TRIP B2: NATURALLY OCCURRING FILTRATION SYSTEMS SEQUESTERING METAL CONTAMINANTS FROM HISTORICAL TAILING WASTES AT THE STERLING LAKE SMELTER COMPLEX, HUDSON HIGHLANDS, NEW YORK

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INTRODUCTION

Mining History

Over 15 million people in New York, New Jersey, Pennsylvania and Connecticut depend on the Highlands Region's (Fig. 1a) 800,000 plus acres of forested watershed for drinking water (Porter, 2008). Large-scale iron mining operations from 1730 to the early 20th century (Smock, 1889; Ransom, 1966) exposed the Highlands to environmental degradation. Although the region is recovering naturally, tailing wastes are still visible and chemically reactive impacting soil and water quality. In addition to iron mining, the Highlands were also exploited for sulfide ores (Gilchrist et al., 2009) but volumetrically spoils from iron mining operations were far greater than sulfide mining operations, the Sterling Lake iron smelter complex is one such example. This area was denuded of its forest to support the smelting operations. Waterfront property owners extract the lake water for potable use. Despite visible tailing wastes chemically decaying in the vicinity, water pH was found to be neutral when measured during a study of this site (Gilchrist et al., 2011). How is this possible if heavy metals are abundant in these tailing wastes?

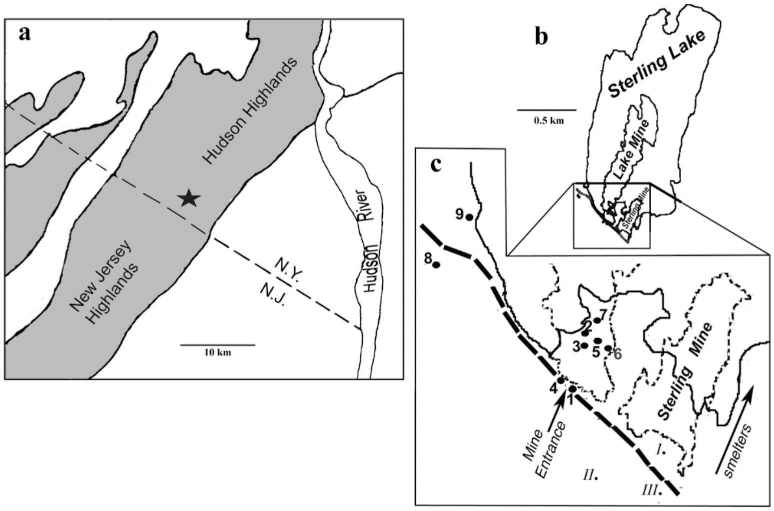

Fig. 1 (a) Study site, (b) Lake Mine and Sterling Mine represented by broken lines. Location of core sample collections indicated by numbered circles. Locations of water sample collections indicated by roman numerals (*I* stream water, *II* still water, *III* spring water). Grab and ash samples collected randomly around former smelter locations. Dashed line represents road. (Adapted from Gilchrist et al., 2011).

Soil cores and water samples were obtained from several locations at the site (Fig. 1b) and chemically analyzed to determine the extent of soil contamination. Geochemical results of the recovered soil cores were compared to regulatory standards and to background soils for the eastern USA (New York State Department of Environmental Conservation (NYSDEC) TAGM 4046, 2009) and the New Jersey Highlands soils (New Jersey Department of Environmental Protection & Energy (NJDEPE), 1993). Chemical analyses suggested that naturally occurring mechanisms are maintaining the neutral water pH. The Highlands Region is a desirable real estate for developers. It is hoped that obtaining answers to the natural recovery of an area impacted by past invasive destructive mining activities will fend off development to protect critical watersheds such as the Highlands region.

An active Panzhihua magnetite mining area in southwestern China yielded high concentrations of Ti, V, Cr, Mn, Zn, Cu, Pb and As in the area's soils (Yanguo et al., 2003) due to airborne depositions from mining and smelting activities. Elevated levels of Cd, Cu, Pb and Zn were found in another but sulfur-rich magnetite mine in central China (Zabowski et al., 2001). These limited studies show that magnetite mining operations can deliver significant metal contaminants to surrounding soils.

