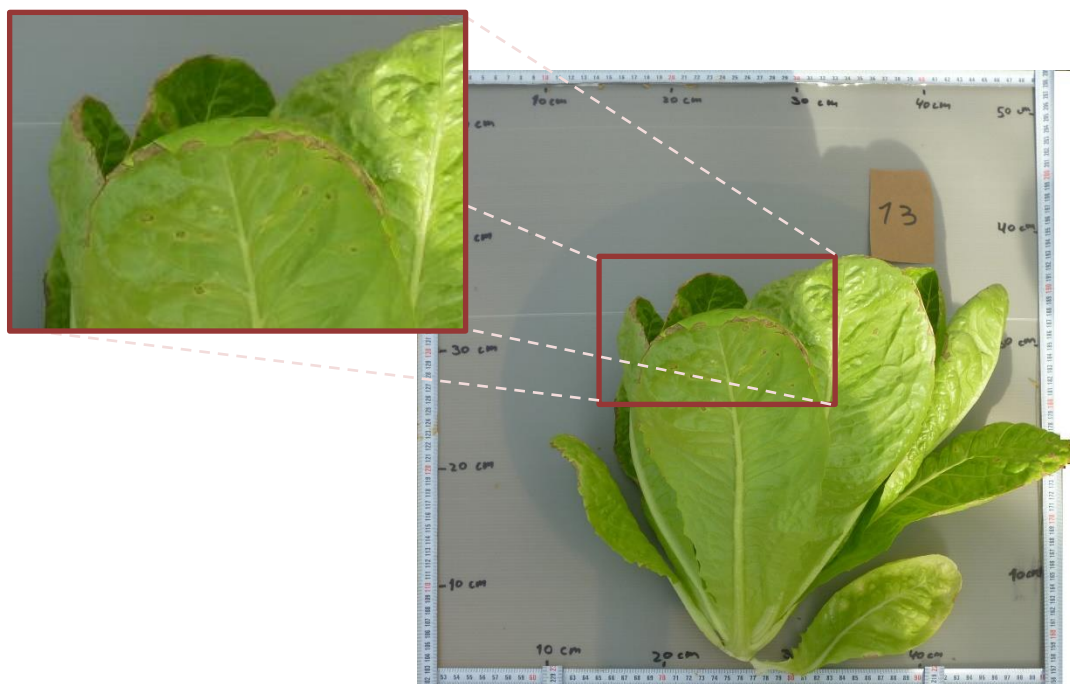


Figure A10: Lettuce leaves with suspicion to B sensitivity.

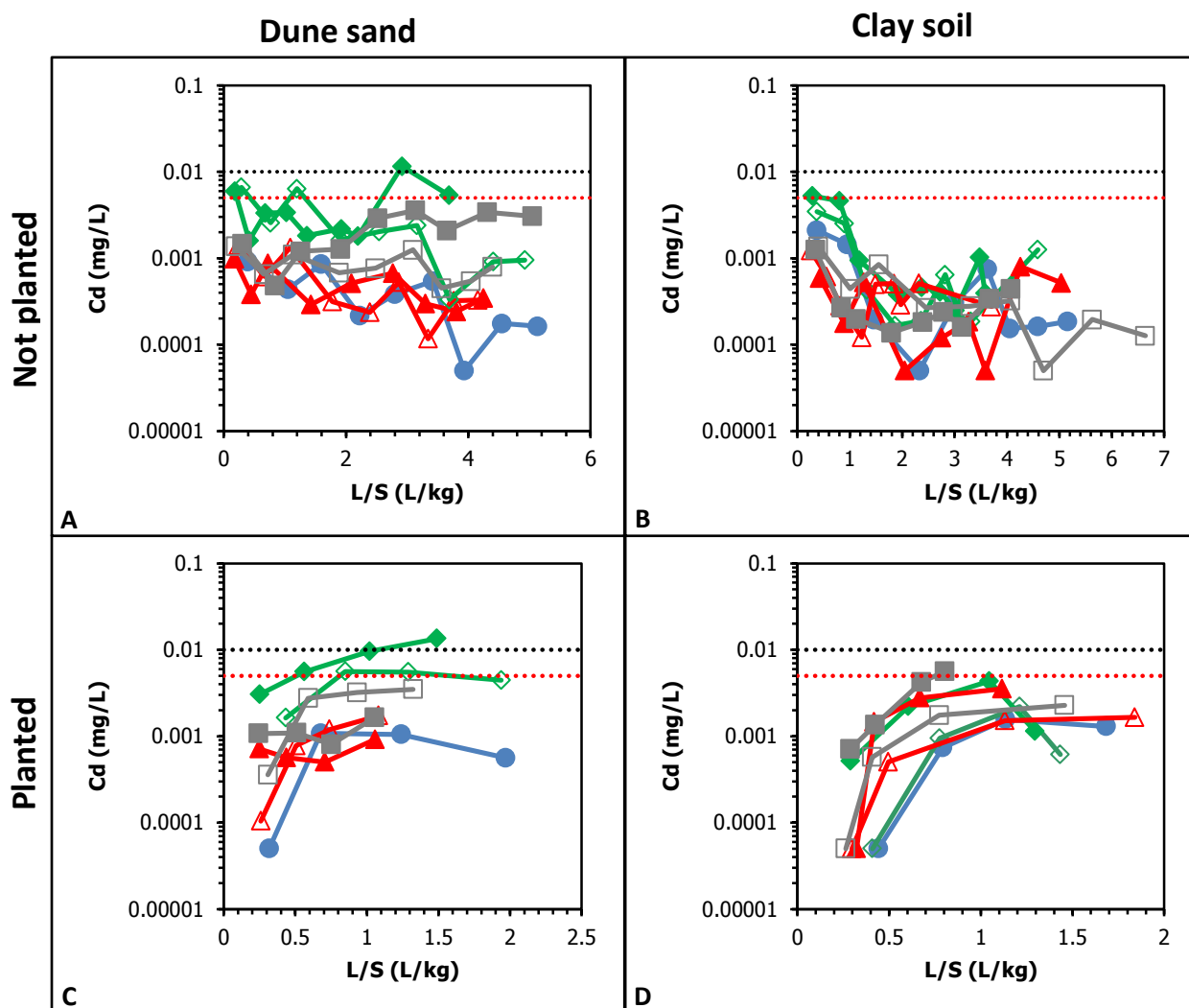


Figure A11: Cadmium leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).

