ACS Scott: Input Level Effects on Crop and Soil Heavy Metal and Metalloid Concentrations

E. Poscher [1], S.A. Brandt [2], M.P. Schellenberg [1], and M.R. Fernandez [1]

[1] Agriculture and Agri-Food Canada, Semiarid Prairie Agricultural Research Centre, P.O. Box 1030, Swift Current, SK S9H 3X2, Canada.
[2] Agriculture and Agri-Food Canada, P.O. Box 10, Scott, SK S0K 4A0, Canada.

Abstract

Different input levels, defined by a combination of tillage intensity and the application of agro-chemicals, affect the availability of heavy metals and metalloids in the soil and subsequently the absorption of heavy metals and metalloids by crops. We studied the effect of organic, high, and reduced input levels in a long-term rotation study on the concentration of 24 heavy metals and metalloids in yellow peas and hard red spring wheat. The Long-Term Agro-Ecosystem Research for the Canadian Prairie Ecozone (Alternative Cropping Systems Project) was established at the AAFC Research Farm in Scott, SK, Canada in 1994, rotating in six-year cycles. We found that selenium concentration in yellow peas and cobalt concentration in hard red spring wheat were highest under the organic input level, while cadmium levels in yellow peas were highest in the high and reduced input levels. The difference in soil heavy metal and metalloid concentration was not significant among input levels but significant between crop types.

Introduction

Desirable and undesirable heavy metal and metalloid concentrations are monitored in crops for human consumption and have been found increasingly elevated in durum wheat (Clarke *et al.* 2002), flax, sunflower (Li *et al.* 1995), potatoes (McLaughlin *et al.* 1994, McLaughlin *et al.* 1995), and yellow peas (Pratt 2006). At the production level, management practices (such as tillage intensity; choices of agricultural input, i.e., animal manure, organic and inorganic fertilizer, pesticides, *inter alia*; or crop type choices) affect soil properties, such as soil organic matter or pH (Lavado *et al.* 2001). This in turn influences the solubility, mobility, and phytoavailability of heavy metals and metalloids that are naturally present in the soil or that are applied or mobilized through management practices (Düring *et al.* 2002).

The Alternative Cropping Systems (ACS) Project at Scott, SK is a long-term rotation study to evaluate the sustainability of conventional and alternative crop production systems in the Canadian Prairie agro-ecosystem (Thomas 2001). This project was established at the AAFC Research Farm in Scott, SK in 1994, as a four-replicate split-plot design with main plot treatments consisting of three input levels (i.e., organic, high, and reduced) and subplots

representing three levels of cropping diversity rotating on a six-year cycle (Ulrich *et al.* 2001). The three input levels are distinguished by a combination of tillage intensity and the application of agro-chemicals. The organic input level includes high tillage intensity, non-chemical pest control and nutrient management practices, and the cultivation of green manure legumes. The high input level uses less tillage intensity than the organic input level; this level also applies agro-chemicals based on conventional recommendations. The reduced input level almost completely excludes tillage and instead relies on the application of significant amounts of herbicides (Ulrich *et al.* 2001).

The objective of this present study was to evaluate the effect of organic, high, and reduced input levels when continuously applied for twelve years (i.e., two rotation cycles) on the concentration of heavy metals and metalloids in crops of yellow pea and hard red spring wheat and accompanying soils.

Materials and Methods

In 2007, we collected paired grain and soil samples of yellow peas (CDC Golden) and hard red spring wheat (Lillian) from each of the three input levels (i.e., organic, high, reduced) at the ACS Project in Scott, SK, Canada. We sampled three replications of the yellow peas from the diversified annual grains (DAG) level, rotating as barley/flax/wheat/canola/spring-wheat/pea in the high (plot numbers 15, 75, 153) and reduced (plot numbers 27, 105, 123) input levels and as barley/sweet-clover (green manure)/mustard/lentil (green manure)/wheat/pea in the organic input level (plots no. 39, 57, 141). We did not include the fourth replication of yellow peas from plots 189 and 213 because we found the crop still green in plot 177. We sampled all four replications of hard red spring wheat. The hard red spring wheat sample was collected from the low diversity (LOW) level, rotating as tillage only (fallow)/canola/wheat/tillage only (fallow)/wheat/wheat in the high input level (plots 9, 87, 159, 195), as tillage only (fallow)/canola/wheat/lentil (green manure)/wheat/wheat in the reduced input level (plot numbers 21, 93, 111, 207), and as lentil (green manure)/mustard/wheat/lentil (green manure)/wheat/wheat in the organic input level (plot numbers 45, 69, 135, 171). The grain samples were collected as close to harvest time as possible: yellow peas on July 30th, 2007 and hard red spring wheat on August 13th, 2007. Soil samples were collected from 0-15 cm depth, immediately adjacent to the plants taken for grain samples.

