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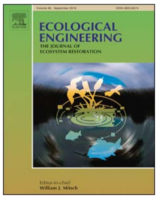

Research paper

Growth and metal uptake of canola and sunflower along a thickness gradient of organic-rich covers over metal mine tailings

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ABSTRACT

We completed a field-scale experiment to determine the thickness thresholds of covers of organic residuals required to grow biofuel crops over low-sulfur metal mine tailings with high metal content. An organic-rich mix made of municipal yard waste composts and wood waste was spread up to ~70 cm thick over low sulfur Ni-Cu tailings. We seeded and fertilized biofuel crops of canola and sunflower across this gradient. We measured biomass production and concentrations of nutrients and trace metals in tailings, organic residuals, and plants. Below the threshold organic cover thickness of 15 cm, macronutrient content was reduced and bioavailable Fe, Ni and Cu were 5–50 times higher as compared to thicker organic covers, apparently as a result of tillage. Bioavailable K and Na increased by an order of magnitude and Mo doubled with increasing thickness of organic covers from 5 and 70 cm thick. The plants showed limited uptake of Ni and Cu, with bioconcentration factors of near 1 for sunflower and 0.6 for canola. Biomass production was not affected by the thickness of the organic cover. Plant rooting depth was deeper over thin organic covers, extending up to 15 cm into the tailings. Low stem Fe in plants over thin covers indicated a potential interaction between trace metals and Fe nutrition. These results support the use of covers of organic residuals as thin as 15 cm thick to grow biofuel crops over circumneutral metal mine tailings. Thin covers will make this approach more economical for mine reclamation managers.

1. Introduction

Organic-rich residual wastes such as biosolids, municipal composts and pulp and paper sludge are increasingly being used as amendments to reclaim and revegetate metal mine tailings facilities (Alvarenga et al., 2009; Brown et al., 2003; Forsberg et al., 2008; Gardner et al., 2010; Hargreaves et al., 2012; Lock et al., 2010; Madejon et al., 2010; Van Rensburg and Morgenthal, 2003; Verdugo et al., 2011). Such organic amendments (i) decrease bulk density of the tailings and provide structure; (ii) improve water holding capacity; (iii) favour root penetration; (iv) provide slow-release nutrients for vegetation and microorganisms; (v) have high cation exchange capacity for nutrient retention; (vi) boost microbial activity through the decomposition and release of labile organic compounds; and (vii) limit the bioavailability of trace metals and metalloids through adsorption, complexation, reduction and volatilization (Larney and Angers, 2012; Park et al., 2011). Organic amendments can also increase the solubilisation of trace metals in tailings (Ribet et al., 1995; Schwab et al., 2007), but the use of circumneutral or alkaline organic amendments, or their mixing with a liming agent, limits the solubility of many trace metals and their bioavailability (Alvarenga et al., 2009; Forsberg et al., 2008; Van Rensburg and Morgenthal, 2003).

Organic residuals may be mixed into the tailings (Alvarenga et al., 2009; Forsberg et al., 2008; Gardner et al., 2010; Madejon et al., 2010; Verdugo et al., 2011) or they may be added as covers on top of mine tailings to act as the principal rooting medium, thus limiting contact with the underlying tailings (Brown et al., 2003; Hargreaves et al., 2012; Lock et al., 2010). If thick enough, covers of organic residuals may also limit oxygen and water ingress into tailings, potentially limiting acid-mine drainage in susceptible tailings (Peppas et al., 2000).

Researchers and reclamation managers primarily use organic residuals on metal mine tailings as part of a phytostabilization strategy, with the intent to establish low productivity vegetation that limits wind and water erosion of the tailings, limits plant metal uptake and brings biodiversity benefits (Alvarenga et al., 2009; Brown et al., 2003; Gardner et al., 2010). In contrast, managers in coal mining and aggregate industries have for decades used organic residuals to reclaim surface mine spoil toward high productivity agricultural land (Sopper,

