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Suitability of an organic residual cover on tailings for bioenergy crop production: A preliminary assessment

Jennifer Hargreaves[1,2], Alan Lock[1,2], Peter Beckett[2], Graeme A. Spiers[1,2], Bryan Tisch[3], Lisa Lanteigne[4], Tamara Posadowski[1,2], and Michael Soenens[5]

[1]MIRARCO, 935 Ramsey Lake Road, Sudbury, Ontario, Canada P3E 2C6; [2]Laurentian University, 935 Ramsey Lake Road, Sudbury, Ontario, Canada P3E 2C6; [3]Natural Resources Canada, 555 Booth Street, Ottawa, Ontario, Canada K1A 0G1; [4]Vale, 337 Power Street, Copper Cliff, Ontario, Canada P0M 1N0; and [5]Green Zone Farms, Azilda, Ontario, Canada P0M 1L0. *Received 5 December 2010, accepted 24 October 2011.*

Hargreaves, J., Lock, A., Beckett, P., Spiers, G. A., Tisch, B, Lanteigne, L., Posadowski, T. and Soenens, M. 2012. **Suitability of an organic residual cover on tailings for bioenergy crop production: A preliminary assessment**. Can. J. Soil Sci. **92**: xxx–xxx. To test the potential for production of bioenergy crops, such as canola and corn, an organic cover was constructed over acid-producing mine tailings containing nickel and copper, belonging to Vale in Sudbury, Ontario, Canada. The 1-m-deep cover was of organic residuals (biosolids) obtained from a regional paper mill.Corn and canola crops were successfully grown using agricultural techniques. Crop yields from each of 2yr from the tailings site were greater than those obtained at an agricultural site in the region. Root, shoot and grain analyses indicated low potential for bioaccumulation of potentially hazardous metals from the organic residual cover or the underlying tailings. Over the short term, there was no evidence of metal movement into the biosolids cover or uptake by the crops from the underlying tailing deposits. Importantly, canola seeds and corn kernels, the feedstocks for biodiesel and ethanol biofuels production, did not accumulate environmentally sensitive metals. This preliminary study demonstrates that the placement of an organic residuals cover on mine tailings to support growth of bioenergy crops is a potential novel reclamation strategy for the mining and smelting industry, or for industrial brownfields in general.

Key words: Reclamation, biosolids, biofuels, metals, energy crops, tailings

Hargreaves, J., Lock, A., Beckett, P., Spiers, G. A., Tisch, B, Lanteigne, L., Posadowski, T. et Soenens, M. 2012. **Recouvrement des stériles par des résidus organiques en vue de la production d'une culture bioénergétique : une évaluation préliminaire**. Can. J. Soil Sci. **92**: xxx–xxx. Les auteurs ont recouvert les stériles acides contenant du nickel et du cuivre d'une mine de la société Vale, à Sudbury (Ontario), avec des résidus organiques pour déterminer si on pourrait y faire pousser des cultures tel le canola ou le maïs pour la production de bioénergie. La couche d'un mètre d'épaisseur était constituée de résidus organiques (biosolides) issus d'une papeterie locale. On a réussi à cultiver le maïs et le canola selon des techniques agricoles. Chacune des deux années où les stériles ont été cultivés, le rendement des cultures dépassait celui obtenu à un site agricole de la région. L'analyse des racines, des pousses et du grain révèle un faible potentiel d'accumulation des métaux éventuellement nocifs à partir de la couche de résidus ou des stériles qu'elle recouvre. À court terme, rien ne prouve que les métaux migrent dans la couche de biosolides ou sont absorbés par la cultures des dépôts situés dans les stériles sous-jacents. Fait plus important, les graines de canola et les grains de maïs, matière première servant à la production de biodiesel et de biocarburants à base d'éthanol, n'accumulent pas de métaux susceptibles d'être dommageables pour l'environnement. Cette étude préliminaire montre que le dépôt de résidus organiques sur des stériles miniers pour favoriser la croissance de cultures bioénergétiques pourrait s'avérer une nouvelle stratégie de restauration des sols pour les sociétés minières et les métallurgies, ou pour les friches industrielles, en général.

Mots clés: Restauration, biosolides, biocarburants, métaux, cultures bioénergétiques, stériles

Globally, the mining industry disturbs large tracts of formally pristine landscapes in environmentally sensitive regions such as the boreal forest of North America and Eurasia. These forested regions also produce abundant waste organic biomass from the fibre extraction industries. The Sudbury region of Ontario, for example, has a large area of mining disturbed lands with approximately 2225 ha utilized to store mining waste rock and tailings residues (Peters 1995; Natural Resources Canada 2009). Successful reclamation of these areas is critical for the surrounding communities because ofassociated environmental and health hazards related to tailings ponds and requirements for industry to meet government regulations. Traditionally, these tailings have been viewed as marginal substrate materials and were reclaimed using vegetative covers, which would not be used for human consumption. Production of edible crops on mine tailings has not appealed to consumers or regulators because of perceived health risks and associated regulatory issues with contaminant accumulation in the products. However, the potential for transformingtailings and brownfields into productive agricultural land may provide a partial solution to the food versus fuel debate by minimizing the need to use only agricultural grade lands to grow energy crops. To reclaim these tailings to support energy crop growth, nutrients and organic materials are needed.