After drying and grinding, our crop samples were ground and packed, while our soil samples were packed. All samples were then shipped for analysis to Testmark Laboratories, in Garson, ON. All samples were analyzed for Al, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Mo, Ni, Se, Ag, Sr, Th, Sn, Ti, U, V, and Zn concentrations. Heavy metals and metalloids in crop samples were determined by ICP-MS with microwave digestion, while heavy metals and metalloids in soil samples were determined by ICP-MS with Aqua Regia Digest. The physical (grain size below 75μm) and chemical properties (alkalinity, cation exchange capacity, electrical conductivity of the saturated soil paste, pH, carbonates, and soil organic matter) of the soils were determined by standard methods.

We used univariate ANOVA for data analysis. Means and standard errors were estimated. Duncan's Multiple Range Test was applied to determine differing means at $p < 0.05$.

Results and Discussion

Soil heavy metal and metalloid concentrations

Input level had no significant effect on soil heavy metal and metalloid concentrations or on soil parameters, while crop type had a significant effect on soil heavy metal and metalloid concentrations and on soil parameters. In fact, arsenic, boron, selenium, tin, titanium, and vanadium were found significantly higher and iron was found significantly lower in soil under yellow peas, compared to soil under hard red spring wheat (Table 1). Soil under yellow peas showed higher alkalinity, CEC, conductivity, and carbonate percentage, compared to soil under hard red spring wheat (Table 2). We measured a slightly significantly higher pH in soil under hard red spring wheat, compared to the soil pH measured under yellow peas. There was no significant difference in soil organic matter and in grain size below 75μm between crop types.

Table 1. Soil heavy metal and metalloid concentrations (in μg*g^{-1}) under yellow peas (CDC Golden) and hard red spring wheat (Lillian). Sample size for yellow peas n = 3 and for hard red spring wheat n = 4. Numbers represent mean ± SEM. Not significant (n.s.) if p-value > 0.05.

Heavy metal/Metalloid	Peas (DAG) [1,2]	Wheat (LOW) [1,2]	p-value
Aluminium	8607.78 ± 323.50	9736.67 ± 451.40	n.s.
Arsenic	4.51 ± 0.31 [b]	3.38 ± 0.13 [a]	0.002
Barium	144.74 ± 7.42	146.75 ± 2.17	n.s.
Beryllium	0.51 ± 0.01	0.50 ± 0.00	n.s.
Boron	3.94 ± 0.23 [b]	3.15 ± 0.17 [a]	0.010
Cadmium	0.36 ± 0.04	0.40 ± 0.02	n.s.
Chromium	15.23 ± 0.73	14.24 ± 0.33	n.s.
Cobalt	6.40 ± 0.39	6.14 ± 0.14	n.s.
Copper	12.99 ± 1.11	11.65 ± 0.27	n.s.
Iron	9055.56 ± 267.65 [a]	13591.67 ± 245.09 [b]	0.001
Lead	6.73 ± 0.37	7.05 ± 0.17	n.s.
Manganese	453.44 ± 23.62	464.00 ± 11.50	n.s.
Mercury	0.05 ± 0.00	0.05 ± 0.00	n.s.
Molybdenum	0.54 ± 0.02	0.52 ± 0.01	n.s.
Nickel	10.95 ± 0.81	10.96 ± 0.30	n.s.
Selenium	1.04 ± 0.08 [b]	0.50 ± 0.00 [a]	0.001
Silver	0.50 ± 0.00	0.50 ± 0.00	n.s.
Strontium	16.71 ± 0.76	16.48 ± 0.59	n.s.
Thorium	1.09 ± 0.16	1.65 ± 0.12	n.s.
Tin	1.09 ± 0.16 [b]	0.64 ± 0.02 [a]	0.005
Titanium	171.89 ± 6.43 [b]	148.67 ± 3.15 [a]	0.002
Uranium	0.61 ± 0.04	0.61 ± 0.03	n.s.
Vanadium	27.43 ± 1.31 [b]	24.46 ± 0.58 [a]	0.035
Zinc	59.41 ± 7.45	63.89 ± 1.57	n.s.