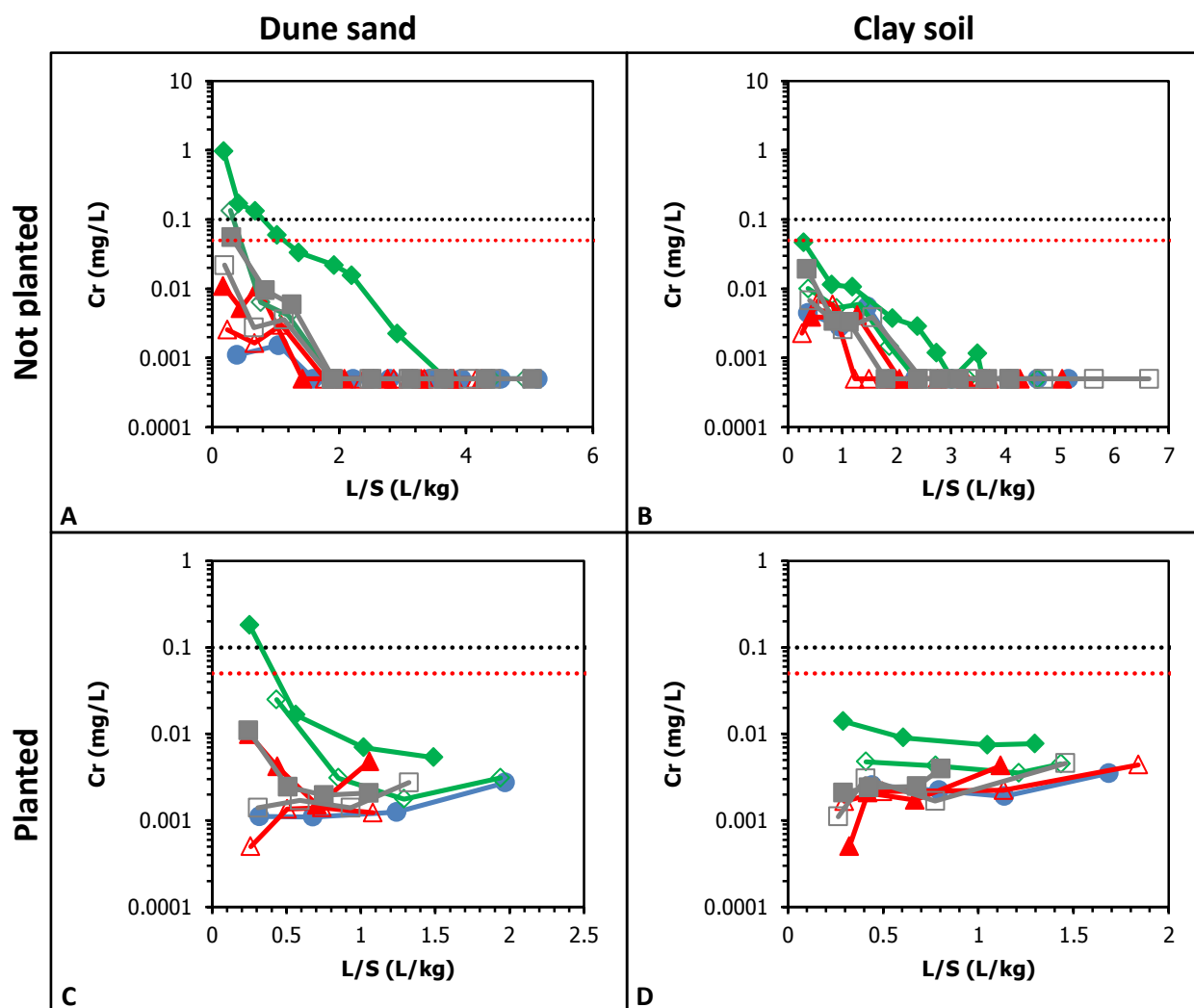
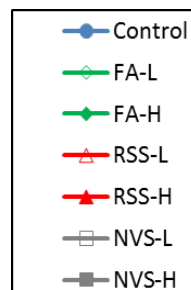


Figure A12: Chromium leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).



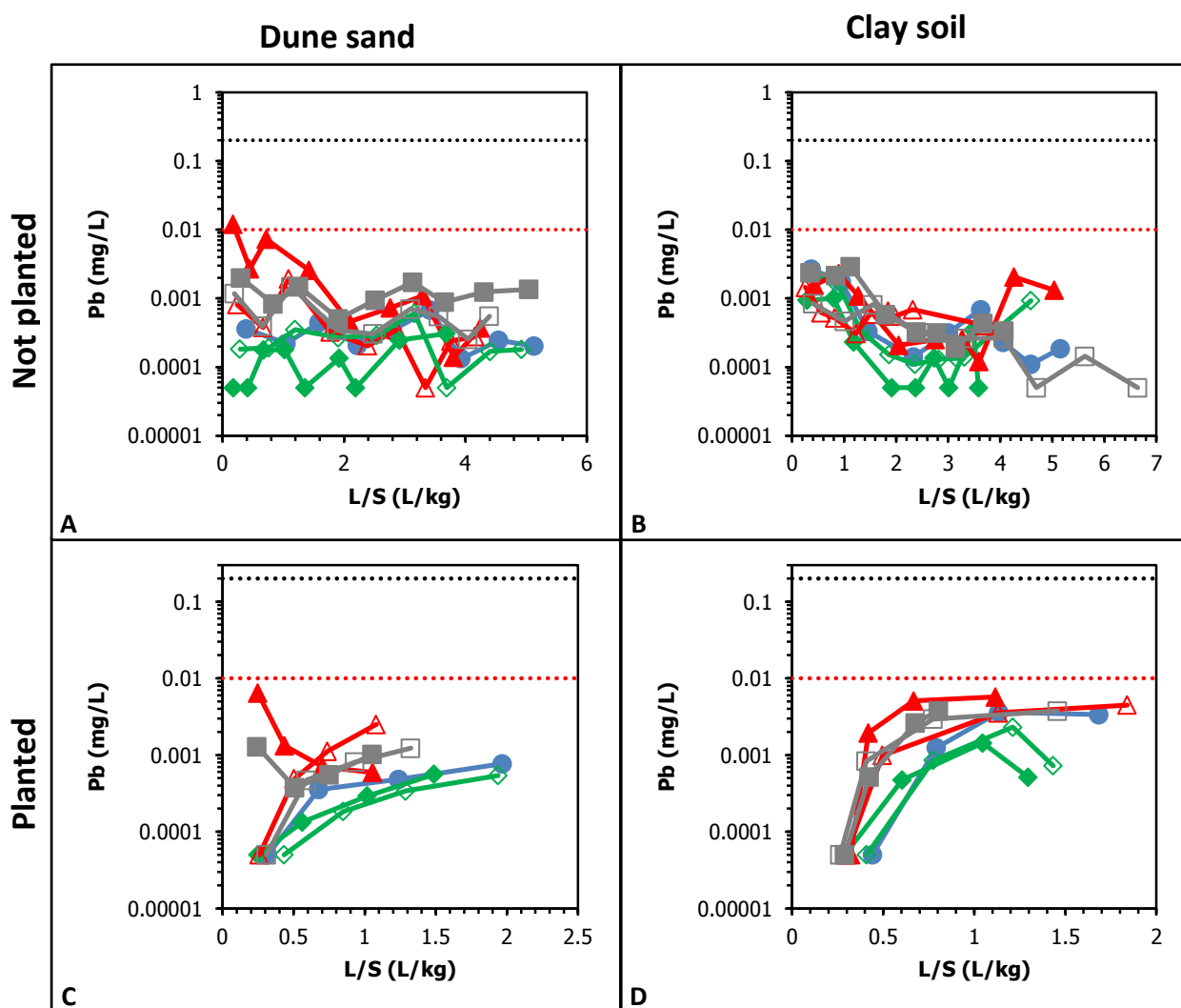
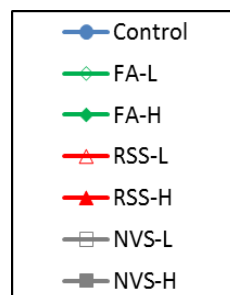


