# Long-Term Trends in Heavy Metal and Metalloid Levels in a Saskatchewan Prairie Soil

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## Abstract

Global heavy metal and metalloid pollution has increased during the last few decades accompanied by marked increases in global population and a rapid increase in metal production. Since the mid-1990s, higher-than-desired levels of some metals have been found in crops, increasingly so. Atmospheric deposition might play a role in these developments. We compared soil samples derived from within a shed that was erected in the 1950s in a semiarid, agricultural location within the Brown soil zone of south-western Saskatchewan with soil samples from the adjacent open prairie, simulating environmental conditions then and now. With this setup, we were able to examine long-term changes in soil heavy metals and metalloid concentrations. We found that chromium, strontium, and vanadium have significantly increased between 1950 and 2007, while cobalt has significantly decreased during this same time frame. With regards to soil parameters, alkalinity and conductivity have increased. Differences in all other heavy metals and metalloids remained insignificant.

## Introduction

Incidents of higher-than-desired levels of heavy metals and metalloids have occurred in agricultural crops grown in the Canadian Prairies. Potential sources of these heavy metals and metalloids are largely unknown. During crop production, excess heavy metals and metalloids may be associated naturally, with the soil, or anthropogenically, with management practices such as agricultural input, tillage intensity, or crop choices. Due to significant increases in metal production during the last 30-40 years (Nriagu 1990), excess heavy metals and metalloids in crops may also be derived from atmospheric wet and dry deposition (Düring *et al.* 2002).

The objective of this study was to evaluate the contribution of atmospheric deposition to soil heavy metal and metalloid concentrations in a Canadian Prairie soil between 1950 and 2007. We investigated soil heavy metal and metalloid concentrations and soil chemical parameters in a location within the semiarid brown soil zone of Saskatchewan.

## Materials and Methods

*Study area.* An agricultural area of 400 $m^2$ located in southwest Saskatchewan was permanently covered by the construction of a shed in the 1950s. The shed was erected on the South Farm of the Semiarid Prairie Agricultural Research Centre in Swift Current and is located at 825 m elevation (N50°15'35.6", W107°44'05.9") in the semiarid brown soil zone of the Palliser Triangle. This shed has protected the soil from any atmospheric input for more than 50 years.
*Soil collection.* In July of 2007, soil samples at two depths (i.e., 0-15 and 15-30 cm) were collected with a manual soil auger from inside the shed and outside the shed, with three replicates.
*Heavy metal and metalloid analyses.* After drying the soil samples, they 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 by ICP-MS with Aqua Regia Digest. Alkalinity, cation exchange capacity (CEC), conductivity, pH, carbonate, soil organic matter (SOM) and below 2µm grain size were determined.
*Statistical Analysis.* Univariate ANOVA was used for data analysis. Means and standard errors were estimated. Duncan's Multiple Range Test was applied to determine differing means at $p < 0.05$. Graphs and tables were prepared with Microsoft Excel.

## Results and Discussion

At 0-15 cm soil depth, there was a significant increase in alkalinity and conductivity between 1950 and 2007 (Table 1), with all other soil parameters remaining insignificant between 1950 and 2007. Differences in heavy metals and metalloids between 1950 and 2007 remained insignificant except for cobalt which has significantly decreased (Table 2).

Table 1. Comparison of soil parameters at 0-15cm depth between 1950 and 2007. Soil samples taken at the South Farm of the Semiarid Prairie Agricultural Research Centre, Swift Current, SK. Sample size n = 3. Numbers represent mean ± SEM. Not significant (n.s.) if p-value > 0.05.

| Soil Parameter (unit) | 1950 [1] | 2007 [1] | p-value |
|---|---|---|---|
| Alkalinity ($mg*g^{-1}$) | 0.05 ± 0.00 [a] | 1.60 ± 0.00 [b] | 0.001 |
| CEC ($cmol(+)*kg^{-1}$) | 20.77 ± 0.72 | 19.67 ± 1.31 | n.s. |
| Conductivity ($\mu S*cm^{-1}$) | 78.1 ± 19.6 [a] | 175.3 ± 6.6 [b] | 0.009 |
| Grain size below 75µm (%) | 40.3 ± 6.4 | 30.7 ± 2.0 | n.s. |
| pH | 5.8 ± 0.1 | 6.1 ± 0.1 | n.s. |
| Carbonate (%) | 0.682 ± 0.080 | 0.889 ± 0.101 | n.s. |
| SOM (%) | 4.25 ± 0.19 | 5.50 ± 0.69 | n.s. |

[1] The letter 'a' indicates a measurement that was significantly lower than the measurement superscripted with the letter 'b', based on Duncan's Multiple Range Test.