[1] Cropping Diversity Level: DAG = diversified annual grains, LOW = low diversity.
[2] The letter 'a' indicates a measurement that was significantly lower than the measurement superscripted with the letter 'b' within rows, based on Duncan's Multiple Range Test.

Table 2. Comparison of soil parameters between yellow peas and hard red spring wheat. Sample size for yellow peas n = 3 and for hard red spring wheat n = 4. Numbers represent mean ± SEM. Not significant (n.s.) if p-value > 0.05.

Soil Parameter (unit)	Peas (DAG) [1,2]	Wheat (LOW) [1,2]	p-value
Alkalinity (mg*g^{-1})	0.40 ± 0.00 [b]	0.07 ± 0.01 [a]	0.001
CEC (cmol(+)*kg^{-1})	24.72 ± 1.05 [b]	19.17 ± 0.46 [a]	0.001
Conductivity (µS*cm^{-1})	179.67 ± 11.60 [b]	88.85 ± 5.74 [a]	0.001
Grain size below 75µm (%)	32.42 ± 2.17	38.04 ± 1.97	n.s.
pH	5.30 ± 0.05 [a]	5.60 ± 0.18 [b]	0.049
Carbonate (%)	1.23 ± 0.10 [b]	0.92 ± 0.08 [a]	0.022
SOM (%)	5.74 ± 0.36	4.97 ± 0.20	n.s.

[1] Cropping Diversity Level: DAG = diversified annual grains, LOW = low diversity.
[2] The letter 'a' indicates a measurement that was significantly lower than the measurement superscripted with the letter 'b' within rows, based on Duncan's Multiple Range Test.

Yellow pea heavy metal and metalloid concentrations

Input level had a significant effect on selenium and cadmium concentration in yellow peas. Selenium concentration was highest in the organically grown yellow peas, medium in the high input level, and lowest in the reduced input level (p = 0.020) (Figure 1). Cadmium concentration was highest in the reduced and high input levels and lowest in the organic input level (p = 0.035) (Figure 2). All other heavy metals and metalloids in yellow peas remained not significant among input levels. Mean concentrations of heavy metals and metalloids in yellow pea seeds are summarized in Table 3.
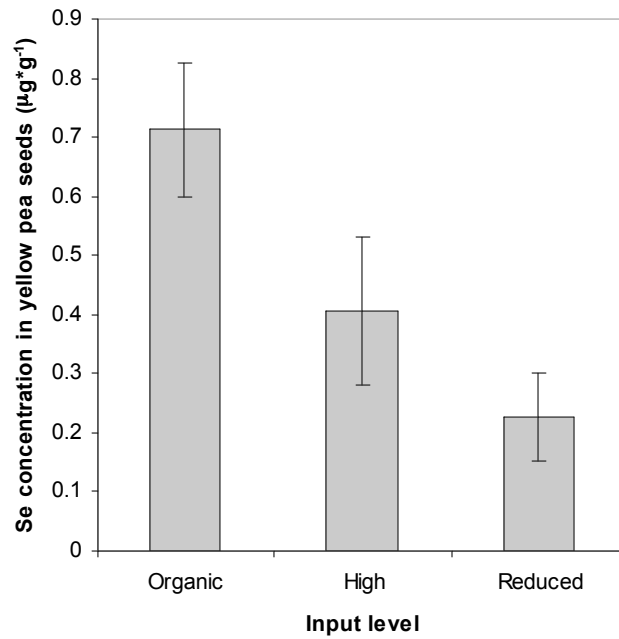
Figure 1. Selenium concentration ($\mu g*g^{-1}$) in yellow peas (CDC Golden) grown at three input levels (organic, high, and reduced) at the Scott Research Farm, SK. Bars indicate mean ± SEM. Sample size n = 3.