Figure A13: Lead leachability from planted and non-planted mini-lysimeters, using clay soil and dune sand as controls and these soils mixed with FA, RSS, and NVS in both low (L) and high (H) loads. The L/S is the ratio between the leachate volume and the weight of the soil in the ML. The two dotted lines represent Israeli water standards for drinking water quality (red) and long-term irrigation (black).



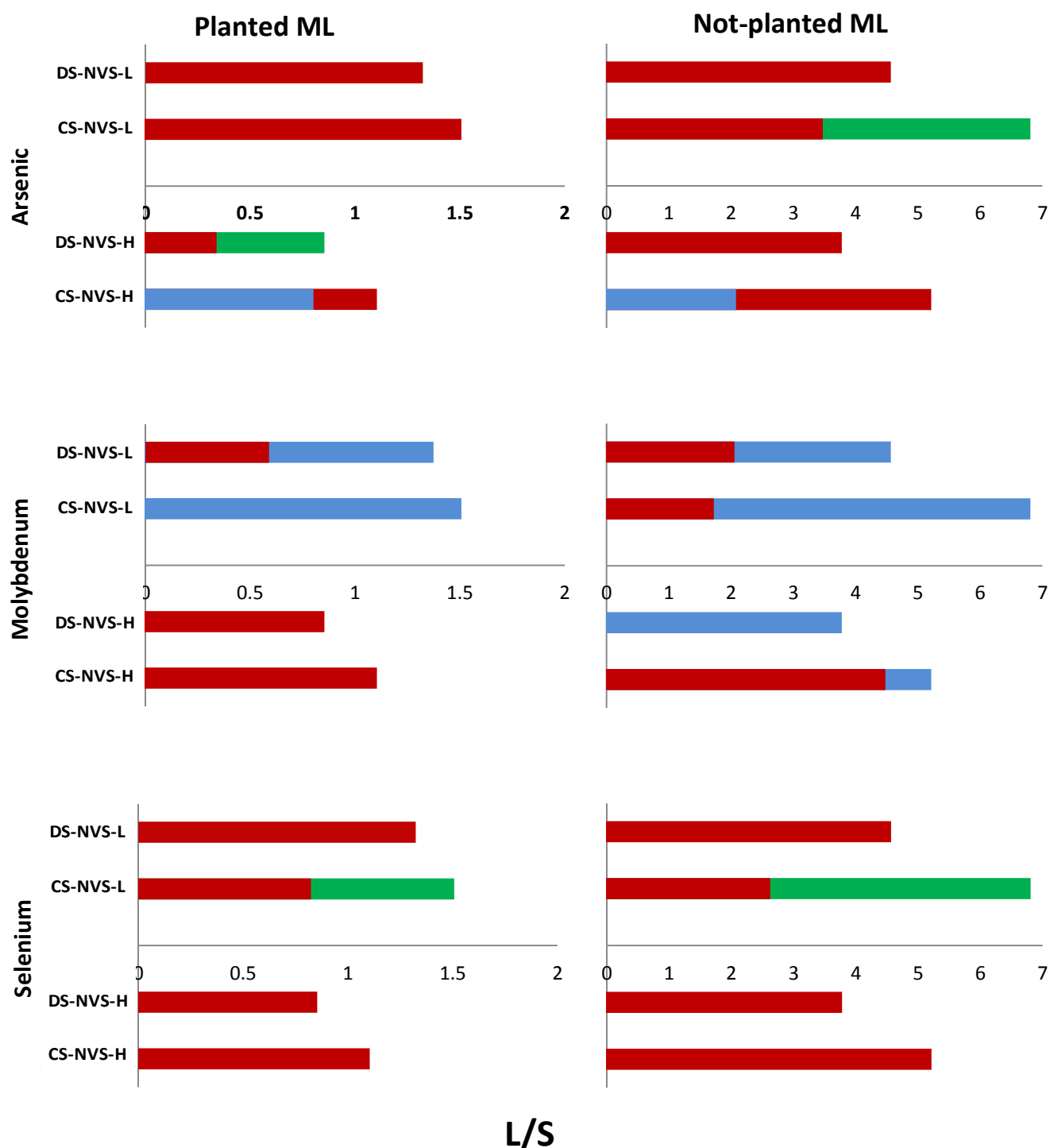
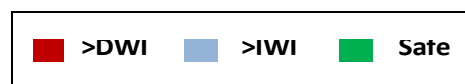


Figure A14: Concentration changes of As, Mo and Se as a function of L/S for the NVS applications. Each column represents the concentrations released according to regulatory standards (drinking and irrigation water) at each L/S applied to the ML. The left column represent planted ML and the right not-planted ML.