Site geology

This paper will provide a brief summary of the study conducted at the Sterling mines for purposes of the field trip scheduled for this conference. Detailed information can be found in Gilchrist et al. (2011). At this site, two abandoned iron mines belonging to the Sterling Lake group of iron mines in the Hudson Highlands of southeastern New York co-exist side by side (Smock, 1889; Hagner et al., 1963). Sterling Mine begins at the surface and continues under the lake (Colony, 1923; Hotz, 1953). The Lake Mine entrance begins at the surface and continues 1160 m out under the lake at a vertical depth of about 300 m below the lake surface (Colony, 1923; Hotz, 1953). Precambrian high-grade metamorphic and igneous crystalline rocks with embedded magnetite deposits are the primary rock types (Drake, 1984) at these sites. When mining operations ceased (1896 to 1921 (Ransom, 1966)) tailing wastes composed of calc-silicate gneiss, meta-volcanic gneiss, pegmatite and the magnetite ore were left abandoned and exposed to weather conditions. Ash and slag relics from surrounding historical furnaces located within the mining area are also visible.

Methods

Soil sampling

Detailed soil sampling method and analyses of soil cores, and water samples can be found in Gilchrist et al. (2011). Briefly, two sets of soil core samples were collected (Fig. 1b): Group A cores were collected at the most impacted areas from heavy mining activities and Group B core samples were collected at passive impacted areas. Each core was sub-sectioned, and prepared for ICP-OES analysis using the flux fusion method and acid digestion to determine chemical composition at various depths of the core (Fig. 2). Loss on ignition (LOI) analysis yielded soil organic matter content. Soil pH was measured using the slurry method (Eckert and Sims, 1995).

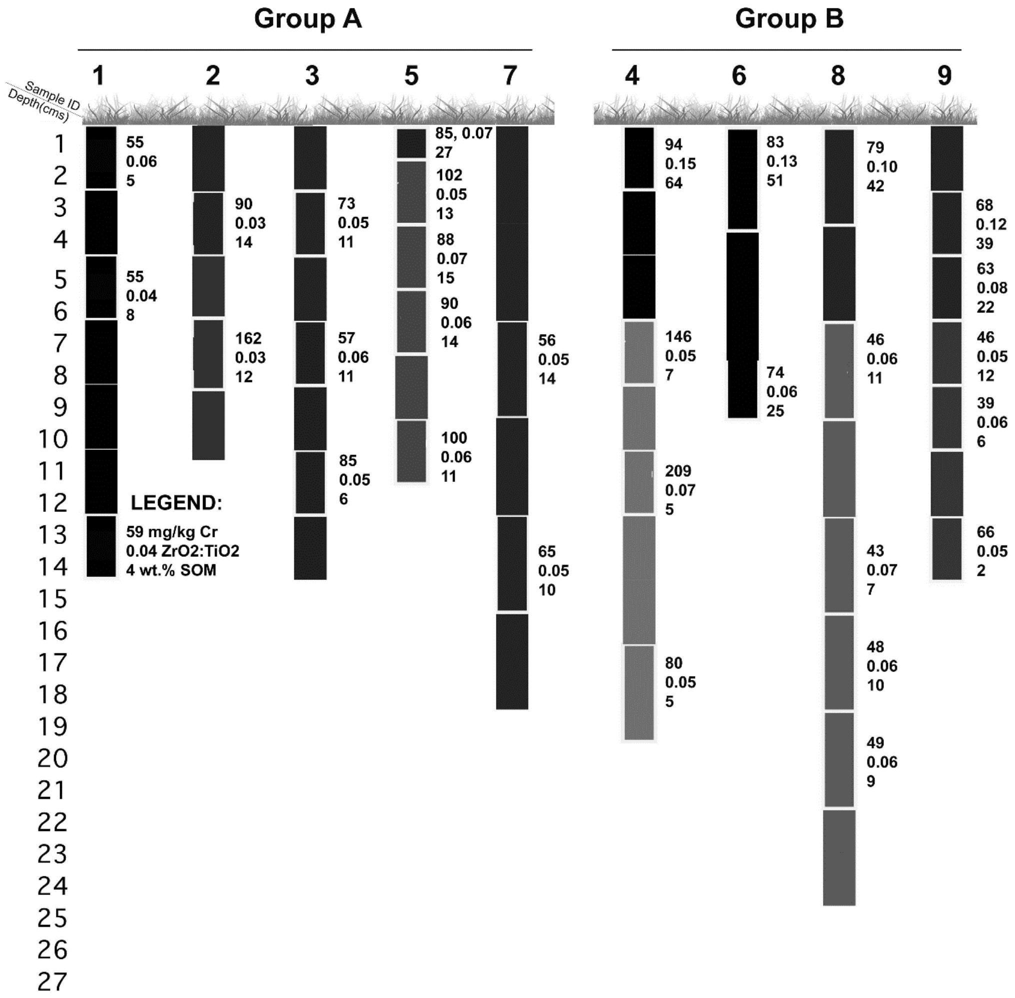

Fig. 2 Sample cores for Groups A and B. Values indicate Cr (mg/kg), ZrO2:TiO2 and SOM (wt%) in analyzed sub-sections. O-horizons are defined from 0–7 cm from the surface. (Adapted from Gilchrist et al 2011)

