

Short Communication

ELEMENTAL CONTENT OF MANUFACTURED SOILS

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ABSTRACT

Information on plot-specific background concentrations of trace metals in manufactured soils is critical for evaluating performance of soil manufacturing recipes and for monitoring the annual bio-availability of trace metals. In this project, total concentrations of trace metals (Cu, Fe, Mn, Ni, Pb, and Zn) and macro nutrients (Ca, Mg, K, P, N) in manufactured soil samples were determined. Seven soil samples were analyzed for pH, cation exchange capacity (CEC), extractable phosphate and sulfate, total concentrations of trace metals (Cu, Fe, Mn, Ni, Pb, and Zn) and macro nutrients (Ca, Mg, K, P). A subset of these metals (Cu, Fe, Mn, Ni, and Pb) are indicators of contamination by acid mine drainage or manufacturing byproducts in the manufactured soil recipe.

Average precision for elements Cu, Mg, Fe, Mn, K, and Zn were < 15% relative standard deviation (RSD) using Method 3051.

Keywords: Manufactured soils, trace elements, soil health and sustainability.

INTRODUCTION

The present study is the continuation of years of discussion and study of the effects of manufactured soils on soil/plant health. The size consistency (soil texture) of the mineral fraction in native soil varies from clay-size to coarse sand-size. The carbon- and nitrogen-rich organic matter contains the monomers and polymers, the main constituents of the humus complex. Soil is a necessary intermediate substrate in the regulation of the Biosphere activity. Estimates of the loss of US soil resources due erosion to range from 2 billion to 6.8 billion tons annually (GAO, 1977; Barlowe, 1979). Worldwide estimates indicate that between 10-15 million hectares of arable land are rendered unproductive annually due soil losses (Lal and Stewart, 1990). Rehabilitation of the soil cover is a global problem that could be solved in cooperation with such disciplines as mineralogy, soil science, biology, ecology, agrochemistry, and biochemistry.

Numerous researchers are concerned with the damage that acid mine drainage does to the soil, water, and biological communities. Janzen *et al.* (2008), described the impact of acid mine drainage on microbial community diversity and stream chemistry in the Shamokin Creek Watershed, PA. It is a well known fact that diatoms as representatives of biodiversity indicate the health of a particular environment. Bacterial presence also indicates the level of ecological balance. The authors concluded that in AMD

where the concentrations of iron are high, the predominant bacteria will be from phylum *Bacteroidetes*, and were closely related to known biofilm community members from acidic environments where they have been demonstrated to be involved in sulfur oxidation. Other bacterial species were closely related to *Sphingomonas* species. Soil ecology damage due to AMD has the potential to have a cascade of negative effects including the loss of vegetation leading to the loss of topsoil due to erosion.

In our prior study (Kalevitch and Kefeli, 2006), the proposed recipes of fabricated soils are based on the carbon-nitrogen balance in the soil as well as on the transformation of carbon products such as glucose, phenolics, and plant polymers such as cellulose and lignin in the humus (polymers which are tightly connected to the aluminosilicate matrix of the soil micelle). This research continues a long term study of the soil health of an area damaged by AMD.

Macronutrients (Summary Table 1) can be broken into two more groups: primary and secondary nutrients. The following macro and micro nutrients were selected for this study in order to assess the overall health of the soil and to trace deficiencies or excesses in nutrient levels.

Information on plot-specific background concentrations of trace metals in manufactured soils is critical for evaluating performance of soil manufacturing recipes and for monitoring the annual bio-availability of trace metals.

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Table 1. Importance of Soil Nutrients for Plant Growth.

