IS FIELD CROP CONTAMINATION WITH HEAVY MEATALS AN EMERGING CONCERN?

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ABSTRACT

Heavy metal contamination of food, particularly food consumed by infants and young children, with arsenic (As), cadmium (Cd), and lead (Pb), is a major food safety concern and is beginning to draw heightened regulatory scrutiny in the United States. Improved strategies, including fertilizer management, are needed to better understand and minimize the risks of heavy metal uptake. The objective was to: 1) evaluate the effectiveness of soil amendments in minimizing winter wheat (*Triticum aestivum* L.) uptake of heavy metals, and 2) visualize the spatial distribution of As, Cd, and Pb in winter wheat grain using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-TOF-MS). A randomized complete block design with four replications was established in Lansing, MI. Treatments investigated included: 1) control, 2) pre-plant agricultural lime (2 T A^{-1}), 3) pre-plant dairy compost (5 T A^{-1}), 4) pre-plant biochar (2 T A^{-1}), 5) pre-plant gypsum (1 T A^{-1}), 6) pre-plant granular $ZnSO_4$ (10 lbs. Zn A^{-1}) and foliar $ZnSO_4$ (1 pint A^{-2}) at Feekes (FK) 9, 7) low N (50 lbs. N A^{-1}) at FK 4, 8) moderate N (100 lbs. N A^{-1}) at FK 4, 9) high N (150 lbs. N A^{-1}) at FK 4, and 10) biodegradable chelating agent ethylenediaminedisuccinic acid (EDDS) sprays with a 2 mmol L^{-1} concentration applied at FK 5, FK 5 + 1 week, and FK 5 + 2 weeks. Autumn starter fertilizer was top-dressed to provide 15 lbs. N and 12.5 lbs. S A^{-1}, respectively, at planting. All treatments received a base green-up N application rate of 100 lbs. N A^{-1} of urea (46-0-0) except check and N fertilizer treatments. In both Feekes 4 and harvest soil samples, the order of heavy metal concentrations in soil was Pb > As > Cd. Across sample timings, the order of winter wheat stages with plant tissue Cd levels was Feekes 4 > Feekes 9 > grains at harvest; Feekes 9 > grains at harvest >> Feekes 4 for plant tissue As levels; and Feekes 4 = Feekes 9 > grains at harvest for plant tissue Pb levels.

MATERIALS AND METHODS

Field experiments were established in Lansing, MI (42°41'14.78"N, 84°29'10.15" W). Plots measured 12 rows wide (8.5 ft. width by 25 ft. length by 7.5 inch. row spacing) and planted using a Great Plains 3P600 drill (Great Plains Manufacturing, Salina, KS). Soft red winter wheat 'Wharf' was planted at 1.8 million A^{-1}. Pre-plant soil characteristics (0–8 in.) included 7.1 pH (1:1 soil/water) (Peters et al., 2015), 33 mg kg^{-1} P (Bray-P1) (Frank et al., 2015), 80 mg kg^{-1} K (ammonium acetate method) (Warncke& Brown, 2015), 23 g kg^{-1} soil organic matter (loss-on-ignition) (Combs & Nathan, 2015), and 3.4 mg kg^{-1} Zn (0.1 M HCl) (Whitney, 2015). Soil nitrate concentration (0-30 cm) was collected prior to planting with 3 mg NO_3-N kg^{-1} soil (nitrate electrode method) (Gelderman & Beegle, 2015).

Monthly growing season weather data was obtained from MSU Enviro-weather (https://enviroweather.msu.edu/, MSU, East Lansing, MI). A 30-year mean was compiled using National Oceanic and Atmospheric Administration data (NOAA, 2022). On 01 July 2024, the outer 5 ft. of plots were mowed prior to harvest. Grain yield was collected from the center 5 ft. by 20 ft. in each plot using a plot combine (Kincaid Equipment Manufacturing, Haven, KS). Grain weight, moisture, and test weight were measured to calculate grain yield expressed as bu. A^{-1} at 13.5% moisture.