Rock standards, duplicates of these standards and laboratory blanks were used for precision analysis and recovery of elements in the standards. Results were within acceptable norms: laboratory blanks' values were less than 0.5wt % of any concentration measured for the field samples and recovery of the elements in the standards ranged 87 – 102%.

Water Sampling

An evaluation of metal concentrations in the water to determine whether these are being transported from the soils into the surface and groundwaters. Flowing water samples were collected from a stream flowing through Sterling Mine. Still water samples were collected from around the main entrance of Sterling Mine. Groundwater samples were collected from a spring that receives water through the tailing piles (Fig. 1b). Collected samples were analyzed for heavy and trace metals by USGS laboratory in Denver, Colorado, using ICP-MS.

Determining metal source

Magnetite ($Fe^{+2}Fe^{+3}{}_2O_4$) and ilmenite ($Fe^{+2}TiO_3$) minerals are present at the site in the tailing piles and Cr can occur with these minerals (IETEG 2005). At Montclair State University, XRD was used to determine Cr-bearing minerals. When tailing piles oxidize and breakdown, Cr is released to the soils. Recalcitrant Cr-bearing minerals can also settle out into the slag and ash materials from ore smelting activities. Slag and ash wastes at the smelter complex were collected for Cr content determination.

To determine Cr content in the magnetite, samples were collected from magnetite-bearing waste rocks. Ilmenite, rare and less abundant than magnetite, was not studied for Cr content. At Montclair State University, samples of the collected magnetite minerals were subjected to a Vibrating Sample Magnetometer (VSM) to determine their purity. If pure, a characteristic hysteresis curve will be revealed.

Results and discussions

Soil characterization

At the most impacted areas (Group A), soil color ranged from dark grayish color to dark brown soils and at the less passively impacted areas (Group B) soil color ranged from very dark gray with yellowish brown and dark olive brown (Fig. 2). Several of the cores were enriched in soil organic matter i.e. greater than 5%, mostly in the top 7 cm from the surface. Whether the high SOM was a result of natural processes or contribution from charcoal-making activity during the mining era is unknown.

Soil pH

Soil pH values showed high spatial variability between Groups A and B and within each group (Table 1A). Sulfur contents were low in the soils and sulfate in waters were not significantly present, indicating sulfur minerals (Table 1B) are not prevalent or exist in insufficient quantities to contribute to soil acidity. It is thus believed that SOM may account for the soil acidity. Positive correlation of SOM with metals suggests retention of metals in soils as soluble chelates (Kabata-Pendias and Pendias, 1992).

Table 1A. Soil pH measurements of core samples. (Adapted from Gilchrist et al 2011)

	Group A cores					Group B cores			
	1	2	3	5	7	4	6	8	9
DI water	7.05	4.85	5.81	6.13	5.04	6.56	6.17	5.64	4.58
$CaCl_2 \cdot 2H_2O$ (0.01M)	5.91	3.9	4.46	4.76	3.95	5.69	4.79	4.53	3.65

Metals in soils

Cr, Ni and some major elements (i.e. Si, Ti, Al, Mg and P) exceed background soils of the New Jersey Highlands or the eastern USA (Table 1B). Group A soil samples showed higher concentrations of major metal-oxides than Group B soil samples. The concentrations were mainly in the O-horizons (Table 2). Iron was enriched in Group A soils, evident of slag and ash (Fe residuum rich) mixed into these soils.