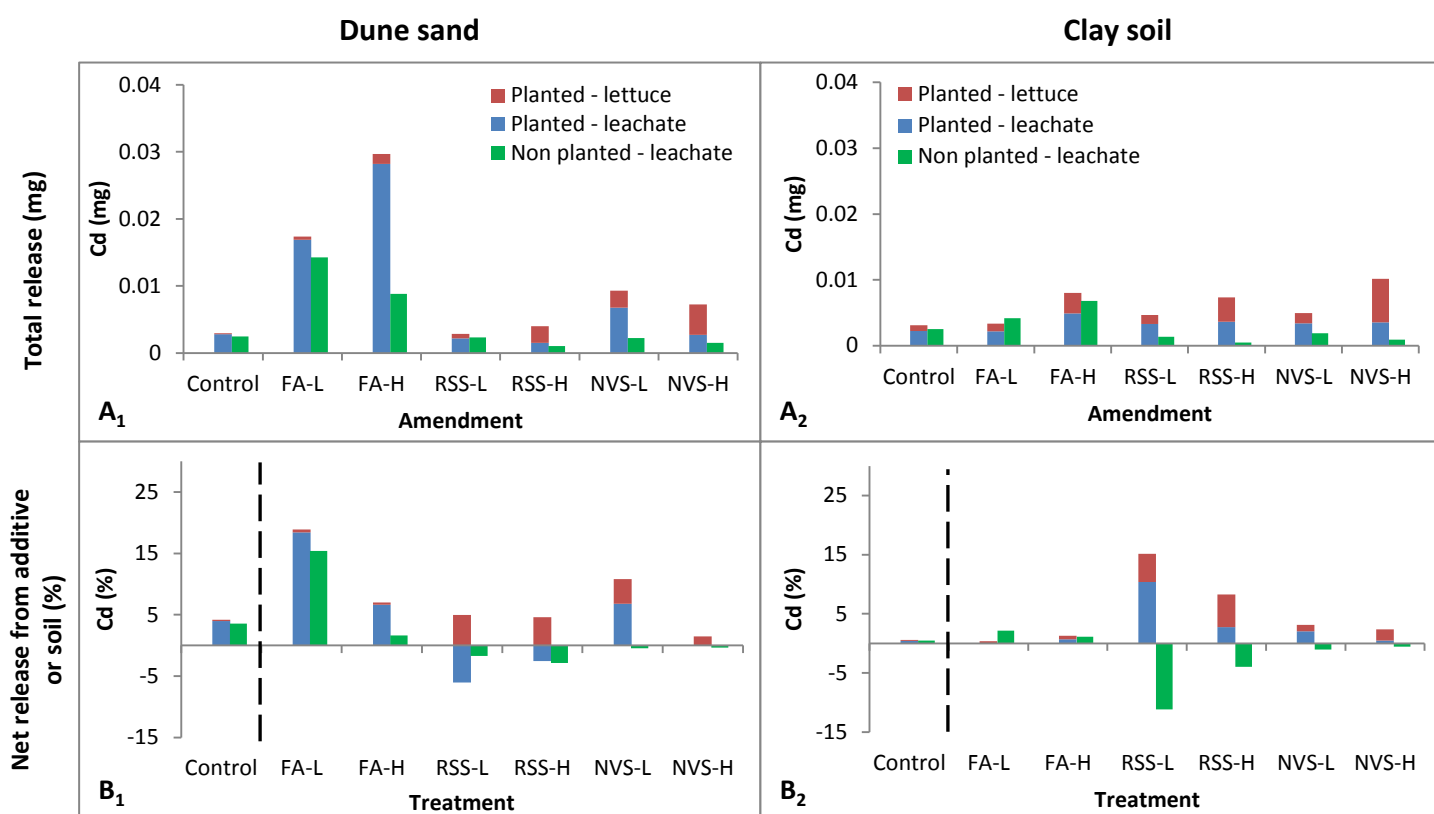


Figure A15: Cadmium mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁&A₂ show the overall amount released and B₁&B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A10.

