Changes During a Century in Trace Element and Macronutrient Concentrations of an Agricultural Soil

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Abstract: Surface soil and subsoil samples collected in 2012 from a long-term agronomic experimental field at Cornell University were digested in concentrated nitric-perchloric acid and analyzed for macronutrient and trace element concentrations by ICP-OES (inductively coupled plasma optical emission spectrometry) and ICP-MS (inductively coupled plasma mass spectrometry). Archived soil samples, taken from the same field nearly a century earlier (1913), were simultaneously analyzed by the same methods to determine any temporal trends in acid-soluble soil elemental composition that might have resulted from agricultural practices and amendments or from diffuse pollution at this semirural site. Modest increases in surface soil concentrations of several macronutrients (P, Ca, Mg, K) were observed between 1913 and 2012, probably attributable to fertilizer and lime amendments. Most trace elements showed either no significant concentration increase (Zn, Ba, Mn) or a small increase (Ni, Cr) in the surface soil. The greatest relative increase in surface soil trace metal concentrations was for arsenic (81%), followed by lead (40%) and cadmium (33%), although acid-soluble concentrations of these toxic metals in 2012 remained in the range considered typical for background levels in uncontaminated agricultural soils of this region. Cadmium measured in acid digests by ICP-OES was shown to overestimate total soil Cd at these low near-background concentrations, with both ICP-MS and a flame atomic absorption method using a preconcentration step for Cd in extracts providing results more consistent with known total soil Cd concentrations of certified standards.

Key Words: Trace elements, soils, cadmium, arsenic, lead, long-term changes.

The elemental composition of soils is a critical property that not only has important implications for soil health and fertility but also records information about past contamination from anthropogenic sources. In most northern regions of North America, glaciation has resulted in geologically young soil with elemental composition strongly reflecting the composition of the predominant minerals of the earth's crust (McBride, 1994). Weathering processes have had insufficient time to significantly alter these minerals and leach more mobile elements. Anthropogenic impacts on elements in agricultural soils, both intentional (e.g., fertilizer, manure, lime, waste applications such as fly ash and sewage sludge) and unintended (e.g., aerial deposition

from fossil fuel combustion, vehicle emission, incinerator emission, etc.), can, in contrast, change both macronutrients (e.g., P, Ca, Mg, K, S) and trace element concentrations (e.g., Cu, Zn, Pb, As, Cd) in the soil at a much more rapid pace, with measureable changes in total elements known to occur on the time scale of decades to centuries (Jones et al., 1987a; Gyori et al., 1996; Nicholson et al., 2006). In agricultural soils of densely populated postindustrial countries, trace metal additions from both atmospheric deposition and direct application have been much greater than removal by crop harvest and leaching (Moolenaar et al., 1998; Nicholson et al., 2006). Therefore, soils are not at steady state, and substantial increases above background of soil Cd, Pb, and other metals up to 50% or more have been documented for periods of a century or longer using archived soil collections to retrospectively determine changes in topsoil concentrations of these trace metals (Jones et al., 1987a, 1987b; Gyori et al., 1996).

Because no estimates of change in trace element and macronutrient compositions of North American agricultural soils on the time scale of a century or longer have been made to our knowledge, we undertook an initial investigation of soil composition using archived and present-day soil samples from an experimental field near Cornell University with a relatively well-known history of continuous cropping. It is worth noting, however, that the nearby Cornell University Central Heating Plant, constructed in 1922, used bituminous coal as its primary energy source, with substantial emissions of sulfur dioxide until converting to natural gas in 2009. This power plant is situated about 1.5 km west of Caldwell Field and is therefore a potential source of soil contamination by sulfur and metals emitted during coal combustion, including As, Pb, Zn, and Cd (Klein et al., 1975; Xu et al., 2003).

The intent was to test two hypotheses during the time frame of 100 years:
1) Continuous cropping using conventional agronomic management had substantial effects on macronutrient or micronutrient concentrations in topsoil or subsoil.
2) Some soil contamination by toxic metals such as Cd, As, and Pb occurred despite the relatively rural nature of the site.