Pulp and paper mill by-products have been used for amending agricultural soils and producing crops including corn (O'Brien et al. 2003; Camberato et al. 2006). The concept of growing agronomic crops on tailings builds on previous successes using paper mill biosolids to restore mine waste management areas (Koski 2005). The first full-scale application in Ontario of a shallow biosolids cover to brownfields was on copper uranium tailings at the Pronto Mine near Elliot Lake, Ontario, which supported excellent vegetation growth over a 10-yr period (Tisch and Beckett 1999; Okonski and Spiers 2001; Okonski et al. 2003). Thick organic covers over tailings prevent wind-generated fugitive dust emissions and act as a hydraulic barrier, slowing or eliminating water movement to the tailings below (Lock et al. 2010). The potential for organic covers to act as oxygen barriers has also been reported (Tasse et al. 1997). The development of a reducing environment at the biosolids-tailings interface can limit sulphide oxidation, acid generation and consequently the release of metals into tailings pore waters (Pierce et al. 1994). The effect of organic residuals, agricultural practices and energy crop development on mobility of tailings bound metals has not been sufficiently studied.

The objective of the current long-term multi-stakeholder research initiative is to develop a sustainable reclamation strategy by creating biosolids covers using waste materials from regional forest fibre industries to provide fertile productive covers over the infertile mining wastes (Tisch and Ednie 2007; Tisch 2008; Spiers et al. 2010; Hargreaves et al. 2011). To support vegetative crops the organic residual materials were applied as surface covers to accommodate the large root volumes of energy crops such as canola, corn, switch grass and woody fibre crops. This study describes the first 2yr of a long-term investigation that compares biofuel crops (canola and corn) grown in biosolids covers over tailings to those grown on local agriculturalland.

MATERIALS AND METHODS

Approximately 4000 tonnes of fresh paper mill biosolids were trucked from St. Mary's Paper Ltd. in Sault Ste. Marie, 300 km from Sudbury, Ontario. The biosolidswere used to construct a 150 m × 25 m × 1 m thickexperimental area within an existing extensive and closed tailings cell during winter 2007–2008 at the Vale waste management facility in Copper Cliff, Ontario (approximately 6 km west of Sudbury, Ontario) (Posadowski 2011). The tailings cell had been closed to fresh tailings addition for at least10 yr. An agricultural reference site (approximately one-third hectare of 150 m × 25 m) was developed from a timothy (*Phleumpratense* L.) clover (*Trifolium* L.) hay pasture on HumicGleysols, the regionally representative Class 3W soils (Agriculture and Agri-Food Canada 1998) in Azilda, Ontario (approximately 12 km northwest of the Valesite). The chemical properties of the biosolids and tailings are shown in Table 1.

The agricultural plot was moldboard ploughed, tilled with an S-tyne cultivator and double roll harrowed prior to planting in both years, whereas the tailings plot at Vale was compacted and tilledwith an S-tyne cultivator and double roll harrowed prior in 2008, and ploughed and tilled in 2009. Following tillage, corn (Canamaize COPOP1) (*Zea mays* L.) a dwarf hybrid and canola (InVigor 5030) (*Brassica napus* L.) were sown at both sites with a conventional agricultural seed drill (6200 Case International) in 2008 and 2009. Plot management details are shown in Table 2, with standard regional farm practice based on soil sample analyses and crop demand guiding fertilizer application rates through the growing season.

Each experimental area was divided into four subplots of approximately 750 m^2, with two diagonally opposed subplots planted with corn and two with canola. All subplots were divided into smaller cells (5 × 5 m), with detailedsampling infive randomly selected cells of each subplot in both years at both sites. Biomass at maximum growth and soil sampling occurred in September each year. Above-ground biomass was harvested from 1 m^2 from each cell ($n = 5$ for each sub-plot), including shoots and grain, with shears by snipping at ground level. Subsequently, composite samples of 10 cores of biosolid covers at Vale and soil at Azilda were sampled with a Star soil probe (www.starqualitysamplers.com) to a depth of 15 cm from five cells in each sub-plot. The biosolids cover was also sampled from pits in 15-cm depth increments through the cover into the tailings.