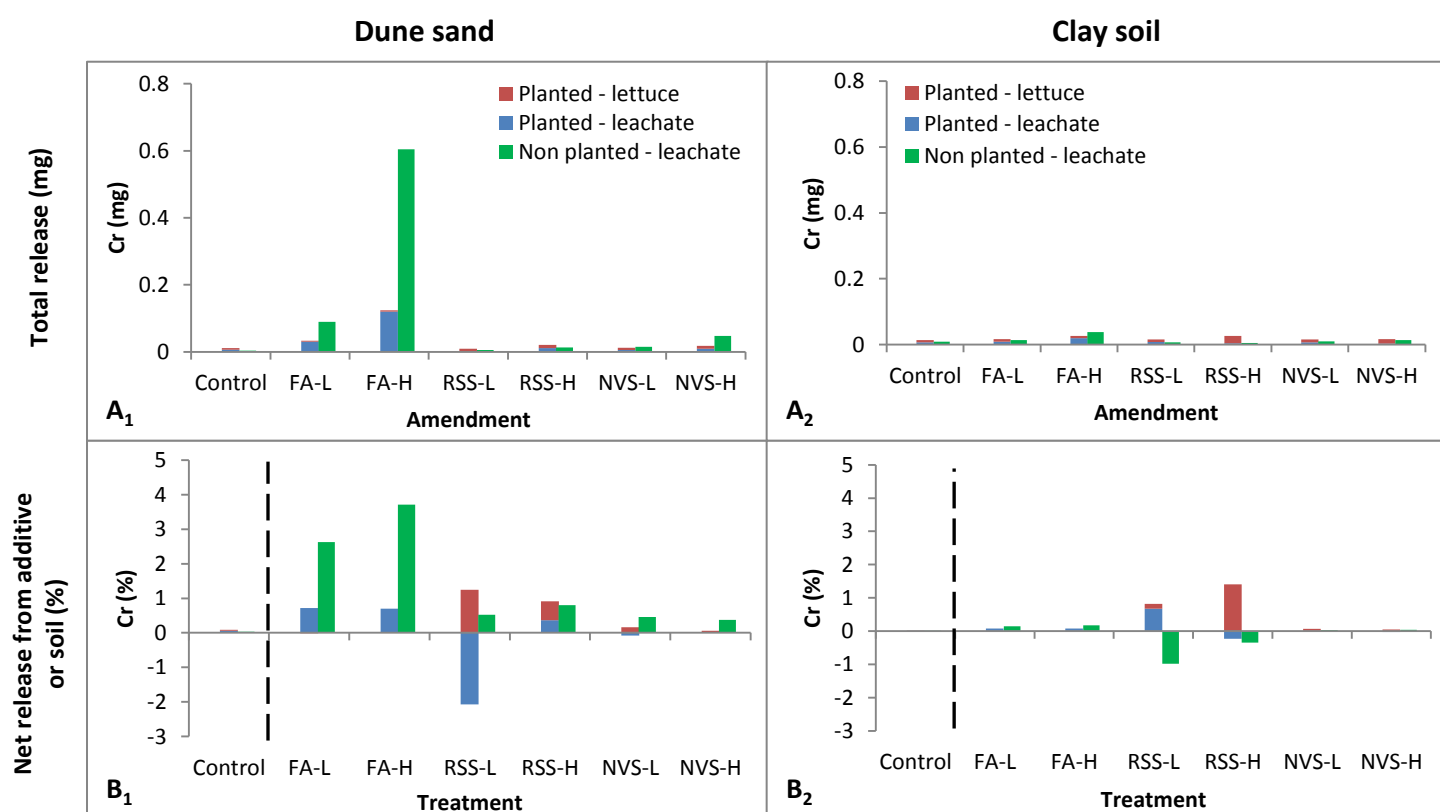


Figure A16: Chromium mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁ & A₂ show the overall amount released and B₁ & B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A11.

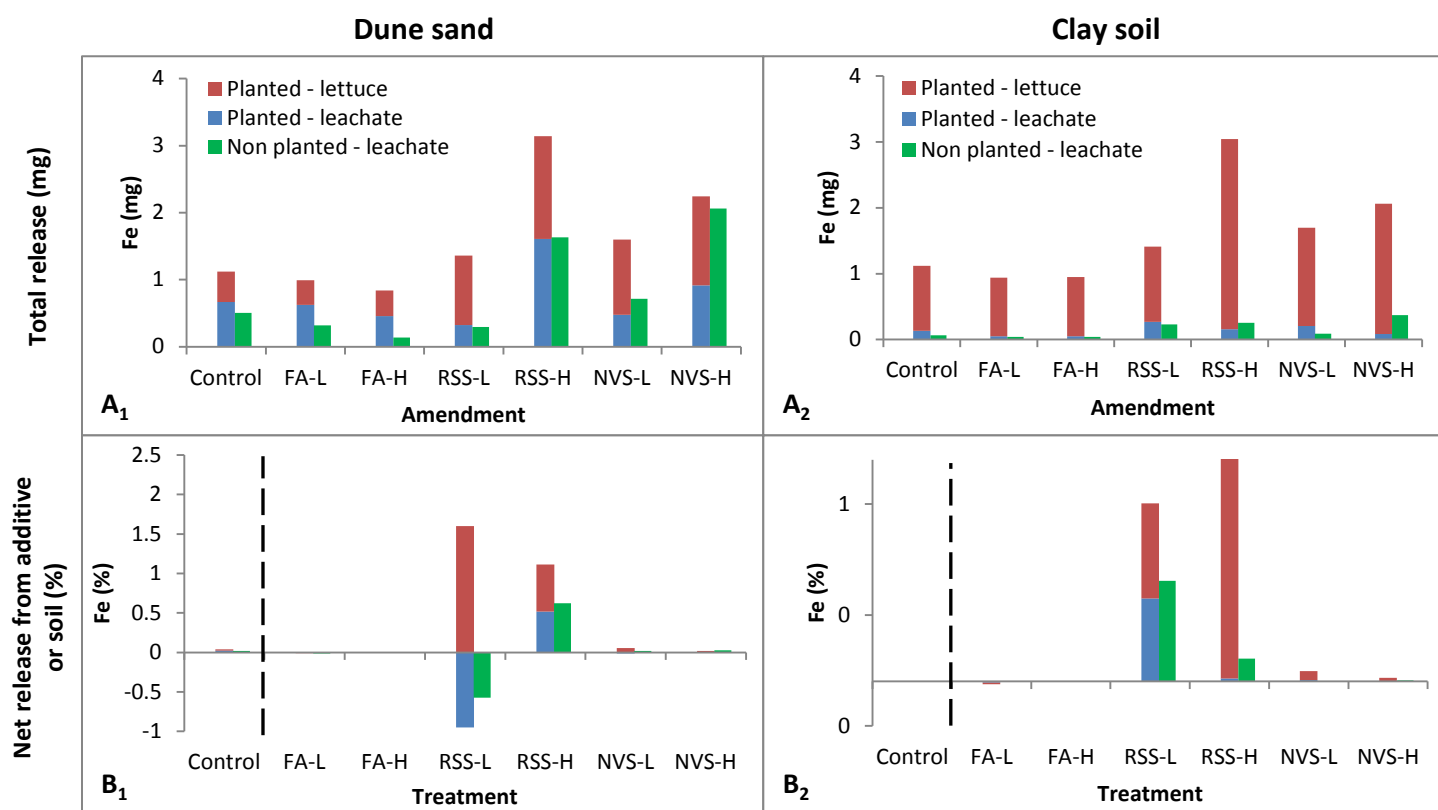


Figure A17: Iron mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁&A₂ show the overall amount released and B₁&B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A12.