MATERIALS AND METHODS

The experimental field site at the eastern edge of the Cornell University campus was established in 1903 when the university acquired the Mitchell farm property. Referred to as Caldwell Field since about 1908, it has since been used by the Agronomy (now Crop and Soil Sciences) and Plant Breeding departments to conduct experiments with small grains and forages until the present. Although a detailed history of cropping and amendments with fertilizer and farm manure cannot be reconstructed because of lost and incomplete records, it is likely that conventional agricultural practices were followed throughout the history of the site.

A collection of 60 soil samples taken from two depths (0–20 cm and 20–40 cm) within Caldwell Field in 1913 had been archived as dry powders in glass jars sealed with cork-lined aluminum lids in the Department of Crop and Soil Sciences.

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TABLE 1. Concentrations of Macronutrients (mg kg^{-1}, $n = 6$) in A-Horizon (0–20 cm) and B-Horizon (20–40 cm) of the Archived and Present-Day Soils as Measured by ICP-OES

		P	S	Na	Ca	Mg	K
1913 soil	A	471 ± 57	73 ± 12	4,343 ± 226	1,544 ± 159	1,658 ± 283	9,889 ± 767
	B	354 ± 42	28 ± 11	4,230 ± 423	1,116 ± 225	2,187 ± 204	11,220 ± 582
2012 soil	A	646 ± 44	57 ± 12	4,797 ± 189	1,840 ± 278	2,318 ± 206	12,052 ± 1,066
	B	631 ± 61	47 ± 11	4,174 ± 519	2,012 ± 520	2,642 ± 424	12,874 ± 1,352
P	A	0.003	0.04	0.03	NS	0.009	0.006
	B	0.000	NS	NS	0.02	0.05	0.04
SRM2709		553	661	7,937	14,898	7,984	13,509

P value for *t* test comparing between topsoil (A) and subsoil (B) of the archived and present-day soils.

NS: not significant; SRM2709: NIST standard reference soil material.

This collection was subsampled by taking six surface and six matching subsurface samples at random from the larger collection. The soil samples, already well homogenized, were saved for acid digestion and elemental analysis.

Although surviving records did not allow us to precisely locate the sampling positions of the archived 1913 soils, we decided to collect soil samples in the fall of 2012 from near the center of Caldwell Field, approximately 250 m away from the most heavily trafficked road in the area, State Route 366; this road has existed since 1908 (initially created as Route 9, average daily vehicular traffic was about 8,000 in 2003 according to the New York Department of Transportation). Using a Dutch auger, we sampled at 0- to 20-cm and 20- to 40-cm depths at six equally spaced locations along an east-west transect running from the eastern end of Caldwell Field for a distance of about 150 m. The soil samples were then air-dried, mixed, sieved (<2 mm), and stored in closed cardboard containers.

The archived and recently collected Caldwell Field soils were acid digested by an identical methodology using an automated hot plate method with HNO$_3$ and HClO$_4$. This method does not achieve complete dissolution of all soil elements because it does not use HF but is comparable to the EPA 3050 method that provides a "pseudo total." Any elemental fraction not dissolved by this type of digestion is probably entrained in highly insoluble minerals and completely unavailable. These digests were then analyzed for a wide range of elements (Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Zn) using inductively coupled plasma optical emission spectrometry (ICP-OES). Because of the sensitivity limitations of ICP-OES for some trace elements of particular interest, specifically Cd, As, and Pb, the surface soil (0–20 cm) digests were further

analyzed by inductively coupled plasma mass spectrometry (ICP-MS), a method with higher intrinsic sensitivity. Last, Cd extractable by 1 *M* HNO$_3$ from the archived and recent soil samples was measured by flame atomic absorption spectrometry (FAAS) using the Aliquat-heptanone phase extraction method described by McBride (2011). This method, shown to be sufficiently sensitive to quantify soil Cd at low background concentrations found in uncontaminated soils, was used to provide further confirmation of any differences detected in Cd levels for the soils collected 100 years apart.

A certified reference soil standard (SRM 2709) was included in all analytical methods to provide quality assurance on trace element analysis. A two-tailed Student *t* test was used to test for significant differences between the elemental concentrations in topsoil and subsoil of the archived and present-day soils.