Table 1. Chemieal properties of the St Mary's biosolids material used as a cover on the Vale tailings at Copper Cliff, Ontario

	St. Marys	SD^z	Vale tailings	SD
pH	7.45	0.07	2.30	0.05
Loss on ignition (%)	35.6	2.92		
Carbon (%)	262667	5508	1467	57.7
Nitrogen (%)	1900	0.00		
Sulphur (%)	227	162	33167	321
Calcium (mg kg^{-1})	51767	4562	38600	6601
Cadmium (mg kg^{-1})	4.50	0.00	32.0	2.00
Cobalt (mg kg^{-1})	2.33	0.58	30.3	1.15
Copper (mg kg^{-1})	26.7	1.53	419	13.3
Iron (mg kg^{-1})	6183	997	183733	4365
Potassium (mg kg^{-1})	6293	680	9420	416
Magnesium (mg kg^{-1})	4853	985	16967	650
Manganese (mg kg^{-1})	1,793	58.6	744	30.5
Nickel (mg kg^{-1})	14.7	3.05	431	15.9
Phosphorus (mg kg^{-1})	2507	32.1	413	17.7
Lead (mg kg^{-1})	20.7	2.31	88.0	2.65
Zinc (mg kg^{-1})	147	9.54	73.0	4.36

^{z}SD, standard deviation.

Table 2. Management details of the Azilda agricultural reference site and Vale tailings site

Site	Crop	Planting date	Fertilizer rate
		2008	
Azilda	Canola and corn	Jul. 01	At planting: 170 kg ha^{-1} 5-20-20; August: 225 kg ha^{-1} 46-0-0
Vale	Canola and corn	Jul. 01	At planting: 170 kg ha^{-1} 5-20-20; August: 225 kg ha^{-1} 46-0-0
		2009	
Azilda	Canola and corn	Jun. 24	At planting: 170 kg ha^{-1} 5-20-20; July: 225 kg ha^{-1} 46-0-0
Vale	Canola and corn	May 25	At planting: 170 kg ha^{-1} 5-20-20; July: 225 kg ha^{-1} 46-0-0

All samples were oven dried at 65°C for 48 h and ground to pass a 2-mm sieve, sub-sampled and digested for 3 h at 105°C with a concentrated nitric and hydrochloric acid mixture ($3{:}1HNO_3{:}HCl$). Solutions were analyzed for nutrients and metals (calcium, cadmium, cobalt, copper, iron, potassium, magnesium, manganese, nickel, phosphorus, lead and zinc) by ICP-AES (Spiers et al. 1983), with a quality control program completed in an ISO 17025 accredited facility to include analysis of duplicates, acceptance of certified reference material data within ±10% of accepted values, procedural and calibration blanks, matrix matched standards, matrix spikes, continuous calibration verification and use of internal standards to compensate for matrix suppression and instrumental drift during analysis. All concentrations were calculated in mass/mass dry soil/plant basis. Bioavailable nutrients and metals (calcium, cadmium, cobalt, copper, iron, potassium, magnesium, manganese, nickel, phosphorus, lead and zinc) were extracted from biosolids and soil samples using a lithium nitrate (0.01M $LiNO_3$) solution (Abedin et al. 2009; Abedin et al. 2011), centrifuged at 3000 rpm for 10 min, filtered through Whatman 44 filter papers, acidified with nitric acid and analyzed by plasma spectrometry (Spiers et al. 1983), with a quality control program including analysis of duplicates, procedural and calibration blanks, matrix matched standards, matrix spikes, continuous calibration verification and the use of internal standards to compensate for matrix suppression and instrumental drift during the analysis.

STATISTICA^{TM} Release 6 was used to perform all statistical analyses, with the Kruskal-Wallis non-parametric ANOVA and multiple comparison tests based on the Nemenyi approach (Statsoft 2011) beingused to test for differences since on testing some data were not normally distributed.

RESULTS

Pooled total and bioavailable metal and nutrient concentrations in the top 15 cm of the biosolids and agricultural soil are presented in Tables 3a and 3b. Only 2009 results are shown as 2008 results were very similar, except for carbon, nitrogen and sulphur for which 2008 data were reported. All total and bioavailable nutrients and metals followed similar trends; bioavailable metal concentrations mirrored total concentrations. Total

Table 3a. Total concentrations of nutrients and metals in the surface 15cm of the St Mary's biosolidscover at the Valetailings site and the HumicGleysolsoil at the Azildaagricultural site (mean ± SD, $n = 20$)