Sample Preparation

Four random soil cores (0-8 in.) were sampled from each plot before planting, Feekes 4, and post-harvest, then air-dried for 72 hours, ground, and sieved through a 2 mm sieve. Tillers at Feekes 4 and Feekes 9 flag leaf were washed with tap water to remove soil particles followed by two washings with deionized water. At Feekes 4, tillers were separated into shoots and roots using a Teflon knife after air drying. The shoots were retained while the roots were discarded. Wheat shoots and flag leaves were dried at 158 °F for 72 hours before being ground to 1 mm (UDY Cyclone sample mill). Grain samples were manually cleaned by removing excess husk. Winter wheat grain (50g) was ground into a coarse powder using an electric coffee grinder (Hamilton Beach®, Richmond, VA) for 1 minute.

Microwave digestion and dilution

Due to differences in microwave digestion protocols, samples were digested in separate batches: (1) soil and (2) plant tissue (i.e., biomass at Feekes 4, flag leaf at Feekes 9, grains at harvest). Soil samples were digested using a microwave-assisted digestion method following EPA Method 3051 (U.S. EPA, 2007). Plant tissue samples and fertilizers were digested using EPA Method 3052 (U.S. EPA, 2007). Grains were digested at 200 °C (ramp time = 15 min., hold time = 15 min., 800 psi, power = 900-1,050 W).

Elemental analyses using ICP-QQQ-MS

The total Cd, As, and Pb concentrations were determined using Triple Quadrupole Inductively Coupled Plasma Mass Spectroscopy (ICP-QQQ-MS, 8900 Triple Quadrupole ICP-MS, Agilent Technologies, Santa Clara, CA). The isotopes used for each element followed the FDA Elemental Analysis Manual Section 4.7 ICP-MS Method. A certified reference material (NIST 1517a tomato leaves) from the National Institute of Standards and Technology (Gaithersburg, MD) and at least one blank run was used for quality control of plant tissue and grain analysis.

Translocation indicator

The plant uptake factor (PUF) indicates the plant's capacity to absorb a specific element. The PUF was calculated as the plant tissue elemental concentration divided by the soil elemental concentration, where w(plant) is the plant tissue elemental concentration (mg kg^{-1}) and w(soil) is the soil elemental concentration (mg kg^{-1}).

RESULTS

3.1 Weather

Compared to 30-year air temperature and precipitation averages, growing conditions in 2023-2024 had normal air temperatures (avg. 38.3-52.3 °F), wet early (Oct., + 49%) and dry late autumn (Nov., -52%). From December 2023 to March 2024, temperatures were warm (+ 5.4 °F) and moisture plentiful (+ 9%). April to May 2024 had warm temperatures (+2.7 °F) and dry spring conditons (-33%). June 2024 had normal air temperature (avg. 69.4 °F) but deficit precipitation (-10%) **(data not shown).**

3.2 Grain yield

Grain yield ranged from 18.2-109.2 bu. A^{-1} with a mean of 83.6 bu. A^{-1}. Low N decreased grain yield ($P < 0.0001$) by 19.1-35.8 bu. A^{-1} compared to the remaining soil amendments **(data not shown).**

3.3 Effects of soil amendments on bulk soil samples

The experimental site was established on a Conover loam soil (Fine-loamy, mixed, active, mesic *Aquic Hapludalfs*) with a surface layer of 41.6% sand, 39.2% silt and 19.2% clay (National Cooperative Soil Survey, 2018). Prior to the field experiment, the average soil cadmium (Cd), arsenic (As), and lead (Pb) concentrations were 0.46, 5.50, and 13.46 mg kg^{-1} soil.

Bulk soil sampling of soil amendment treatments at Feekes 4 had comparable soil Cd, As, and Pb levels with check **(Table 3.1).** Soil Cd levels ranged from 0.13-0.36 mg kg^{-1} soil with a mean of 0.25 mg kg^{-1} soil. Soil As levels ranged from 2.58-3.89 mg kg^{-1} soil with a mean of 3.27 mg kg^{-1} soil greater than the statewide average of 2.50 mg kg^{-1} soil (State of Michigan, 2023). Soil Pb levels ranged from 8.52-25.37 mg kg^{-1} soil with a mean of 12.06 mg kg^{-1} soil.