Figure 2. Cadmium concentration ($\mu g*g^{-1}$) in yellow peas (CDC Golden) grown at three input levels (organic, high, and reduced) at the Scott Research Farm, SK. Bars indicate mean ± SEM. Sample size n = 3.
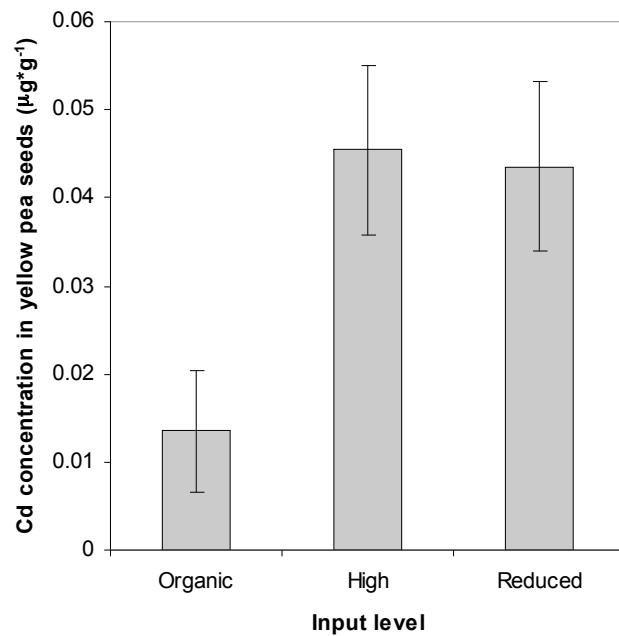
Table 3. Yellow pea heavy metal and metalloid concentrations (in $\mu g*g^{-1}$) when grown under organic, high, and reduced input levels; sample size n = 3. Not significant (n.s.) if p-value > 0.05. Grand mean represents all input levels (n = 9). Numbers represent mean ± SEM.

Heavy metal/Metalloid	Input Level[1] organic	high	reduced	p-value	Grand mean[2]
Aluminium	0.349 ± 0.145	0.460 ± 0.284	0.156 ± 0.045	n.s.	0.322 ± 0.103 [a]
Arsenic	0.018 ± 0.012	0.006 ± 0.000	0.006 ± 0.000	n.s.	0.010 ± 0.004
Barium	5.713 ± 0.673	6.710 ± 0.668	5.690 ± 0.153	n.s.	6.038 ± 0.324
Beryllium	0.029 ± 0.000	0.028 ± 0.000	0.029 ± 0.000	n.s.	0.028 ± 0.000 [a]
Boron	9.887 ± 0.502	10.527 ± 0.537	10.367 ± 0.167	n.s.	10.260 ± 0.238 [b]
Cadmium	0.014 ± 0.006[a]	0.046 ± 0.008[b]	0.044 ± 0.008[b]	0.035	0.034 ± 0.006
Chromium	0.677 ± 0.201	0.911 ± 0.236	0.891 ± 0.280	n.s.	0.826 ± 0.126 [b]
Cobalt	0.106 ± 0.002	0.088 ± 0.014	0.088 ± 0.005	n.s.	0.094 ± 0.005 [b]
Copper	4.930 ± 0.555	5.313 ± 0.795	4.377 ± 0.424	n.s.	4.873 ± 0.334
Iron	0.293 ± 0.003	0.290 ± 0.000	1.773 ± 1.483	n.s.	0.786 ± 0.494 [a]
Lead	0.039 ± 0.020	0.019 ± 0.000	0.019 ± 0.000	n.s.	0.026 ± 0.007
Manganese	12.033 ± 0.285	12.867 ± 0.273	12.667 ± 0.376	n.s.	12.522 ± 0.201 [a]
Mercury	0.010 ± 0.000	0.009 ± 0.000	0.009 ± 0.000	n.s.	0.010 ± 0.000 [a]
Molybdenum	0.665 ± 0.152	0.595 ± 0.113	0.918 ± 0.225	n.s.	0.726 ± 0.098
Nickel	0.019 ± 0.000	0.019 ± 0.000	0.019 ± 0.000	n.s.	0.019 ± 0.000 [a]
Selenium	0.712 ± 0.091[b]	0.407 ± 0.101[a]	0.227 ± 0.062[a]	0.020	0.448 ± 0.083 [a]
Silver	0.002 ± 0.000	0.005 ± 0.003	0.008 ± 0.006	n.s.	0.005 ± 0.002
Strontium	2.263 ± 0.148	2.410 ± 0.246	1.993 ± 0.046	n.s.	2.222 ± 0.104
Thorium	0.003 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	n.s.	0.003 ± 0.000 [a]
Tin	0.008 ± 0.005	0.022 ± 0.014	0.005 ± 0.002	n.s.	0.012 ± 0.005
Titanium	12.357 ± 0.867	13.933 ± 0.669	14.600 ± 0.231	n.s.	13.633 ± 0.462 [a]
Uranium	0.001 ± 0.000	0.001 ± 0.000	0.001 ± 0.000	n.s.	0.001 ± 0.000 [a]
Vanadium	0.004 ± 0.001	0.005 ± 0.001	0.003 ± 0.000	n.s.	0.004 ± 0.001
Zinc	75.367 ± 21.855	45.767 ± 6.528	57.000 ± 3.702	n.s.	59.378 ± 7.944

[1] Different letters within rows indicate significant difference among input levels.
[2] Different letters between the Grand Mean of Table 3 and Table 4 indicate significant differences between crop types. Mean ± SEM superscripted with the letter 'a' is significantly lower than mean ± SEM superscripted with the letter 'b', based on Duncan's Multiple Range Test.