	Vale		Azilda	
	2008			
pH	6.56	0.22	6.97	0.12
Carbon (g kg^{-1})	231	35.9	19.1	1.00
Nitrogen (g kg^{-1})	7.00	0.70	1.60	0.10
Sulphur (g kg^{-1})	1.90	0.20	0.30	0.00
	2009			
Calcium (mg kg^{-1})	30,474	3,879	6,730	308
Cadmium (mg kg^{-1})	0.75	0.37	0.25	0.07
Cobalt (mg kg^{-1})	4.13	1.05	8.66	0.28
Copper (mg kg^{-1})	83.6	51.7	44.5	2.78
Iron (mg kg^{-1})	9,718	3,961	13,663	388
Potassium (mg kg^{-1})	2,736	494	231	28.4
Magnesium (mg kg^{-1})	3,165	520	4,475	105
Manganese (mg kg^{-1})	2,478	301	264	17.5
Nickel (mg kg^{-1})	35.2	16.5	63.4	2.35
Phosphorus (mg kg^{-1})	2,606	330	421	20.4
Lead (mg kg^{-1})	21.8	3.96	11.1	0.73
Zinc (mg kg^{-1})	330	29.5	160	28.9

Table 3b. Bioavailable concentrations of nutrients and metals in the surface 15cm of the St Mary's biosolids cover at the Vale tailings site and the HumicGleysol soil at the Azilda agricultural site (mean ± SD, $n = 20$)

	Vale		Azilda	
	2009			
Calcium (mg kg^{-1})	1,708	298	450	50.6
Cadmium (mg kg^{-1})	0.01	0.007	0.002	0.002
Cobalt (mg kg^{-1})	0.01	0.01	0.03	0.01
Copper (mg kg^{-1})	0.72	0.18	0.65	0.04
Iron (mg kg^{-1})	3.75	1.32	6.77	1.32
Potassium (mg kg^{-1})	256	73.8	8.86	1.23
Magnesium (mg kg^{-1})	327	64.8	106	11.4
Manganese (mg kg^{-1})	78.3	14.0	5.01	1.66
Nickel (mg kg^{-1})	0.12	0.14	0.44	0.04
Phosphorus (mg kg^{-1})	146	24.9	7.06	0.59
Lead (mg kg^{-1})	0.02	0.03	0.02	0.02
Zinc (mg kg^{-1})	0.76	0.17	0.03	0.01

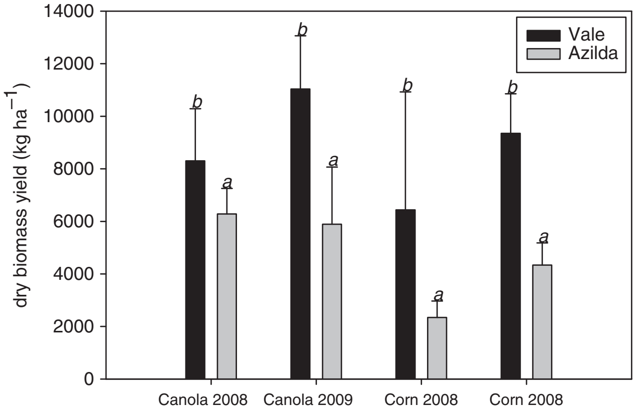

Fig. 1. Dry biomass yields of canola and corn at the Vale experimental site and the Azilda reference site in 2008 and 2009 ($n = 10$). Means marked with different letters indicate significant differences ($P < 0.05$).

iron, magnesium and nickel concentrations were greater in Azilda soil than biosolids at the Vale site but their bioavailable concentrations in soils and biosolids were similar. Notable differences included the much greater total and bioavailable concentrations of potassium and phosphorus at the Vale site than at the Azilda reference site. The soil at the Azilda site was generally lower in both total and bioavailable nutrients. Specifically, the soil had very low concentrations of total carbon, nitrogen and sulphur; bioavailability of all measured nutrients except iron was also low (Tables 3a and 3b).

Dry biomass for canola and corn were significantly greater at the Vale tailings site than at the Azilda agricultural site in 2008 and 2009 (Fig. 1). Crops at the Vale site (Fig. 2) were visually healthier and lusher than those at the agricultural site, as indicated by their colour and vigour. The corn at the agricultural site was visibly stressed, being very pale greenand showing signs of deficiencies, including paler leaf margins and occasional red streaking. Canola at the tailings site appeared very healthy at all growth stages without visible deficiency symptoms (Fig. 2).

Nitrogen concentrations in canola tissue from the tailings site were higher than those from the agricultural site (Table 4), but similar between sites in corn tissue (Table 5). Canola root and shoot tissues from the tailings site had much higher concentrations of potassium than those from the agricultural site (Table 4), whereas concentrations in corn shoots and roots were higher if grown in tailings. Kernel potassium concentrations were similar from the two sites (Table 5). Magnesium concentrations in all canola and corn tissue were higher for crops grown in biosolidsthan in the agricultural site (Tables 4 and 5). Canola and corn tissue grown in biosolidshad higher concentrations of cadmium in most plant parts compared crop tissue samples from the agricultural site. Root tissue concentrations of iron in both canola and corn plants grown in biosolids were lower than those grown in agricultural soil (Tables 4 and 5).