Table 2. Comparison of soil (0-15cm) heavy metal and metalloid concentrations (in $\mu g*g^{-1}$) between 1950 and 2007. Soil samples taken at the South Farm of the Semiarid Prairie Agricultural Research Centre, Swift Current, SK. Sample size n = 3. Numbers represent mean ± SEM. Not significant (n.s.) if p-value > 0.05.

| Heavy metal/Metalloid | 1950 [1] | 2007 [1] | p-value |
|---|---|---|---|
| Aluminium | 12667 ± 291 | 11900 ± 346 | n.s. |
| Arsenic | 4.58 ± 0.34 | 4.07 ± 0.20 | n.s. |
| Barium | 183.33 ± 1.45 | 181.00 ± 3.51 | n.s. |
| Beryllium | 0.65 ± 0.03 | 0.58 ± 0.02 | n.s. |
| Boron | 5.80 ± 0.51 | 5.43 ± 0.41 | n.s. |
| Cadmium | 0.33 ± 0.02 | 0.34 ± 0.01 | n.s. |
| Chromium | 19.57 ± 0.46 | 18.63 ± 0.23 | n.s. |
| Cobalt | 7.92 ± 0.07 [b] | 7.39 ± 0.15 [a] | 0.030 |
| Copper | 13.43 ± 0.49 | 13.07 ± 0.13 | n.s. |
| Iron | 11366 ± 318 | 10700 ± 346 | n.s. |
| Lead | 9.04 ± 0.14 | 10.86 ± 1.03 | n.s. |
| Manganese | 564.7 ± 16.4 | 551.3 ± 20.3 | n.s. |
| Mercury | < 0.490 | < 0.490 | n.s. |
| Molybdenum | 0.369 ± 0.161 | 0.523 ± 0.023 | n.s. |
| Nickel | 15.30 ± 0.17 | 15.60 ± 0.90 | n.s. |
| Selenium | < 0.490 | < 0.490 | n.s. |
| Silver | < 0.490 | < 0.490 | n.s. |
| Strontium | 19.27 ± 0.24 | 20.03 ± 0.43 | n.s. |
| Thorium | < 0.490 | < 0.490 | n.s. |
| Tin | < 0.490 | < 0.490 | n.s. |
| Titanium | 269.0 ± 13.6 | 237.0 ± 35.1 | n.s. |
| Uranium | 0.81 ± 0.01 | 0.76 ± 0.01 | n.s. |
| Vanadium | 32.1 ± 0.80 | 31.1 ± 0.78 | n.s. |
| Zinc | 69.7 ± 0.32 | 72.83 ± 2.26 | n.s. |

[1] The letter ‘a’ indicates a measurement that was significantly lower than the measurement superscripted with the letter ‘b’, based on Duncan’s Multiple Range Test.

At 15-30 cm soil depth, we found half of the percentage of soil grain size below 75μm in 2007 compared to 1950 (Table 3). Chromium, strontium, and vanadium significantly increased between 1950 and 2007 (Table 4). All other differences in heavy metals and metalloids and soil parameters between 1950 and 2007 remained insignificant.

Table 3. Comparison of soil parameters at 0-15cm depth between 1950 and 2007. Soil samples taken at the South Farm of the Semiarid Prairie Agricultural Research Centre, Swift Current, SK. Sample size n = 3. Numbers represent mean ± SEM. Not significant (n.s.) if p-value > 0.05.

| Soil Parameter (unit) | 1950 [1] | 2007 [1] | p-value |
|---|---|---|---|
| Alkalinity ($mg*g^{-1}$) | 0.283 ± 0.117 | 0.333 ± 0.067 | n.s. |
| CEC ($cmol(+)*kg^{-1}$) | 16.17 ± 1.96 | 21.83 ± 3.11 | n.s. |
| Conductivity ($\mu S*cm^{-1}$) | 116.3 ± 17.2 | 83.9 ± 16.8 | n.s. |
| Grain size below 75µm (%) | 57.1 ± 3.9 [b] | 31.6 ± 2.0 [a] | 0.004 |
| pH | 6.0 ± 0.1 | 6.2 ± 0.1 | n.s. |
| Carbonate (%) | 0.836 ± 0.259 | 2.322 ± 1.894 | n.s. |
| SOM (%) | 3.56 ± 0.18 | 3.36 ± 0.90 | n.s. |

[1] The letter 'a' indicates a measurement that was significantly lower than the measurement superscripted with the letter 'b', based on Duncan's Multiple Range Test.