Hard red spring wheat heavy metal and metalloid concentrations

   Input level had a significant effect on crop Co concentration, all other heavy metals and metalloids remaining not significant among input levels. Cobalt concentration was highest in the organically grown hard red spring wheat, medium in the reduced level, and lowest in the high input level (p = 0.022) (Figure 3). Mean concentrations of heavy metals and metalloids in yellow pea seeds are summarized in Table 4.
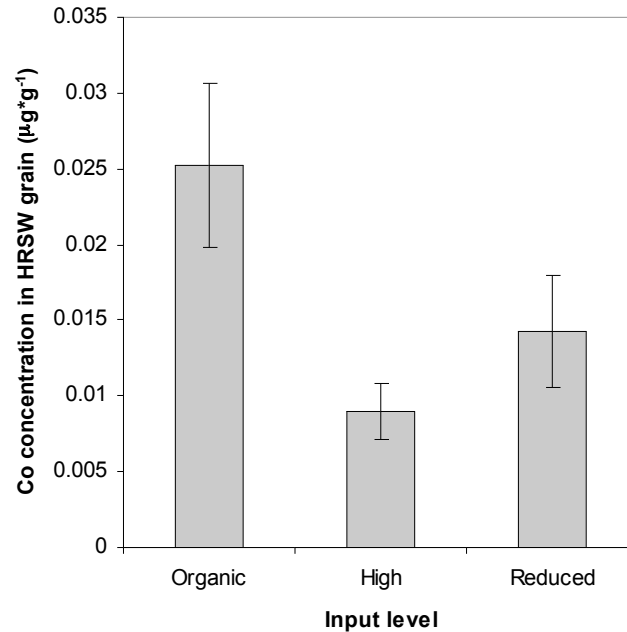

Figure 3. Cobalt concentration ($\mu g*g^{-1}$) in hard red spring wheat (Lillian) grown at three input levels (organic, high, and reduced) at the Scott Research Farm, SK. Bars indicate mean ± SEM. Sample size n = 4.

Table 4. Hard red spring wheat heavy metal and metalloid concentrations (in $\mu g \cdot g^{-1}$) when grown under organic, high, and reduced input levels; sample size n = 4. Not significant (n.s.) if p-value > 0.05. Grand mean represents all input levels (n = 12). Numbers represent mean ± SEM.