Table 1B. Chemical composition of Groups A and B soil core samples. (Adapted from Gilchrist et al., 2011)

	Mean values[a]				EPA SSL[c] (residential)	Eastern USA[d] Background Soil Levels (NYSDEC)	NJDEPE[e] (Highland soils) Mean Values	World Soils[f] Median Values
	Group A (1,2,3,5 & 7)		Group B (4,6,8 & 9)					
Soil depth	0 – 6 cms	7 – 24 cms	0 – 6 cms	7 – 24 cms				
No. of sub-sections	(n = 8)[b]	(n = 8)	(n = 5)	(n = 11)				
Major Oxides (wt.%)								
Si	28.14	29.78	19.41	32.70	--[g]	--	--	28
Ti	0.48	0.52	0.31	0.43	--	--	--	0.4
Al	5.33	6.33	3.51	5.31	--	3.3	--	8
Fe	5.68	4.40	2.28	3.41	--	55 (max)	--	3.5
Mn	0.06	0.08	0.04	0.04	--	0.5 (max)	0.05	0.05
Mg	1.39	1.20	0.69	0.99	--	0.5 (max)	--	0.9
Ca	1.74	1.40	1.05	0.89	--	3.5 (max)	--	1.4
Na	0.87	1.00	0.61	0.88	--	0.8 (max)	--	1.0
K	0.97	1.12	0.62	1.01	--	4.3 (max)[h]	--	1.4
P	0.12	0.10	0.11	0.05	--	--	--	0.08
Trace Elements (mg/kg)								
Cr	79.80	84.30	77.31	76.99	230	40 (max)[h]	10	80
V	151.79	127.51	107.74	92.24	550	300 (max)	--	90
S (wt.%)	0.02	0.02	0.1	0.04	--	--	--	0.08
Zr	305.27	300.38	434.53	307.20	--	--	--	230
Ba	318.22	334.04	341.16	260.07	5500	600	--	500
Ni	52.96	51.74	45.49	45.62	1600	25 (max)	12	20

[a] Mean values of the analyte in all sampled sub-sections.

[b] n = number of sub-sections analyzed within the group.

[c] EPA SSL (soil screening levels, 2002) for residential soils. Cr value refers to total Cr.

[d] Eastern USA Background soil levels listed in NYSDEC TAGM 4046 (2009) for heavy metals.

[e] Soil data (n=17) extracted from counties (n=3) within the Highlands region compiled by NJDEPE (1993).

[f] World soil data compiled by Reimann and Caritat (1998).

[g] Dashed lines indicate no data available or not applicable because element is not considered a contaminant.

[h] New York State Background Levels also listed in NYSDEC TAGM 4046 (2009) for heavy metals.

Table 2. Mean concentrations of Cr, Oxides, SOM and divalent metals. Values in parentheses indicate correlation of oxides, SOM or divalent metals with Cr. (Adapted from Gilchrist et al 2011)

V	**Cr (mg^{-kg})**	**Fe_2O_3 (wt.%)**	**Al_2O_3 (wt.%)**	**MnO (wt.%)**	**SOM (wt.%)**	**Ni (mg^{-kg})**
Group A core samples (1,2,3,5 and 7)						
Upper soil sub-sections (0-6cms; n=8)	79.8	8.12 ***(0.17)***	10.07 ***(-0.49)***	0.08 ***(-0.28)***	13.37 ***(0.50)***	53.0 ***(0.52)***
Lower soil sub-sections (7-24cms; n=8)	87.1	6.29 ***(0.74)*****	11.95 ***(0.92)******	0.1 ***(-0.12)***	10.22 ***(0.32)***	51.74 ***(0.70)****
Group B core samples (4,6,8 and 9)						
Upper soil sub-sections (0-6cms; n=5)	77.31	3.26 ***(-0.66)***	6.63 ***(-0.92)***	0.05 ***(-0.49)***	43.59 ***(0.96)******	45.49 ***((0.99)******
Lower soil sub-sections (7-24cms; n=11)	77.0	4.87 ***(0.64)*****	10.04 ***(0.49)***	0.05 ***(0.36)***	8.97 ***(-0.19)***	45.62 ***(((0.98)*******

p-values: *p < .05. **p < .025. ***p < .005. ****p < .0005.

Chromium

Among the trace metals, Cr was more widespread than Ni and, hence, more emphasis was placed studying Cr source and its distribution at the site. Core samples contained elevated levels of Cr (Fig. 2). Group A soil profiled an irregular Cr distribution pattern while Group B showed Cr concentration in the top soils higher than at increasing depths. Passively impacted areas (i.e. Group B) are rich in SOM, which evidently resulted in a high correlation between SOM and Cr ($r = 0.96$, $p < 0.005$) in the O-horizons of these areas. The uppermost organic-rich layers at the site appear to act like a filtration/retention system for Cr, preventing vertical transportation. In the surface and ground waters, Cr concentrations were less than 1.5 ug/L, further evidence that the site's topsoil serve as filters and sinks for Cr released from the tailing piles and past ore-smelting operations. Manganese III, IV -(hydr)oxides are known to oxidize Chromium(III) to mobile Cr(VI) (Bartlett and James, 1979; Fendorf 1995; Stepniewska et al., 2004). But the absence of a negative correlation between Mn-Cr at the site indicates that some other factors may be inhibiting this association.