RESULTS AND DISCUSSION

Acid-Soluble Macronutrient and Trace Element Concentrations in Soils

The acid-soluble macronutrient (P, S, K, Ca, Mg, and Na) concentrations in the topsoil (0–20 cm) and subsoil (20–40 cm) of the archived and present-day soils, as determined by ICP-OES, are listed in Table 1. Some of the macronutrients (P, K, Ca, and Mg) in the topsoil and subsoil of the present-day soils were at concentrations higher than those in corresponding layers of the archived soils, possibly as a result of regular use of phosphatic fertilizers and lime for many years. However, the near-doubling of subsoil Ca concentrations could be caused by the effects of deeper tillage practiced in modern times in North America to counteract "traffic" or "plow" pans created by heavier farm equipment used

TABLE 2. Concentrations of Micronutrients and Heavy Metals (mg kg^{-1}, $n = 6$) in A-Horizon (0–20 cm) and B-Horizon (20–40 cm) of the Archived and Present-Day Soils as Measured by ICP-OES

		Mn	Ba	Co	Ni	Cu	Pb	As	Cr	Zn	Cd
1913 soil	A	631 ± 97	278 ± 16	12 ± 0.86	18 ± 1.93	16 ± 1.45	10 ± 0.44	3.81 ± 0.54	31 ± 3.29	72 ± 8.39	0.82 ± 0.04
	B	439 ± 97	280 ± 19	14 ± 0.85	22 ± 1.77	14 ± 2.28	10 ± 0.64	5.57 ± 0.74	36 ± 2.55	68 ± 3.37	1.00 ± 0.08
2012 soil	A	453 ± 36	296 ± 20	14 ± 0.69	23 ± 1.93	19 ± 1.36	14 ± 1.20	6.89 ± 0.45	37 ± 2.59	75 ± 2.42	1.09 ± 0.04
	B	503 ± 66	302 ± 32	14 ± 1.09	25 ± 3.26	20 ± 2.56	14 ± 1.52	7.30 ± 0.94	39 ± 4.70	73 ± 11	1.14 ± 0.24
P	A	0.01	NS	0.05	0.003	0.02	0.0005	0.0000	0.01	NS	0.0000
	B	NS	NS	NS	NS	0.006	0.003	0.004	NS	NS	NS
SRM2709		453	739	15	66	29	8.9	15	81	105	1.17

P value for *t* test comparing between topsoil (A) and subsoil (B) of the archived and present-day soils.

NS: not significant; SRM2709: NIST standard reference soil material.

TABLE 3. Soil Analysis Results for Acid-Soluble Cd, Pb, and As by ICP-OES and ICP-MS (mg kg^{-1})

	ICP-OES			ICP-MS		
	As	**Cd**	**Pb**	**As**	**Cd**	**Pb**
1913 soil	3.81 ± 0.54	0.82 ± 0.04	10 ± 0.44	3.34 ± 0.34	0.10 ± 0.01	6.00 ± 0.28
2012 soil	6.89 ± 0.45	1.09 ± 0.04	14 ± 1.20	5.41 ± 0.12	0.12 ± 0.02	9.30 ± 0.92
SRM2709 observed values	14.5	1.17	8.88	10.7	0.23	8.94
SRM2709 certified value	17.7	0.38	18.9	17.7	0.38	18.9

in recent decades (Reicosky and Archer, 2007; Hussain et al., 1999). Bioturbation may also have contributed at least in part to the increased subsoil Ca because earthworms are able to mix elements such as Ca and P to considerable depths in soil profiles (Resner et al., 2011). Undisturbed soils of the area studied commonly have free calcium carbonate in the C-horizon of the profile. Although surface soil S declined from 73 mg kg^{-1} in 1913 to 57 mg kg^{-1} in 2012, at the same time, the S content of subsoil increased from 28 to 47 mg kg^{-1}. Because S deposition from the nearby coal power plant must have occurred for many decades at this site, these results suggest that the deposited S may have migrated deeper into the soil profile within 100 years possibly by bioturbation or by sulfate leaching.