Bulk soil sampling of soil amendment treatments at harvest had comparable soil As and Pb levels with check **(Table 3.1).** Among soil amendments, $ZnSO_4$ increased soil Cd level by 0.047 mg kg^{-1} soil. Soil Cd levels ranged from 0.15-0.43 mg kg^{-1} soil with a mean of 0.24 mg kg^{-1} soil. Soil As levels ranged from 1.56-3.99 mg kg^{-1} soil with a mean of 2.47 mg kg^{-1} soil. Soil Pb levels ranged from 7.76-12.11 mg kg^{-1} soil with a mean of 9.91 mg kg^{-1} soil. Soils were considered non-contaminated based on the Pb threshold of 39 mg kg^{-1} soil for gardening use of soils in Michigan (State of Michigan, 2023). Across both sampling periods, the order of heavy metal concentrations in soil was Pb > As > Cd. Further, Feekes 4 had greater As and Pb soil levels than at harvest while soil Cd levels remained comparable.

3.4 Effects of soil amendments on biomass and grain heavy metal concentrations

Cadmium, As, and Pb concentrations in winter wheat biomass at Feekes 4 and flag leaf at Feekes 9 were expressed in mg kg^{-1} of dry weight (dw) while grains at harvest were expressed in mg kg^{-1} of fresh weight (fw). At both Feekes 4 and 9, Pb was the most prevalent heavy metal followed by Cd and As. On the other hand, Cd was the most dominant heavy metal at harvest followed by Pb and As.

Wheat biomass from soil amendments at Feekes 4 and grain at harvest had comparable Cd levels with check **(Table 3.3).** Cadmium accumulation in biomass at Feekes 4 ranged from 0.22-0.60 mg kg^{-1} dw with a mean of 0.34 mg kg^{-1} dw. At Feekes

9, all soil amendments decreased flag leaf Cd level by 0.26-0.28 mg kg^{-1} with lime showing the greatest reduction compared to the control. Flag leaf total Cd levels ranged from 0.04-0.99 mg kg^{-1} dw with a mean of 0.15 mg kg^{-1} dw. Grain total Cd levels at harvest ranged from 0.019-0.053 mg kg^{-1} fw with a mean of 0.033 mg kg^{-1} fw. Across sampling, the order of winter wheat stages with plant tissue Cd levels was Feekes 4 > Feekes 9 > grains at harvest.

Biomass total As levels were below the detection limit (< 1.736 x 10^{-6} mg kg^{-1}) at Feekes 4. Arsenic accumulation began in the flag leaf at Feekes 9 ranging from 0.06-0.64 mg kg^{-1} dw with a mean of 0.16 mg kg^{-1} dw **(Table 3.3).** Soil amendments reduced flag leaf As levels by 18-24 mg kg^{-1} at Feekes 9 compared to the check plot. Grains at harvest had comparable As levels with check ranging from 0.002-0.006 mg kg^{-1} fw with an average of 0.003 mg kg^{-1} fw. Across sampling, the order of winter wheat stages with plant tissue As levels was Feekes 9 > grains at harvest >> Feekes 4.

Wheat Feekes 4 biomass and grain at harvest had comparable Pb levels with check **(Table 3.3).** Lead accumulation began in biomass at Feekes 4 ranging from 0.34-3.54 mg kg^{-1} dw with a mean of 1.33 mg kg^{-1} dw. At Feekes 9, the addition of $ZnSO_4$ decreased flag leaf Pb level by 2.90 mg kg^{-1} dw. Flag leaf total Pb levels ranged from 0.06-7.71 mg kg^{-1} dw with a mean of 1.57 mg kg^{-1} dw. Grain total Pb levels at harvest ranged from 0.003-0.073 mg kg^{-1} fw with a mean of 0.016 mg kg^{-1} fw. Among the mean grain Pb concentrations from soil amendments, lime (0.010 mg kg^{-1}) and gypsum (0.006 mg kg^{-1}) were within the allowable limit set by FDA (0.010 mg kg^{-1}). Across sampling, the order of winter wheat stages with plant tissue Pb levels was Feekes 4 = Feekes 9 > grains at harvest.