Chemical analysis for Cr in slag (100 mg/kg) and ash (200 mg/kg) materials confirmed these as possible Cr sources. Chromite can occur as an accessory mineral with magnetite ($Fe^{+2}Fe^{+3}_2O_4$) and ilmenite ($Fe^{+2}TiO_3$), which are present in calc-silicate rocks (Volkert and Drake, 1999), with magnetite more abundant (avg: 2.24–3.23wt.%) than ilmenite (avg: 1.1–1.37wt.%). If exposed to surface conditions, these chromite-bearing minerals can be a source of low-Cr in soils.

Two modes of Cr transportation from the sources are proposed: (1) Cr released from mining activities complexes with SOM and immobilizes as soluble chelates in the O-horizon, forming a first layer of a naturally occurring filtration/retention system; (2) Cr released in-situ in the lower soil horizons not complexed by SOM are sorbed and retained by soil-rich sesquioxides, forming a second layer of filtration/retention system.

Nickel

Several cores contained high Ni concentrations. Nickel retention is influenced by the abundance or lack of SOM, clay minerals and oxides in the soils (Nachtegaal and Sparks, 2003; Karathanasis and Pils, 2005). In this study, Ni showed a binding behavior similar to Cr. Nickel–SOM is strongly correlated when SOM is high relative to oxides, and vice-versa. A strong Ni-Fe correlation and a strong Ni-Al correlation were revealed in the lower layers of Group B soils as SOM decreases with depth. Ash contained 90 mg/kg of Ni compared to 50 mg/kg in the slag.

CONCLUSIONS

Against all odds, the once extensively mined area recovered with the return of the forest, a clean lake and streams with neutral pH waters. This is undoubtedly due to the naturally occurring filtration/retention systems at the site, both by the SOM and the sesquioxides in the lower soil horizons. The study was able to trace the Cr sources from the slag/ash to breakdown of the parent rock bearing magnetite and other Cr-bearing minerals. Whether these types of Cr filtration/retention systems can efficiently remove Cr in areas severely impacted by Cr contamination requires further study.

ACKNOWLEDGMENTS

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FIELD GUIDE AND ROAD LOG

Meeting Point: Museum/Visitors Center (aka Frank L. Lautenberg Visitor Center) at 116 Old Forge Road, Tuxedo, NY 10987

Meeting Point Coordinates: 41.199^0 N, 74.255^{0}W

Meeting Date and Time: Sunday, October 2nd, 2016 at 9:00 AM

Directions from the conference (Distance in miles (km))

Cumulative	Point to Point	Route Description

1.3 (0.5)	1.3 (0.5)	Begin going east on Route 59 Take ramp onto Palisades Interstate Pkwy North (toward Bear Mt)
12.1 (19.5)	10.8 (17.4)	Take I-87 (NY Thruway) Westbound (toward Albany)
13.8 (22.2)	1.7 (2.7)	Take Exit 15A (NY17, toward NY-59/Sloatsburg/Suffern) and turn left onto Route 17.
16.9 (27.2)	3.1(5.0)	Take ramp toward Ringwood/Sterling Forest/West Milford and merge onto Sterling Mine Road.
20.5 (33.0)	3.6 (5.8)	Turn right onto Long Meadow Rd (Hwy 84)
20.8 (33.5)	0.3 (0.5)	Turn left onto Old Forge Rd *(If you reach Sterling Lake Corp you have gone a bit too far)*
21 (33.8)	0.3 (0.5)	Take first right to stay on Old Forge Rd *(If you reach Harriman Ct you went about 0.1 mile too far)*
		116 Old Forge Rd, Tuxedo Park, NY *(If you reach Reception Rd you have gone a bit too far)*

All 4 – 5 stops are short walking distances around the mining complex, including the visitors' center, which showcases a model of the underground mines and aboveground facilities before the whole operation was abandoned in the early 20th C. The exhibits also include samples of the rock types mined and other mining paraphernalia.