The biosolids pH of 6.2 was higher than that of the underlying acid-generating tailings with pH of 2.8 (Table 6a). Total concentrations of nutrients and metals generally increased with depth, although calcium, cadmium, manganese, phosphorus and zinc decreased with depth (Table 6a). Bioavailabity of nutrient and metals displayed different trends (Table 6b). Bioavailable potassium concentrations were lower in tailings

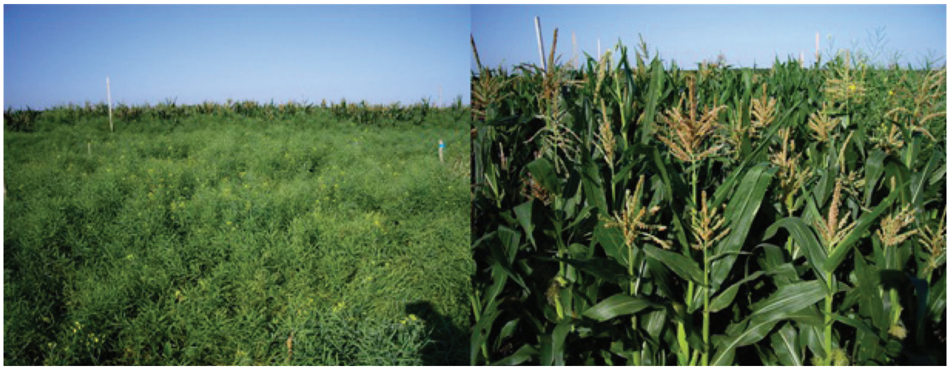

Fig. 2. Canola (left) and corn (right) crops grown at the Vale experimental site, July, 2009.

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Table 4. Nutrient and metal concentrations (mg kg^{-1}) in canola shoots, roots and seeds in plants from the Vale tailings site and the Azildaagricultural site ($n = 10$)

	Shoots				Roots				Seeds			
	Vale	SD	Azilda	SD	Vale	SD	Azilda	SD	Vale	SD	Azilda	SD
2008												
Carbon	408000	8800*	441000	5700	435000	7100*	453000	11000	520000	37000*	441000	63200
Nitrogen	21500	3000*	9600	2300	9700	2400*	6200	1,200	383000	1500	28500	9500
Sulphur	4400	1400*	3700	900	1300	500*	2100	400	4500	700*	6600	1500
2009												
Calcium	15360	2708	13871	1222	4309	1073	4634	620	5734	440*	4265	226
Cadmium	<0.015		<0.015		<0.015		0.16	0.07	<0.015		<0.015	
Cobalt	<0.015	0.00	<0.015		<0.015		<0.015		<0.015		<0.015	
Copper	4.19	1.77	3.10	0.86	4.04	1.52*	1.16	1.61	1.60	1.64	2.46	1.61
Iron	263	256*	56.3	10.5	39.3	25.6*	467	93.5	46.5	13.8	52.8	8.90
Potassium	22552	3024*	12449	1920	19023	3297*	9058	2255	8463	390*	7956	245
Magnesium	2703	556*	2,613	305	885	212*	1347	260	5385	269*	3931	199
Manganese	33.1	8.86*	10.9	1.60	18.3	8.14*	7.71	2.11	70.0	6.40*	50.4	3.61
Nickel	1.18	1.86*	<0.015		0.04	0.07*	2.28	0.65	<0.015	*	0.59	0.79
Phosphorus	NA[z]		NA		3861	887*	878	163	10039	625*	6518	558
Lead	264	258*	56.5	10.3	0.11	0.17	0.11	0.17	<0.03		<0.03	
Zinc	141	25.0*	98.0	37.4	108	38.6	114	33.5	175	21.1	185	30.4

[z] NA, not available.

*Means followed by an asterisk indicate significant differences ($P < 0.05$) between sites.

than in biosolids. Bioavailable concentrations of cobalt and iron decreased within the 0- to 15-cm depth increment, while copper concentrations increased (Table 6b). In the 15- to 30-cm depth increment, concentrations of bioavailable calcium, cadmium, manganese and nickel increased. For all nutrients and metals the bioavailable portion was less than 1% of the total concentration (Tables 6a and 6b).