| Heavy metal/Metalloid | Input Level[1] | | | p-value | Grand mean[2] |
	organic	high	reduced		
Aluminium	3.510 ± 0.589	3.903 ± 0.416	3.203 ± 0.284	n.s.	3.538 ± 0.282 [b]
Arsenic	0.021 ± 0.011	0.010 ± 0.000	0.015 ± 0.000	n.s.	0.015 ± 0.004
Barium	5.222 ± 0.466	5.775 ± 0.286	4.983 ± 0.540	n.s.	5.328 ± 0.253
Beryllium	0.050 ± 0.000	0.050 ± 0.000	0.050 ± 0.000	n.s.	0.050 ± 0.000 [b]
Boron	2.175 ± 0.221	2.450 ± 0.065	2.575 ± 0.103	n.s.	2.400 ± 0.091 [a]
Cadmium	0.033 ± 0.015	0.009 ± 0.001	0.059 ± 0.034	n.s.	0.034 ± 0.013
Chromium	0.499 ± 0.201	0.465 ± 0.015	0.480 ± 0.069	n.s.	0.481 ± 0.036 [a]
Cobalt	0.025 ± 0.002[b]	0.009 ± 0.002[a]	0.014 ± 0.003[a]	0.022	0.016 ± 0.003 [a]
Copper	6.975 ± 0.555	5.020 ± 1.033	6.328 ± 0.976	n.s.	6.108 ± 0.608
Iron	60.375 ± 3.880	65.050 ± 6.861	50.400 ± 16.275	n.s.	58.608 ± 5.750 [b]
Lead	0.033 ± 0.020	0.033 ± 0.000	0.034 ± 0.001	n.s.	0.033 ± 0.000
Manganese	116.500 ± 3.096	103.725 ± 15.295	108.750 ± 2.287	n.s.	109.658 ± 5.012 [b]
Mercury	0.017 ± 0.000	0.017 ± 0.000	0.017 ± 0.000	n.s.	0.017 ± 0.000 [b]
Molybdenum	0.698 ± 0.228	0.649 ± 0.239	0.432 ± 0.113	n.s.	0.593 ± 0.113
Nickel	0.859 ± 0.068	0.641 ± 0.087	0.729 ± 0.641	n.s.	0.743 ± 0.046 [b]
Selenium	1.208 ± 0.544	0.720 ± 0.402	1.708 ± 0.392	n.s.	1.212 ± 0.265 [b]
Silver	0.003 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	n.s.	0.003 ± 0.000
Strontium	1.663 ± 0.208	1.995 ± 0.181	2.053 ± 0.239	n.s.	1.883 ± 0.120
Thorium	0.005 ± 0.000	0.005 ± 0.000	0.005 ± 0.000	n.s.	0.005 ± 0.000 [b]
Tin	0.005 ± 0.000	0.005 ± 0.000	0.005 ± 0.000	n.s.	0.005 ± 0.000
Titanium	19.975 ± 0.466	21.300 ± 0.512	20.275 ± 0.581	n.s.	20.517 ± 0.322 [b]
Uranium	0.002 ± 0.000	0.002 ± 0.000	0.002 ± 0.000	n.s.	0.002 ± 0.000 [b]
Vanadium	0.009 ± 0.004	0.007 ± 0.002	0.007 ± 0.002	n.s.	0.008 ± 0.001
Zinc	47.575 ± 1.772	55.0225 ± 4.462	42.625 ± 3.611	n.s.	48.408 ± 2.375

[1] Different letters within rows indicate significant difference among input levels.
[2] Different letters between the Grand Mean of Table 3 and Table 4 indicate significant differences between crop types. Mean ± SEM superscripted with the letter 'a' is significantly lower than mean ± SEM superscripted with the letter 'b', based on Duncan's Multiple Range Test.

Conclusions

(1) We found no difference in soil chemistry (i.e., heavy metal and metalloid concentrations, alkalinity, CEC, conductivity, pH, carbonate, soil organic matter) and soil physics (i.e., grain size below 75μm) among organic, high, and reduced input levels. These input levels had been applied for two preceding six-year-cycles.

(2) In spite of the lack of difference in soil metal concentrations among input levels, we found differences in crop heavy metal and metalloid concentrations among input levels. In fact, selenium in yellow peas and cobalt in hard red spring wheat were highest in the organic input level, compared to reduced and high input levels. Also, cadmium in yellow peas was highest in the high and reduced input levels. This could be explained by the fact that high tillage intensity might increase the phytoavailability of certain heavy metals and metalloids, such as selenium and cobalt. Higher concentrations of cadmium were probably the result of contaminants in agricultural inputs (i.e., organic and inorganic fertilizer, herbicides, pesticides), applied into the high and reduced input levels of this study.

(3) We found significant differences in soil chemistry between crop types. Crop type influences soil chemistry which in turn affects heavy metal and metalloid uptake and extraction ability of the current crop or the following crop in a rotation. Symbiotic rhizobia in legumes might greatly influence soil microclimate. As this study shows, peas had a significantly different soil microclimate, compared with the soil microclimate of hard red spring wheat.

(4) On a dry weight basis, yellow peas contained significantly higher levels of boron, chromium, and cobalt compared to hard red spring wheat. Hard red spring wheat contained significantly higher levels of aluminium, beryllium, iron, manganese, mercury, nickel, selenium, thorium, titanium, and uranium, compared to yellow peas on a dry weight basis of the seed.

(5) Estimating exposure risk for humans: the Tolerable Upper Intake Level (UL) is 11mg per day for manganese and 400μg per day for selenium (NRC 2005, Table 2.2 Toxicity Assessments of Nutrients for Humans Based on Food and Nutrition Board Assessments, p. 14). Combining these recommendations with our results, more than 94.4g of hard red spring wheat daily grown under the organic input level would be above the UL for manganese and more than 234.2g of hard red spring wheat daily grown under the reduced input level would be above the UL for selenium.

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