Table 4. Comparison of soil (15-30cm) heavy metal and metalloid concentrations (in $\mu g*g^{-1}$) between 1950 and 2007. Soil samples taken at the South Farm of the Semiarid Prairie Agricultural Research Centre, Swift Current, SK. Sample size n = 3. Numbers represent mean ± SEM. Not significant (n.s.) if p-value > 0.05.

| Heavy metal/Metalloid | 1950 [1] | 2007 [1] | p-value |
|---|---|---|---|
| Aluminium | 12267 ± 67 | 12767 ± 353 | n.s. |
| Arsenic | 4.47 ± 0.09 | 4.73 ± 0.07 | n.s. |
| Barium | 180.67 ± 3.53 | 176.00 ± 0.58 | n.s. |
| Beryllium | 0.63 ± 0.08 | 0.71 ± 0.02 | n.s. |
| Boron | 5.23 ± 0.32 | 6.03 ± 0.26 | n.s. |
| Cadmium | 0.30 ± 0.04 | 0.27 ± 0.01 | n.s. |
| Chromium | 19.33 ± 0.19 [a] | 20.37 ± 0.22 [b] | 0.023 |
| Cobalt | 8.09 ± 0.08 | 8.11 ± 0.11 | n.s. |
| Copper | 13.0 ± 0.15 | 12.73 ± 0.22 | n.s. |
| Iron | 11333 ± 67 | 11267 ± 145 | n.s. |
| Lead | 9.21 ± 0.12 | 9.37 ± 0.18 | n.s. |
| Manganese | 533.0 ± 15.7 | 518.3 ± 30.0 | n.s. |
| Mercury | < 0.490 | < 0.490 | n.s. |
| Molybdenum | 0.503 ± 0.009 [a] | 0.493 ± 0.003 [b] | n.s. |
| Nickel | 16.77 ± 0.55 | 17.37 ± 0.20 | n.s. |
| Selenium | < 0.490 | < 0.490 | n.s. |
| Silver | < 0.490 | < 0.490 | n.s. |
| Strontium | 19.13 ± 0.27 [a] | 20.77 ± 0.33 [b] | 0.019 |
| Thorium | < 0.490 | < 0.490 | n.s. |
| Tin | < 0.490 | < 0.490 | n.s. |
| Titanium | 229.7 ± 17.2 | 263.7 ± 11.8 | n.s. |
| Uranium | 0.81 ± 0.03 | 0.79 ± 0.02 | n.s. |
| Vanadium | 32.8 ± 0.60 [a] | 35.8 ± 0.72 [b] | 0.032 |
| Zinc | 68.13 ± 1.85 | 67.8 ± 1.15 | n.s. |

[1] The letter 'a' indicates a measurement that was significantly lower than the measurement superscripted with the letter 'b', based on Duncan's Multiple Range Test.

## Conclusions

(1) We found a decrease in cobalt at 0-15 cm soil depth and an increase in chromium, strontium, and vanadium at 15-30 cm soil depth between 1950 and 2007. Decreasing soil cobalt concentrations may be due to worldwide reduced cobalt mining operations. Increasing soil chromium concentrations could be associated with increased energy production, manufacturing processes, and waste incineration due to increasing needs by the global population. The increase in strontium is related to fallout from nuclear tests taking place during the 1950s and 1960s. Similar to chromium, vanadium results as a by-product in burning fossil fuel and in industrial-urban emissions.

(2) While alkalinity and conductivity increased at 0-15cm soil depth, grain size below 75μm decreased at 15-30cm soil depth between 1950 and 2007. Agricultural activities have influenced this development.

(3) In this study location, there were no significant differences in soil concentrations of Al, As, Ba, Be, Bo, Cd, Cu, Fe, Pb, Mn, Hg, Mo, Ni, Se, Ag, Th, Sn Ti, and Zn between 1950 and 2007. Agricultural input, such as animal manure, organic and inorganic fertilizers, pesticides, and sewage sludge, may have contained heavy metals and metalloids. The potential and subsequent removal of heavy metals and metalloids by crops, surface runoff, leaching, and/or other processes, however, is unknown.

## References

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