N	Nitrogen helps form amino acids which are building blocks of protein	Cu	Copper is necessary for chlorophyll formation and also acts as a catalyst for other plant reactions.
P	Phosphorus is utilized in the formation of nucleic acids and other chemicals which help in the development of health root systems, early growth, early maturity and seed production.	Fe	Iron also acts as a catalyst for chlorophyll formation and also carries oxygen. It also helps form certain respiratory enzyme systems. These functions make it critical to photosynthesis.
K	Potassium is similar to phosphorus in root formation and also appears to promote disease resistance. It increases the size and quality of fruits.	Mn	Manganese activates many metabolic reactions in plants and is directly involved in photosynthesis. It accelerates germination and maturity and increases the availability of phosphorus and calcium.
Ca	Calcium is used in root system and leaf development and is combined with other elements to form cell walls. It also helps by activating other enzyme systems.	Ni	Nickel is a micronutrient which is necessary for proper germination and seed development. (Brown <i>et al.</i> , 1987)
Mg	Magnesium is the central atom of the chlorophyll molecule which makes it absolutely necessary for photosynthesis. It also plays a role in phosphate metabolism, plant respiration and enzyme systems.	Zn	Zinc is necessary for the production of chlorophyll and carbohydrates and aids in the creation of plant growth substances, enzyme systems, and metabolic reactions.

In this project, total concentrations of trace metals (Cu, Fe, Mn, Ni, Pb, and Zn) and macro nutrients (Ca, Mg, K, P, N) in manufactured soil samples were determined. Subsets of these metals (Cu, Fe, Mn, Ni, and Pb) are indicators of contamination by AMD residue or by manufacturing byproducts in the manufactured soil recipe.

The goal of this study is to evaluate the mineral content of soils from an abandoned strip mine site remediated with fabricated soil amendments.

MATERIALS AND METHODS

Study Site

The study site is located in Butler County, Pennsylvania, USA. The site was strip mined in the 1950's and has experienced acid mine drainage in the subsequent years. The resulting site has remained sparsely vegetated since the original mining. To remediate this site, a fabricated soil amendment, a natural mixture of decaying substrates rich in aluminosilicate, carbon, nitrogen, phosphorus and potassium sources, was added to test plots. Eight soil samples were collected from the reclaimed mining site; seven samples were collected from test plots with fabricated soil or topsoil and one from abandoned mining soil.

Sample Analysis

Samples were allowed to air-dry and were then crushed and screened to pass through a 2.0 mm-mesh sieve. Soils were analyzed for pH, Cation Exchange Capacity (CEC), total nitrogen, extractable phosphate and sulfate, total

concentrations of trace metals (Cu, Fe, Mn, Ni, Pb, and Zn) and macro nutrients (Ca, Mg, K, P).

Soil pH was measured as a slurry at a 1:2 soil/water ratio with a Fisher Accumet 25 pH meter. Cation Exchange Capacity (CEC) was determined following the method of Robertson *et al.* (1999). Exchangeable ion concentrations were analyzed on a Perkin Elmer AAnalyst 100 utilizing air/acetylene flame with the appropriate hollow cathode lamp utilizing standard conditions and optimized for lamp alignment, burner head alignment, and nebulizer flow. Exchangeable aluminum and acidity was determined by titration of KCl extracts with NaOH. Results from exchangeable ion concentrations and exchangeable acidity were converted to cmol charge per kg dry soil to determine total CEC.

Total nitrogen and phosphorous concentrations were determined following digestion according to the method of Parkinson and Allen (1975). After sample digestion, total nitrogen concentrations were determined on a BioTek Elx808 well plate reader according to the method of Sims *et al.* (1995). Phosphorous concentrations were determined on a BioTek Elx808 well plate reader. Extractable phosphate and sulfate concentrations were determined by ion chromatography (IC) according to a modified Olsen method (Olsen and Summers, 1982).

To determine total metal concentrations, samples were digested in a block digester using EPA Method 3050B. AA and AE analysis were completed on a Perkin Elmer AAnalyst 100 utilizing air/acetylene flame with the

Table 2. pH, exchangeable sulfate and phosphate and cation exchange capacity in the Tested Soils (mean +/- standard error).