3.5 Effects of soil amendments on plant uptake factor of heavy metals

Plant uptake factor reflects the capacity of winter wheat to absorb heavy metals at certain crop stages. The PUF of heavy metals on biomass at Feekes 4 and grains at harvest showed that Cd was most absorbed followed by Pb and As **(Table 3.2).** Biomass exhibited greater PUF values for Cd accumulation than grains. Nonetheless, biomass Cd PUF values remained comparable with check (P = 0.3668). At harvest, all soil amendments, except for the high N rate and gypsum, were significantly different from the check (P = 0.0858). On the other hand, the addition of lime and biochar provided the lowest grain Cd PUF values. Grain As (P = 0.7903), biomass Pb (P = 0.5933) and grain Pb (P = 0.6133) PUF values remained comparable across treatments.

PRELIMINARY CONCLUSIONS

Initial results demonstrate the spatial distribution and temporal variation of Cd, As, and Pb in winter wheat. As plant growth progressed, As levels increased while Cd and Pb levels declined. Additionally, Cd was more readily transported from soil to grain compared to As and Pb. The potential of soil amendments to reduce heavy metal uptake was observed. Agricultural lime or biochar application resulted in lower grain Cd PUF values and Pb levels (< FDA action level 0.01 mg Pb kg^{-1}). The inherent properties of agricultural lime and biochar had a greater heavy metal immobilization impact than the other soil amendments.

Table 3.1 Cadmium, arsenic, and lead levels (mg kg^{-1}) in bulk soils at Feekes 4 and harvest. Mean Cd, As, and Pb levels of check plots were displayed. All other treatments display change in Cd, As, and Pb levels using Dunnett's test.

Treatment	Bulk soil at Feekes 4[a]			Bulk soil at harvest[b]		
	Cd	As	Pb	Cd	As	Pb
	mg kg^{-1} soil					
Check	0.25	3.29	12.48	0.22	2.56	9.77
Lime	-0.016^{ns}§	+0.18^{ns}	+2.12^{ns}	+0.035^{ns}	-0.20^{ns}	-0.19^{ns}
Dairy compost	+0.019^{ns}	+0.10^{ns}	-1.39^{ns}	+0.031^{ns}	+0.42^{ns}	+0.61^{ns}
Biochar	+0.001^{ns}	+0.02^{ns}	-1.26^{ns}	+0.021^{ns}	-0.24^{ns}	+0.44^{ns}
Gypsum	-0.016^{ns}	-0.16^{ns}	-0.55^{ns}	+0.014^{ns}	-0.36^{ns}	-0.03^{ns}
$ZnSO^4$	-0.040^{ns}	-0.26^{ns}	-0.96^{ns}	+0.047*	-0.25^{ns}	+0.54^{ns}
Low N	NA ¶	NA	NA	+0.028^{ns}	0.37^{ns}	+0.35^{ns}
Moderate N	NA	NA	NA	+0.017^{ns}	-0.22^{ns}	+0.26^{ns}
High N	NA	NA	NA	-0.016^{ns}	-0.02^{ns}	-0.15^{ns}
EDDS	NA	NA	NA	-0.011^{ns}	-0.35^{ns}	-0.25^{ns}
Range	0.13-0.36	2.58-3.89	8.52-25.37	0.15-0.43	1.56-3.99	7.76-12.11
Overall mean	0.25	3.27	12.06	0.24	2.47	9.91

[a] Dunnett's test degrees of freedom = 18.
[b] Dunnett's test degrees of freedom = 27
§ Asterisks indicate thresholds of significance (NS, P > 0.10; *, P < 0.10; **, P < 0.05; ***, P < 0.001).
¶ NA - not applicable, treatments were excluded since they had not been applied before the Feekes 4 sampling.

Table 3.2 Plant uptake factor of heavy metals on biomass at Feekes 4 and grains at harvest as influenced by soil amendments.