DISCUSSION

The higher yield and healthier crops at the tailings site compared with the agricultural site may be reflective of the greater abundance and availability of nutrients in the biosolids cover. The agricultural soil test indicated low plant available phosphorus, potassium, manganese and zinc concentrations while the biosolids were low in zinc for field crops [Ontario Ministry of Agriculture,

Table 5. Nutrient and metal concentrations (mg kg^{-1}) of corn shoots, roots and kernels in plants from the Vale tailings site and the Azildaagricultural reference site ($n = 10$)

	Shoots				Roots				Kernels			
	Vale	SD	Azilda	SD	Vale	SD	Azilda	SD	Vale	SD	Azilda	SD
2008												
Carbon	418000	6200*	435000	4800	422000	9000*	408000	10400	449000	9900*	455000	3200
Nitrogen	15600	2000	15200	1800	10000	1800*	7600	600	25100	1600*	30200	2700
Sulphur	1600	300	1700	200	1000	200	1000	100	2000	200*	2200	200
2009												
Calcium	5028	696	4909	373	3011	635	3208	347	1595	373*	1829	269
Cadmium	0.20	0.18*	<0.015		<0.015	*	0.16	0.07	<0.015		<0.015	
Cobalt	<0.015		<0.015		<0.015		0.03	0.04	<0.015		<0.015	
Copper	6.60	1.84*	9.31	2.52	7.22	1.95*	14.6	4.17	6.17	1.93*	9.59	3.45
Iron	179	99.4	224	80.0	201	77.7*	1989	527	64.0	9.75*	134	112
Potassium	19953	1494*	6358	978	27013	3242*	5255	1544	12907	856*	11172	1262
Magnesium	2565	442*	5159	538	1809	292*	2544	290	2822	143*	3943	515
Manganese	62.1	24.8*	20.7	5.58	77.4	17.6*	35.8	9.80	42.5	6.51*	22.9	3.78
Nickel	0.22	0.35	0.05	0.07	0.21	0.43*	13.6	2.24	<0.015	0.00*	16.9	51.6
Phosphorus	NA[z]		NA		3123	938*	1291	158	5662	422	5774	563
Lead	175	95.6	225	80.9	0.58	0.58*	1.64	0.72	1.15	0.89	2.77	3.77
Zinc	192	34.2*	151	29.3	125	43.4	124.1	18.7	144	12.1*	123	20.2

[z] NA not available.

*Means followed by an asterisk indicate significant differences ($P < 0.05$) between sites.

Table 6a. Total nutrient and metal concentrations in the profile of the biosolids cover and underlying tailings at the Vale tailings site (mg kg^{-1}) ($n = 4$)

	Depth										
	0–15 cm	SD	15–30 cm	SD	30–45 cm	SD	45–60 cm^z	Interface	SD	Tailings	SD
					2009						
pH	6.43	0.21	6.50	0.13	6.69	0.06	6.69	6.35	0.43	2.78	0.56
Calcium	28668	5135	27132	5727	29234	3087	30813	23072	5882	14002	2792
Cadmium	0.53	0.26	0.45	0.28	0.26	0.28	0.67	0.12	0.21	<0.015	
Cobalt	2.52	0.61	2.29	0.64	2.31	0.51	2.26	5.13	1.86	10.3	1.15
Copper	49.5*ab*	9.72	40.4*a*	15.1	38.6*ab*	7.93	32.2*ab*	137*ab*	56.7	292*b*	52.1
Iron	6986	1310	5923	2422	4879	322	4,751	40705	24693	65850	5900
Potassium	1687	673	1708	687	1934	385	2296	1775	591	3615	938
Magnesium	2263	656	2262	767	2472	773	2942	2432	610	4538	1276
Manganese	2275*b*	292	2092*ab*	441	263*ab*	601	2135*ab*	1493*ab*	471	486*a*	37.2
Nickel	17.0*ab*	7.61	12.6*ab*	5.38	8.23*a*	0.55	7.72*ab*	93.9*ab*	73.8	174*b*	16.6
Phosphorus	2507*b*	215	2453*ab*	217	2384*ab*	75.8	2614*ab*	2023*ab*	495	488*a*	66.1
Lead	19.2*ab*	6.92	17.7*a*	5.14	21.3*ab*	2.47	26.2*ab*	23.2*ab*	3.91	32.5*b*	4.37
Zinc	302	61.0	290	44.2	312	28.2	328	263	49.6	159	17.5

Table 6b. Plant available nutrients and metals in the profile of the biosolids covers and underlying tailings at the Vale tailings site (mg kg^{-1}) ($n = 4$)