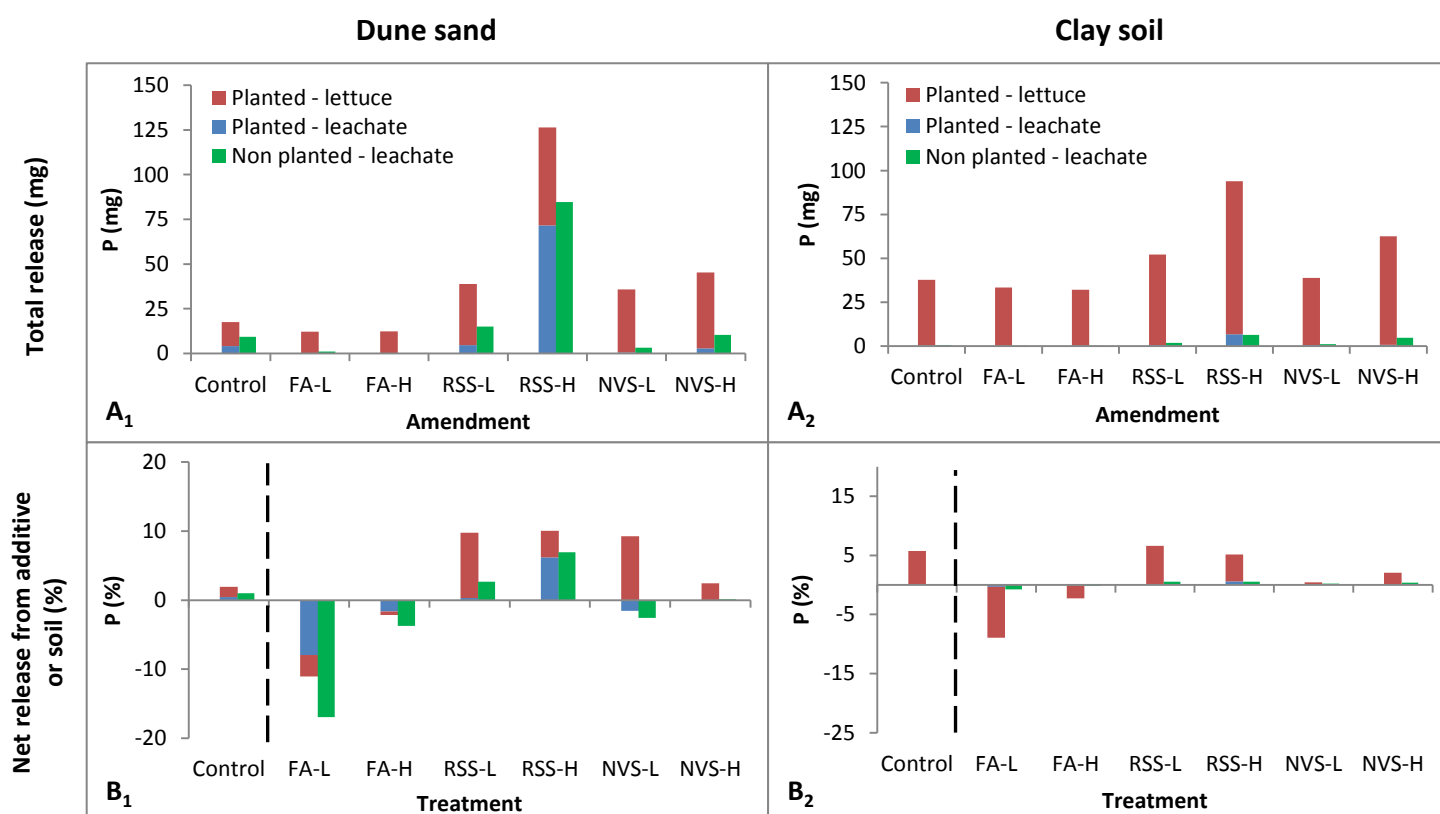


Figure A18: Phosphorus mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A1&A2 show the overall amount released and B1&B2 represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A15.

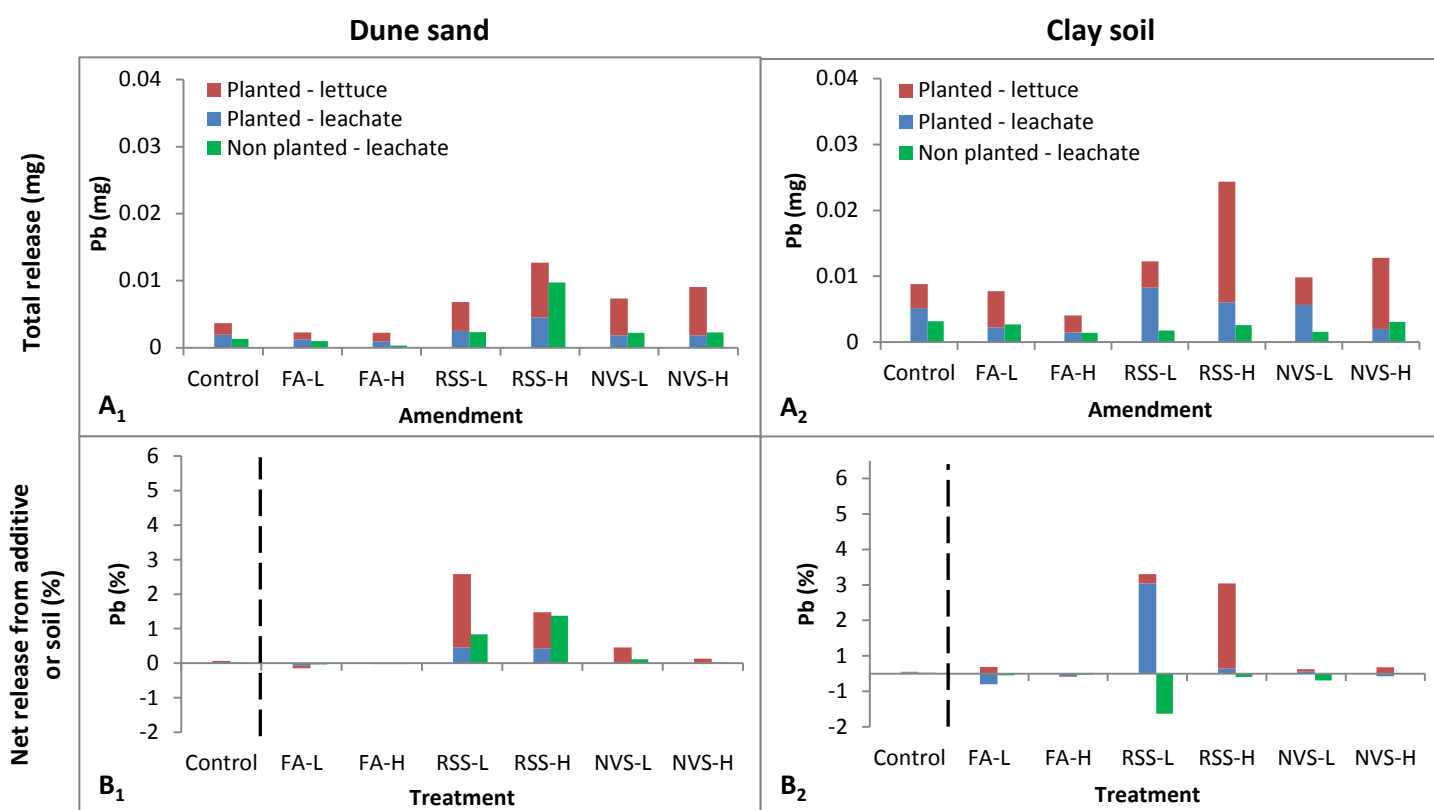


Figure A19: Lead mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A1&A2 show the overall amount released and B1&B2 represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A13.