Soil	pH	Exchangeable Phosphate (mg/kg soil)	Exchangeable Sulfate (mg/kg soil)	CEC (cmolc/kg soil)
07-1	6.4	6.0 (4)	3.5 (4)	9.5 (1.7)
07-2	5.6	0.8	5.8 (4)	8.5 (1.7)
07-3	8.5	1.7 (0.8)	3.9 (4)	39 (11.0)
07-4	8.4	1.2 (0.6)	5.6 (4)	38 (12.0)
07-5	6.9	36 (13)	6.6 (4)	33 (7.0)
07-6	6.8	32 (13)	10.7 (4)	36 (6.0)
07-7	7.4		181 (4)	48 (11.0)
07-8	3.1	3.8 (1.8)	37 (4)	8.9 (0.5)

appropriate hollow cathode lamp. The instrument was equipped with a 10 cm burner head. All elements were analyzed utilizing standard conditions and optimized for lamp alignment, burner head alignment, and nebulizer flow. Sample concentrations were corrected for matrix effects. Four replicates of each sample were analyzed to determine average concentration and relative standard deviation for each element.

Validation of precision and accuracy of methods for trace metals and macro nutrients were performed by two internal standards, an external SRM from the National Institute of Standards and Technology (NIST), and comparison to external analysis results conducted by inductively coupled plasma spectrometry (ICP).

Data Analysis

Because the study focuses on one specific area within which soil remediation treatments were completed, the study is necessarily qualitative in nature. Results from exchangeable ion concentrations and exchangeable acidity were converted to c_{mol} charge per kg dry soil to determine total CEC. All metal and nutrient concentrations were converted to mg/kg soil for comparison. Soil data was qualitatively compared to historical data from the Butler and Allegheny county region obtained from the USGS PLUTO soils database (<http://tin.er.usgs.gov/pluto/soil/>) and background concentrations for naturally occurring inorganic chemicals in surface and subsurface soil (Risk Assessment Information System, <http://rais.ornl.gov/>).

RESULTS

The evaluation of eight soil samples consisted of testing for the presence of the nine minerals. Five soils represented natural soil with a topsoil cover, two soils were manufactured, and there was also one mineral soil sample taken from a mining soil plot.

Table 2 demonstrates the presence of exchangeable phosphorus and sulfate in the samples along with the cation exchange capacity.

According to the background concentrations for naturally occurring inorganic chemicals in surface and subsurface soil (Risk Assessment Information System, <http://rais.ornl.gov/>) (Table 3), the concentration for calcium in tested soil was well below the normal (200,000 mg/kg), it ranged from 60 to 11,000 mg/kg in different samples (Table 4). The maximum concentration was shown on plot 07-7, and the lowest was for the mining soil plot, 07-8.

Table 3. Background Concentrations for Naturally Occurring Inorganic Chemicals in Surface and Subsurface Soil (Risk Assessment Information System, <http://rais.ornl.gov/>)

Analyte	Background Value ^b	
	Surface	Subsurface
Inorganic Chemicals (mg/kg) ^a		
Aluminum	13,000	12,000
Calcium	200,000	6,100
Copper	19	25
Iron	28,000	28,000
Lead	36	23
Magnesium	7,700	2,100
Manganese	1,500	820
Nickel	21	22
Potassium	1,300	950
Zinc	65	60

Concentration for copper ranged from 11.8 to 63 mg/kg with 19 mg/kg being the mean. Five plots had copper concentration higher than normal with two plots being within or below normal range.

Concentration of iron (Table 5) was within the normal range: 10,247- 24,300 mg/kg with a mean of 28,000 mg/kg of iron. There was one plot (07-4) where the

Table 4. Elemental Analysis for the Tested Soils (mean +/- standard error).

Sample	Ca	Co	Cu	Zn	Mg
07-1	80 ± 40	19±3	20±3	100±11	1578±100
07-2	20±30	12.2±2	11.8±1	67.1±1	1450±30
07-3	24000±7000	11.8±1	30±20	50±8	12300±1700
07-4	32000±3000	10.4±2	63±4	54.7±2	13400±1600
07-5	7700±800	2±3	24.7±1	47±3	1020±70
07-6	9000±1200	6±7	30±2	51.8±1.1	740±70
07-7	110000±30000	1274±100	20.8±1	1300±50	3700±300
07-8	-60±20	9±5	53.6±1	56±6	100±30

Table 5. Elemental Analysis of the Tested Soils-Continued (mean +/- standard error).