	Depth										
	0–15 cm	SD	15–30 cm	SD	30–45 cm	SD	45–60 cm	Interface	SD	Tailings	SD
					2009						
Calcium	2205	385	1858	300	1217	150	1,538	4,717	2727	4578	221
Cadmium	0.014	0.016	0.015	0.005	0.015	0.005	0.017	0.022	0.008	0.163	0.06
Cobalt	0.002	0.002	0.018	0.007	0.012	0.017	0.028	0.034	0.017	1.35	1.25
Copper	0.60	0.09	0.70	0.06	0.91	0.00	0.79	0.49	0.25	12.7	12.1
Iron	1.66	0.11	1.85	0.40	2.39	1.16	4.98	1.87	1.42	1239	1449
Potassium	293	82.3	334	52.7	394	16.0	425	342	183	301	203
Magnesium	354	40.6	335	45.5	319	64.4	444	363	65.5	303	49.1
Manganese	78.4	38.9	67.1	19.8	45.7	8.83	40.5	110	62.0	163	39.8
Nickel	0.16	0.10	0.15	0.04	0.16	0.005	0.14	0.36	0.20	23.1	20.0
Phosphorus	91.9	19.3	103	30.4	116	7.64	90.5	41.4	34.4	2.07	1.46
Lead	0.06	0.05	0.02	0.03	<0.0012		0.02	0.02	0.02	0.14	0.02
Zinc	0.61	0.25	0.66	0.15	0.80	0.21	0.77	0.76	0.16	12.7	4.27

^{z}Only one sample collected at this depth that did not represent the interface.
a, *b* Means followed by different letters indicate significant differences ($P < 0.05$).

Food and Rural Affairs (OMAFRA) 2010]. In 2009 the shorter growing season of crops on the agricultural site (Table 2) due to late planting because of wet conditions may have contributed to the lower yield. Field observations also showed that germination was faster on the biosolids cover.

Contrary to our study, O'Brien et al. (2002) found increasing the proportion of paper mill biosolids used as soil amendments suppressed growth of corn due to immobilization of nitrogen and phosphorus. Gagnon et al. (2010) found that paper mill sludge had greater than average nutrient concentrations, producing a higher corn yield with increasing amounts of biosolids amendment incorporated into the soil. Crops at the Vale tailings site were grown in 100% biosolids with a carbon:nitrogen ratio greater than 20 (Table 3a), a ratio which generally will inducenitrogen immobilization (Mkahabel and Warman 2005). Camberato et al. (2006) observed that many studies utilizing paper mill biosolids as crop amendments found nitrogen availability was reduced, despite addition of nitrogen fertilizer. Since biosolids from each mill site are different plant response differences might be expected.

Corn at the agricultural site was nitrogen, phosphorus and potassium (Table 5) deficient (2008 and 2009) at harvest according to published nutrient sufficiency criteria for high yield hybrid corn (OMAFRA 2009). Canola plants (Table 4) at both sites were nitrogen (<2.5%) and sulphur (<0.5–0.6%) deficient in 2008, but had sufficient calcium, magnesium and phosphorus (Canola Council of Canada 2003). Canola grown at the agricultural site was potassium deficient both years (Brennan and Bolland 2007); the crop grown at the tailings site was potassium deficient in 2009. Distribution of potassium in canola plants from the agricultural site in 2008 may be symptomatic of soil potassium deficiencies or metal sensitivities (Table 4). Potassium, being very mobile in plants, is often redistributed to younger tissues (Mengel and Kirkby 1982). At the agricultural site, where potassium was deficient, only canola showed translocation of potassium to seeds, a response not observed in corn plants (Table 5). Uptake of potassium is influenced by the size of the root system relative to the shoots (Engels and Marschner 1992). The root system of plants grown at the agricultural site was muchsmaller in size than those at the tailings site (field observations, data not shown).

Although the higher metal concentration in the biosolids cover did not generally lead to increased metal uptake by the crops, the higher lead and zinc concentrations observed in canola tissue on the biosolids (Table 4) were within documented ranges (lead: 30–300 mg kg^{-1}; zinc: 100–400 mg kg^{-1}) (McBride 1994). Canola species exhibit metal tolerance and have been used for phytoremediation because of their capacity for metal accumulation. For example, Marchiol et al. (2004) found lead accumulation to 472 mg kg^{-1} in canola root tissue and zinc accumulation to 1305 mg kg^{-1} in canola shoots (Marchiol et al. 2004; Angelova et al. 2008). In corn, lead tended to accumulate in the shoots, which is in disagreement with previous studies that have shown lead to have very limited mobility in the canola plant and accumulated in root tissue (Gigliotti et al. 1996; Marchiol et al. 2004; Angelova et al. 2008).