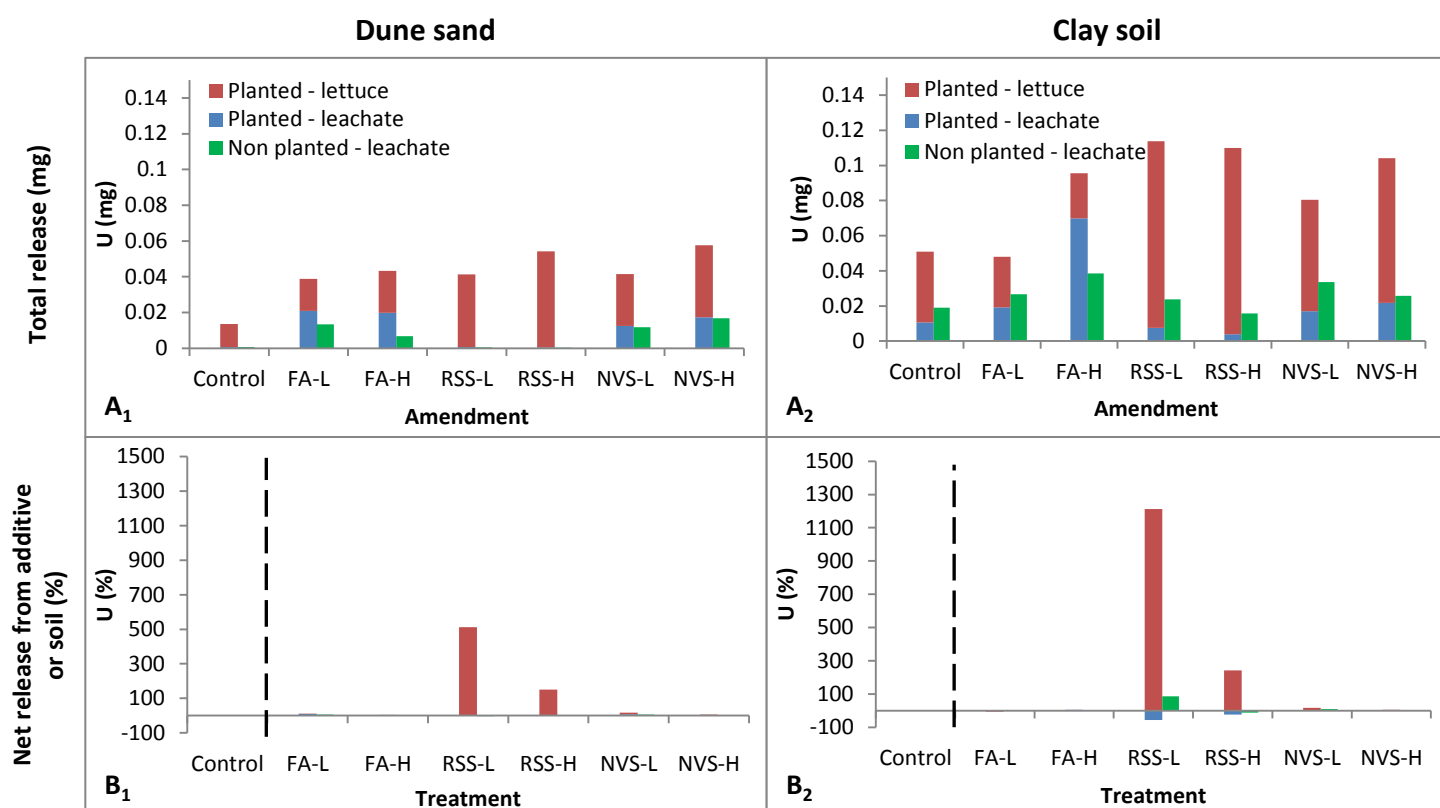


Figure A20: Uranium mass balance. Each paired graphs represent release of the element to leaching and uptake from dune sand (figures 1) and clay soil (figures 2). A₁&A₂ show the overall amount released and B₁&B₂ represent the percent of element released from each additive; or from the soil, in the case of the non-amended controls, which are presented to the left of the broken line. Negative values in Figs. B result from higher release from the non-amended soil (+ fertigation) than from the amended soil. In Figs. B, the calculated percentage release in the control treatments is from the total content only. The As mass balance statistical significance scale (HSD) is presented in table A14.

חישובי מאזן מסה של קרקעות מטופלות ולא מטופלות עם וללא צמח הכוללים קליטה על ידי הצמח ומיצוי לנקז של המזהמים הפוטנציאליים מצביעים כי אפר הפחם בבמס"א אינו משחרר מזהמים פוטנציאליים בכמות גבוהה ולכן הוא בטוח ליישום חקלאי. החלק היחסי של כל יסוד אשר השתחרר מקרקעות בתוספת אפר פחם או במס"א היה נמוך בהרבה עבור הקרקע חרסיתית מאשר בחולית. הכמות המקסימלית של מוליבדן, בורון, ארסן וסלן שהשתחררה כתוצאה מיישום אפר פחם ובמס"א בקרקע חרסיתית בשמונת שבועות גידול החסות (יחסי מוצק/נוזל בטווח 0.3-2) שקולה ל- 4%, 13%, 34% ו- 7% מתוך התכולה הכללית, בהתאמה. לעומת זאת, הכמויות שהשתחררו מתערובת במס"א ואפר עם קרקע חולית היו גבוהות בהרבה (11%, 65%, 84% ו- 29%, בהתאמה).