Sample	Fe	Pb	Mn	K	Ni
07-1	19510±1000	60±30	1310±160	700±120	17±10
07-2	19900±300	30±20	1329±18	710±80	20±13
07-3	24300±1100	6±17	1268±13	1100±500	147±16
07-4	30000±3000	9±18	1380±20	1100±200	180±20
07-5	14800±110	30±30	240±30	2490±160	20±20
07-6	15870±1000	23±11	300±50	2800±200	21±7
07-7	17200±1200	20±30	136800±10000	860±150	900±700
07-8	10247±100	13±3	29±8	3000±200	20±7

concentration of iron was slightly elevated to 30,000 mg/kg. This, however, is within the relative standard deviation of the measurements.

Lead was below normal (>36 mg/kg) in all samples except sample 07-1 that had 60 mg/kg of lead. In seven of the samples manganese concentration varied overall from 29 mg/kg to 1,380 mg/kg which is within the expected background concentrations, however the concentration of manganese in one soil (07-7) was significantly elevated (136,800 mg/kg).

Potassium concentration was more than doubled in fabricated and mining soil samples ranging from 2,490 to 3,000 mg/kg. The expected background concentration is 1,300 mg/kg (Table 5). Three soils showed an increase in nickel concentration ranging from 147 to 900 mg/kg vs 21 mg/kg as background.

The concentration of zinc was greatest in plot-07-7 (1,300 mg/kg vs 65 mg/kg -normal range), the rest of the samples showed zinc concentrations in the range of 47 to 100 mg/kg.

Samples 07-3 and 07-4 had the highest concentration of magnesium 12,300-13,400 mg/kg vs 7,700 mg/kg at the normal range. The rest of the samples had concentrations of magnesium vary from 110-3,700 mg/kg.

DISCUSSION

Overall, samples collected from the mining site showed the highest concentration of trace elements. They showed

an increase in the following elements: copper, magnesium, iron, manganese, and nickel with concentrations sometimes up to ten times above normal. These soils with elevated mineral contents, especially those with extremely elevated levels zinc and manganese are a concern. For sample 07-7, the concentration of zinc was more than an order of magnitude above the expected value and the concentration of manganese was more than two orders of magnitude above the expected value. This sampling plot was located on an abandoned manganese spoil site.

Table 6. Historical soil reference data obtained the USGS PLUTO database (<http://tin.er.usgs.gov/pluto/soil/select.php>).

Name	Butler County	Allegheny County
Calcium (mg/kg soil)	6083.4	4012.78
Cobalt (mg/kg soil)	15.5	17.82
Copper (mg/kg soil)	37.7	52.23
Zinc (mg/kg soil)	100.8	208.00
Magnesium (mg/kg soil)	9229.9	4914.72
Iron (mg/kg soil)	46916.2	50275.21
Lead (mg/kg soil)	23.5	85.27
Potassium (mg/kg soil)	42305.4	32832.68
Nickel (mg/kg soil)	39.2	44.96

In addition to the high levels of zinc and manganese, the concentration of exchangeable sulfate was more than an order of magnitude greater than the normal topsoil samples. Potentially these elevated levels are due to

residual minerals deposited in the soil from the acid mine drainage that originally damaged the area under study. Another potential source for these elevated mineral levels is from the raw materials which were used to create the manufactured soil. Although it is unknown if this is the case for the area under study, in some cases the components used to create the manufactured soil may contain waste sand from casting foundries. Often foundry sands are contaminated with high levels of metals. Further studies are underway to determine the source of these high levels of trace minerals and the effect that they may have on the bacterial ecology within the soil.

As the environmental damage caused by acid mine drainage and surface mining operations increases, methods must be developed to repair or replace the topsoil in order to support normal ecological development. As soil is a necessary intermediate substrate in the regulation of the Biosphere activity, it is important to understand the long term effects of micronutrient loss and to monitor attempts to amend soils to improve sustainability and viability of the soil. Future work will compare the mineral content of soil with microbial biomass and diversity.

ACKNOWLEDGEMENT

We express our sincere appreciation to the group of students who worked tirelessly with us on this project.

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Received: May 8, 2013; Revised: Aug 14, 2013;
Accepted: Aug 17, 2013