Root tissue of corn grown at the agricultural site had nickel concentrations within documented ranges for plants (10–100 mg kg^{-1}) (McBride 1994). The soil at the agricultural site had greater total and bioavailable concentrations of nickel than the biosolids at the tailings site (Tables 3a and 3b) and thus greater uptake is reasonable. Nickel is among the plant mobile metals, which while generally not translocated to grain, accumulates in shoots (Gigliotti et al. 1996). Iron accumulated in the roots of canola and corn plants grown at the agricultural site, which had much higher total soil iron concentrations compared with the biosolids (Table 4). Corn roots from the Gleysolic soils at the agricultural site had iron concentrations in excess of potential toxicity limits for corn shoots ($>$1000 mg kg^{-1}) (McBride 1994). Iron is relatively immobile in plants and less mobile metals tend to accumulate in roots (Mengel and Kirkby 1982; Gigliotti et al. 1996). Bioavailable iron concentrations of the soil and the biosolids indicated iron was similarly available at both sites.

In biofuel manufacturing, the oil is extracted from canola seeds. Canola seeds from both sites had elevated (2–3 times greater) copper and zinc concentrations (Table 4) compared with values of 5.8 mg copper kg^{-1} and 58 mg zinc kg^{-1} published by the Canola Council of Canada (2010). Canola seeds from the agricultural site had higher than normal nickel concentrations (0.17–2.50 mg kg^{-1}). For corn kernels (Table 5), some metal concentrations were elevated compared with literature values. Cadmium and zinc kernel content was two to three times greater than the ranges of 0.001–0.294 mg 13.0–32.6 mg kg^{-1}, with copper and lead being two to four times higher than the values of 1.32–6.31 mg kg^{-1} and 0.033–0.519 mg kg^{-1}(Pietz et al. 1978; Granato et al. 2004). These comparisons, however, should be considered with caution as literature values were not for the canola and corn varieties used in the present study. As lipids, a key component of any potential seed extracted fuel, from corn (*Zea mays* L.), common wheat (*Triticumaestivum* L.) and peanut (*Arachishypogaea* L.) had low metal concentrations, any potential concern from environmental release of combusted metals in fuels may be minimal as Stefanov et al. (1995) showed that the metals were accumulated in the non-lipid tissues of the seed.

Plant available metal concentrations of biosolids and tailings demonstrate that, while total concentrations of some metals may be increasing slightly in the biosolids, these metals are being more strongly bound by biosolids organic and inorganic compounds compared with the tailings (Table 8). Cadmium, copper and cobalt were more plant available in the tailings than the 0- to 15-cm depth increment of the cover (Table 6a and 6b). While organic matter will eventually decompose, inorganic residues in organic materials can bind metals for decades (McBride 1994), with Fierro et al. (1997) documenting varying half-lives for the degradation of biosolid organic components in soils ranging from 0.4 to 13 yr. However, the tailings at the Pronto waste management area near Elliot Lake, Ontario, covered with 30 cm of pulp and paper biosolids about 15 yr ago, maintained that thickness. The carbon loss due to degradation is potentially being balanced by carbon inputs from both roots and litter fall from the perennial vegetation. A recent study of an age sequence of shallow (~30 cm) pulp and paper mill organic residue covers on non-acid producing gold tailings showed low rates of organic matter decomposition over a 10-yr period (Cousins et al. 2009).

To demonstrate feasibility on a longer temporal and larger spatial scale, additional research is underway using biosolids materials from a variety of sources, and manufactured soils on both acid and non-acid generating tailings. The testing of other crops that play key roles in the biofuel industry, such as perennial grasses [e.g., switch grass (*Panicumvirgatum* L.)] or short rotation shrubs such as willows (*Salix* species), will also be beneficial. This preliminary research has shown that there appears to be no significant uptake of metals into the crops, which is important when using the crops for biofuels or other purposes. The effectiveness of thick covers as potential oxidation barriers needs investigation with larger size plots on tailings. Our preliminary data suggest that ongoing change in many of the monitored parameters is anticipated but stability in the longterm is projected. Although this short-term study did not address the effects of microclimate, water budget, different fertilizer regimes and different soil nutrient concentrations on crop production, growth responses

Author: There is no Table 8.

and tissue concentrations, these variables will be important in ongoingre search following this preliminary study. An understanding of the implications of the decomposition of the biosolids cover and carbon cycling is critical for sustainability of this mining brownfields reclamation approach.

CONCLUSIONS AND IMPLICATIONS FOR RECLAMATION

Corn and canola crops can be successfully grown using agricultural techniques on acid tailings that have a cover of biosolids such as paper mill residues. Over the short term, there was no evidence for metal uptake into the biosolids cover or by the crops from the underlying tailing deposits. Importantly, the seeds of canola and corn kernels did not accumulate environmentally sensitive metals.

This is an important preliminary phase for a novel reclamation practice that has environmental and economic benefits including: the use of one industry's waste (biosolids) to reclaim the wastes (tailings) of another industry; a contribution by the mining industry to sustainable development and community growth; and a contribution towards greenhouse gas reductions through the addition of carbon to an otherwise barren or less productive land.

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