כל יבול החסות שהופק בניסוי העציצים נמצא בטוח למאכל אדם, מאחר וריכוזי היסודות בחסות לא הגיע לערך המרבי המותר בירק עלוותי (יבש) למאכל (1 מ"ג קדמיום/ק"ג, 1.5 מ"ג עופרת/ק"ג ו- 5 מ"ג ארסן/ק"ג). יחד עם זאת, יישומי במס"א ואפר פחם הגדילו את ריכוזי יסודות אלו בחסות בהשוואה לקרקעות לא מטופלות (0.55 לעומת 0.04 מ"ג קדמיום/ק"ג, 0.9 לעומת 0.5 מ"ג עופרת/ק"ג, ו- 0.45 לעומת 0.06 מ"ג ארסן/ק"ג, בהתאמה). תוספת בוצה ובמס"א לקרקעות הגדילה את יבול החסה. מלבד יישום הבוצה בעומס גבוה, לא נמצא מתאם סטטיסטי ביבול החסות (משקל יבש) בין כל שאר הטיפולים, למרות שביישומי בוצה ובמס"א נצפתה התפתחות מוגברת של חסה.

מיצוי המזהמים הפוטנציאליים שנבחנו בעבודה זו מושפע בעיקר מרמת החומציות של הקרקע ולכן במחקרים עתידיים, ניתן להיעזר בשיטת המיצוי תלוית דרגת חומציות, US-EPA 1313, לבחינת תוספי קרקע שונים.

תקציר

בוצה מיוצבת בסיד ואפר פחם (במס"א) הינה תערובת דיסון לקרקעות חקלאיות המורכבת מבוצת שפכים, אפר פחם מרחף וסיד (ביחס של 5:40:55, בהתאמה). במס"א מכילה יסודות קורט ויסודות עיקריים המהווים מקור הזנה יעיל לצמחיה, ומשפרת תכונות פיסיקליות, כימיות וביולוגיות של הקרקע. אולם, אפר הפחם המשמש ליצור הבמס"א עלול להגביר שחרור מתכות רעילות ואת זמינותם לצמח. מטרת מחקר זה היא לבחון את התרומה היחסית של רכיבי הבמס"א (אפר פחם ובוצת שפכים) לשחרור מזהמים פוטנציאליים, קליטתם על ידי צמחיה וחלחול למי תהום. המחקר התמקד בארבעה מזהמים פוטנציאליים ארסן (As), בורון (B), מוליבדן (Mo) וסלן (Se) המנוטרים ע"י המשרד להגנת הסביבה, משרד החקלאות ופיתוח הכפר ומשרד הבריאות. שחרור יסודות לתמיסת הקרקע הוערך בעזרת שני ניסויים שונים: (1) שיטת מיצוי US-EPA 1313 שבוחנת שחרור יסודות כתלות ברמת החומציות (pH) ו- (2) ניסוי מיני-ליזימטרים (ML) בחממת מכון וולקני. בנוסף למיצוי יסודות הקורט, ניסוי העציצים בחן גם את קליטת היסודות ע"י צמחיה תוך שימוש בחסה כצמח בוחן.

המחקר כלל שני סוגי קרקעות: חול דיונה (פלמחים) וקרקע חרסיתית (רבדים), אשר עורבבו עם במס"א, אפר פחם או בוצת שפכים בשתי רמות יישום - נמוכה וגבוהה. רמת היישום הנמוכה נקבעה על פי עומס החנקן השנתי המקסימלי המותר (500 kg N/ha), ורמת היישום הגבוהה הייתה פי חמש מערך זה (2500 kg N/ha). אפר פחם קולומביאני (La-Loma) נבחר לשימוש במחקר זה מאחר והוא מכיל ריכוזים גבוהים במיוחד של מזהמים פוטנציאליים. הבוצה במחקר הינה בוצת שפכים שניונית לא מיוצבת ממכון טיפול השפכים שפד"ן.

תוצאות מיצוי החומרים הגולמיים, בוצה ואפר פחם, כתלות ברמת החומציות הצביעו על שחרור מוגבר של מזהמים פוטנציאליים בטווח חומציות רחב. שחרור יסודות מזהמים אלה מהבמס"א מקורם באפר הפחם, ולכן שחרור יסודות מוגבר מתקיים גם בתערובות הבמס"א עם הקרקעות בכל טווח החומציות. הבוצה אינה מקור משמעותי ליסודות מזהמים.

ריכוזי מוליבדן, בורון וסלן שהשתחררו לנקזי העציצים כתוצאה מיישום במס"א ואפר פחם (בעציצים עם וללא צמח) הלכו וירדו כתלות ביחס השטיפה (מוצק/נוזל; L/S), כצפוי בתהליך שטיפה ראשונה ("first flush"). אולם, ריכוזי הארסן הושפעו פחות מיחס השטיפה. לדוגמא, ביישום במס"א בעומס גבוה בקרקע חולית ללא צמח (DS-NVS-H) פחת שחרור מתכות אלו כתלות ביחס מוצק/נוזל (0.3-5): 7.65 ל- 0.5 מ"ג בורון/ליטר, 1.65 ל- 0.03 מ"ג מוליבדן/ליטר, 0.18 ל- 0.02 מ"ג סלן/ליטר ו- 0.14 ל- 0.06 מ"ג ארסן/ליטר.

נמצאה התאמה טובה בין הריכוזים שנמדדו בניסוי העציצים לבין שיטת US-EPA 1313 עבור שתי הקרקעות בתוספת במס"א בעומס גבוה. ההתאמה המוצלחת ביותר נצפתה עבור ריכוזי סלן. התאמה חיובית זו מצביעה על חשיבות רמת החומציות כמשפיעה על מיצוי מזהמים פוטנציאליים לעומת שינויים ביחסי מוצק/נוזל וסוג הקרקע.



המכון הגיאולוגי
משרד האנרגיה

**מיצוי יסודות קורט ביישום במס"א (בוצה מיוצבת בסיד ואפר פחם)
בקרקות חקלאיות וזמינותם לצמחיה**

אלון משה

עבודה זו הוגשה כחיבור לקבלת תואר "מוסמך" לפקולטה לחקלאות, מזון וסביבה ע"ש רוברט ה. סמית, האוניברסיטה העברית בירושלים.

העבודה נעשתה בהדרכתם של:

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ד"ר פנחס פיין, מינהל המחקר החקלאי, מרכז וולקני.