The elevated acid-soluble concentrations of several trace elements in the surface soil of the present-day soil, shown in Table 2, indicate that some inputs of these elements from soil amendments (particularly fertilizers) and aerial deposition did occur during the period 1913 to 2012. Specifically, the concentrations of Ni, Cr, Pb, As, and Cd in the topsoil of the present-day soils were significantly higher ($P < 0.01$) than in the archived soils. None of the trace element concentrations in the present-day surface soil were significantly different from those in the subsoil, which was not the case for all trace elements in 1913. Again, this homogeneity in the soil profile may simply reflect the deeper tillage in modern agricultural practice. With respect to Ba and Zn, acid-soluble concentrations after a period of 100 years showed no measurable increase for either the topsoil or subsoil ($P > 0.05$). The elements Mn and Zn showed no increases in concentration (surface soil Mn actually decreased), suggesting either that very little addition of these elements to the soil had occurred during a century or that additions were offset by removal by crop harvest. Soil analysis for acid-soluble Cu did indicate a small, but significant, increase in this micronutrient.

Changes of Acid-Soluble Toxic Metal (As, Cd, and Pb) Concentrations in Soils

During the 100-year period of cropping (1913–2012), the soil concentration of As increased from 3.8 to 6.9 mg kg^{-1} in the topsoil and from 5.6 to 7.3 mg kg^{-1} in the subsoil (Table 2). These increases represent relative increases of 31 to 81%, suggesting that atmospheric deposition or contaminants in fertilizers may

have been a significant source of As. It has been reported in the United Kingdom, for example, that more than 50% of As input to agricultural soils was from atmospheric deposition (Adriano, 2001). However, trace metal inputs from phosphatic fertilizers can exceed atmospheric deposition for As, Cd, and Cr, with the reverse being generally true for Zn, Pb, and Ni (Nziguheba and Smolders, 2008). Jones et al. (1987a) calculated a predicted increase of 11% in the plow layer Pb burden for the 20th century, a value derived from estimates of Pb deposition between 1900 and 1987. In the present study, analysis of soils from Caldwell Field shows an increase in Pb concentration from 10 to 14 mg kg^{-1} during 100 years, a rate of increase consistent with widespread Pb deposition from anthropogenic emissions as measured in other industrialized countries (Gyori et al., 1996). Table 2 also shows that the Cd concentration in the plow layer (0–20 cm) soils from Caldwell Field increased by about 33% in the last 100 years. This is a very small increase in the topsoil Cd burden in absolute terms but is a similar relative increase to that reported at the Rothamsted Experimental Station in the United Kingdom (Jones et al., 1987b). At Rothamsted, soil Cd contents increased by between 27 and 55% above the historical background level during a 130-year period (1861–1989).

In summary, the results presented here indicate that a small, but measurable, contamination of agricultural soils by the toxic metals As, Cd, and Pb has occurred at a relatively rural site during a century and could have been largely the cumulative result of atmospheric deposition (from fossil fuel combustion and vehicle emissions) and phosphatic fertilizers (Nicholson and Jones, 1994; Alloway and Steinnes, 1997; Adriano, 2001).

Comparison of As, Cd, Pb Determination by ICP-OES and ICP-MS

Because ICP-OES can produce erroneously high measurements of certain trace metals in soils, most notably Cd and As (Chapnick et al., 2010; McBride, 2011), we decided to test the reliability of the ICP-OES measurements of soil acid-soluble Cd, As, and Pb reported in Table 2 by comparison with alternative methods (ICP-MS for Cd, As, and Pb; FAAS for Cd) to reanalyze the soils for these toxic metals. Inductively coupled plasma mass spectrometry has intrinsically higher sensitivity and fewer spectral interferences than ICP-OES. Although FAAS has poorer

TABLE 4. Comparison of Soil Cd Analysis by ICP-OES, ICP-MS, and FAAS (mg kg^{-1})

		FAAS	**ICP-MS**	**ICP-OES**
1913 soil	A	0.097 ± 0.01	0.10 ± 0.01	0.82 ± 0.04
	B	0.083 ± 0.004	NA	1.00 ± 0.08
2012 soil	A	0.10 ± 0.004	0.12 ± 0.02	1.09 ± 0.04
	B	0.10 ± 0.004	NA	1.14 ± 0.24
SRM values		0.13	0.23	1.17

NA: no analysis.

sensitivity than ICP for Cd, a preconcentration step performed on acid extracts of the soil allows FAAS to achieve superior sensitivity to ICP-OES (McBride, 2011).