Treatment	Biomass Feekes 4		Grains at harvest		
	Cd	Pb	Cd	As	Pb
Check	1.4	0.1	0.20 a	0.001	0.001
Lime	2.1	0.1	0.12 c	0.001	0.001
Dairy compost	1.3	0.1	0.16 abc	0.001	0.001
Biochar	2.0	0.1	0.12 c	0.001	0.003
Gypsum	1.5	0.1	0.17 ab	0.001	0.001
$ZnSO^4$	0.9	0.1	0.14 bc	0.001	0.001
Low N	¶ NA	NA	0.14 bc	0.001	0.003
Moderate N	NA	NA	0.15 bc	0.001	0.002
High N	NA	NA	0.19 a	0.001	0.002
EDDS	NA	NA	0.14 bc	0.001	0.002
P > F §	NS	NS	*	NS	NS

§.Asterisks indicate thresholds of significance (NS, P > 0.10; *, P < 0.10; **, P < 0.05;

***, P < 0.001). Treatments were compared at 0.10 probability level, Fisher's least significant difference (LSD). Values followed by the same lowercase letter are not significantly different.
¶ NA - not applicable, treatments were excluded since they had not been applied before the Feekes 4 sampling.

Table 3.3 Cadmium, arsenic, and lead levels (mg kg^{-1}) in winter wheat biomass at Feekes 4, flag leaf at Feekes 9, and grains at harvest. Mean As, and Pb levels of check plots were displayed. All other treatments display change in Cd, As, and Pb levels using Dunnett's test.

Treatment	Biomass Feekes 4[a]		Flag leaf Feekes 9[b]			Grains at harvest[c]		
	Cd	Pb	Cd	As	Pb	Cd	As	Pb
	mg kg^{-1}							
Check	0.32	1.06	0.39	0.36	3.16	0.041	0.003	0.010
Lime	-0.03^{ns} §	+0.66^{ns}	-0.28*	-0.24**	-1.06^{ns}	-0.012*	-0.0006^{ns}	+0.000^{ns}
Dairy compost	-0.03^{ns}	+0.01^{ns}	-0.25*	-0.21**	-2.34^{ns}	-0.006^{ns}	-0.0006^{ns}	+0.005^{ns}
Biochar	-0.02^{ns}	+0.73^{ns}	-0.26*	-0.23**	-2.26^{ns}	-0.014*	-0.0003^{ns}	+0.017^{ns}
Gypsum	+0.11^{ns}	+0.41^{ns}	-0.27*	-0.21**	-2.39^{ns}	-0.005^{ns}	-0.0004^{ns}	-0.003^{ns}
ZnSO^{4}	+0.05^{ns}	-0.29^{ns}	-0.26*	-0.21**	-2.90*	-0.011*	-0.0004^{ns}	+0.001^{ns}
Low N	NA ¶	NA	-0.27*	-0.18**	-2.38^{ns}	-0.011*	-0.0001^{ns}	+0.017^{ns}
Moderate N	NA	NA	-0.24*	-0.21**	-1.04^{ns}	-0.008^{ns}	+0.0000^{ns}	+0.011^{ns}
High N	NA	NA	-0.26*	-0.20**	-0.86^{ns}	-0.004^{ns}	+0.0004^{ns}	+0.008^{ns}
EDDS	NA	NA	-0.26*	-0.19**	-0.68^{ns}	-0.012*	-0.0002^{ns}	+0.007^{ns}
Range	0.22-0.60	0.34-3.54	0.04-0.99	.06-0.64	0.06-7.71	0.019-0.053	0.002-0.006	0.003-0.073
Overall mean	0.34	1.33	0.15	0.16	1.57	0.033	0.003	0.016

[a] Dunnett's test degrees of freedom = 18.
[b] Dunnett's test degrees of freedom= 27.
[c] Dunnett's test degrees of freedom = 27
§.Asterisks indicate thresholds of significance (NS, P > 0.10; *, P < 0.10; **, P < 0.05; ***, P < 0.001)
¶ NA - not applicable, treatments were excluded since they had not been applied before the Feekes 4 sampling.