The 12 topsoil samples from the previously selected 1913 and 2012 sampling sets were reanalyzed for As, Cd, and Pb using ICP-MS. As shown in Table 3, the total concentrations of As, Cd, and Pb measured by ICP-MS were consistently lower than the concentrations measured by ICP-OES for both the archived and present-day soils. This bias in relative terms was particularly large for Cd. The results agree with our previous study indicating that ICP-OES did not reliably quantify total soil Cd, with cases of both serious overestimation (especially for low-Cd soils) and underestimation (McBride, 2011). Measured values of Pb in the standard reference soil (SRM2709), as determined by ICP-MS and ICP-OES, were in good agreement but were roughly 50% lower than the certified value for total Pb in this reference soil. Although Pb determined by ICP-MS in soil digests gave a lower estimate of soil Pb than ICP-OES, the two analytical methods revealed a similar trend and magnitude of increasing Pb concentration in topsoil since 1913 (~55 and 40% increase in total Pb by ICP-MS and ICP-OES, respectively).

It is standard practice when testing analytical quality assurance in measurement of trace metals in soils to use certified metal concentrations reported for standard reference soils such as SRM2709, but it should be cautioned that the sample digestion and analytical methods used to obtain these certified values may be quite different from the methods used in practice by most soil testing laboratories. Specifically, the certified total As, Pb, and Cd values documented for SRM2709 (see Table 3) were not obtained by standard ICP-OES or ICP-MS or by acid digestion methods used routinely by most laboratories. Therefore, although we obtained a particularly low recovery for Pb in SRM2709 by both ICP-OES and ICP-MS, this discrepancy could be caused by the different acid digestion or analytical methods used. A detailed comparison of different acid digestion methods applied to SRM soils has revealed that incomplete recovery (<70%) of a number of elements (especially Pb, As, Ba, and Cr) can be expected when using digestion methods not involving HF (Chen and Ma, 2001).

In an attempt to improve on the estimation of total soil Cd, which is frequently overestimated by ICP-OES, two more sensitive and less interference-prone methods for Cd were used: ICP-MS analysis of acid digests and FAAS analysis of Cd in 1 M HNO$_3$ extracts with Cd preconcentration into the Aliquat-heptanone phase (McBride, 2011). A comparison of the results for Cd determination in acid digests or acid extracts by ICP-OES, ICP-MS, and FAAS in the selected archived and present-day soils is presented in Table 4. Because the 1-M HNO$_3$-FAAS method produced a low Cd recovery from the SRM (only 34%), it is concluded that the 1-M HNO$_3$ extraction method was not very efficient in extracting Cd from this low-Cd soil, an expected result based on previous work with this method (McBride, 2011). Nevertheless, overall extraction efficiency by 1 M HNO$_3$ for the Caldwell Field soils was in the range of 83 to 97% if compared with soil Cd measured in acid soil digests by ICP-MS. In summary, when estimates of soil Cd by the three methods used in this study are compared (Table 4), it is clear that ICP-OES overestimates total Cd in low-Cd soils, confirming the conclusions from previous studies by McBride (2011).

CONCLUSIONS

In testing the two hypotheses initially proposed for this study, the soil analyses have shown concentrations of acid-extractable P, K, Ca, and Mg in the topsoil and subsoil of the present-day soils to be higher than those in corresponding layers of the archived soils, possibly resulting from regular use of fertilizers and lime during the period 1913 to 2012. Substantial increases in subsoil Ca and S

could be the result of bioturbation or deep tillage, although some leaching of S as sulfate may have occurred during a period of high S deposition rates when the nearby power plant was using coal. The significantly increased acid-extractable concentrations of As, Cd, Ni, Cu, Cr, and Pb in the surface soil of the present-day soil indicate that some inputs of these elements from soil amendments (particularly fertilizers) and/or aerial deposition do occur during a century of cultivation. The present results reveal that anthropogenic activity has caused measurable changes in soil elemental and toxic metal concentrations despite the relatively rural nature of the study site.

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