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1992). Only recently have researchers used organic residuals to target high-productivity agricultural endpoints on metal mine tailings (Hargreaves et al., 2012; Lock et al., 2010), for non-food uses such as biofuel crops. These latter trials have used thicker covers of organic residuals, 40–100 cm thick, to limit water and oxygen ingress into the tailings and minimize plant uptake of contaminants. However, tailings management areas of metal mines can exceed hundreds of hectares, so managers would need plentiful and inexpensive sources of organic residuals for such thick covers. Thin covers of organic residuals would be more economical, but little is known on the potential of using compost covers < 40 cm for biofuel crop production over metal mine tailings. Thinner covers may limit available nutrient pools and increase metal uptake by plants, both of which could affect plant biomass production. Growing oil seed crops such as canola (*Brassica napus* L.) and sunflower (*Helianthus annuus* L.) on thin covers of organic residuals may offer a complementary strategy since both crops are metal-tolerant and have been used to phytoremediate metal-contaminated soils (Lai et al., 2010; Marchiol et al., 2004; Mohammadzadeh et al., 2014; Rivelli et al., 2012; Shaheen and Rinklebe, 2015).

Here we present a field-scale study to test whether growing crops of canola or sunflower on thinner covers of organic residuals over low sulfur Ni-Cu mine tailings affects the availability and uptake of nutrients and contaminants of concern and the production of crop biomass. We constructed a thickness gradient of organic residuals from < 5 to ~70 cm over the metal mine tailings, and then we prepared, seeded and fertilized crops of sunflower and canola across this gradient over two growing seasons. We were interested in identifying the minimum threshold thickness of organic covers that affect nutrients and contaminants in substrates and crop plants and also affect crop growth. We predicted that: (i) the availability of contaminants would increase and nutrients would decline below threshold thicknesses of covers made of organic residuals; (ii) the plant uptake of contaminants would increase below these thresholds; and (iii) the productivity of oilseed crop plants would also drop below these thresholds. Knowing these thresholds thicknesses would allow managers to limit the quantity and cost of organic covers for the reclamation of metal mine tailings facilities to biofuel cropland, while at the same time limiting environmental risks.

2. Materials and methods

The study took place at a Ni-Cu mine tailings facility within the northwest part of the City of Greater Sudbury, Ontario, Canada in the summer 2013, after a preliminary 2012 season. The region has a humid continental climate, with an average annual temperature of 4.1 °C, July average temperature of 19.1 °C, 943.6°-days above 10 °C and 903.3 mm of precipitation annually (Sudbury A station, 41 km E; 1981–2010 climate normals; Environment Canada, 2017). Average temperature and precipitation for July and August 2013 were within half a standard deviation of the climate normals for these months. The tailings facility is ~65 ha in size and flat to very gently domed, with deep tailing deposits (maximum > 15 m) and surrounded by the rolling landscape of Precambrian shield. The tailings originated as waste from the processing and extraction of Cu and Ni-rich phases of massive pentlandite, chalcopyrite, pyrrhotite and pyrite-bearing sulfide deposits (Rousell et al., 2002). The raw sulfide-rich tailings are capped by ~1.5 m of low sulfur tailings produced through a desulfurization process. The surface tailings were slightly alkaline (pH 7.8 ± 0.2), had low organic matter content (0.3 ± 0.1%) and low cation exchange capacity (CEC; 15.7 ± 2.7 cmol (+) 100 g^{-1}; $n = 5$; mean ± SD; K. Nicholls, unpublished data). They also had very low total content of C, N, and P, high total content of Ca, Mg, Fe and Al, and high total content of several elements of concern, namely Ni, Cu, Cr, Mo and Se, well above Canadian environmental guidelines (Table 1).

Table 1
Total concentrations of selected nutrient, major elements and minor elements (μg g^{-1}) within low sulfur tailings (n = 160) and organic covers (n = 39), as determined from ICP-AES (Smith 2012), as compared to Canadian soil quality guidelines for agricultural and industrial uses (CCME, 2016). Bolded mean values in the tailings exceed agricultural soil quality guidelines.

Element	Low sulfur tailings		Organic cover		Soil quality guideline	
	mean	SD	mean	SD	Agricultural	Industrial
P	339	104	1780	577		
K	5560	903	3960	1000		
Ca	12900	2140	40400	9270		
Mg	10800	855	11400	1800		
Fe	32800	4090	13800	1060		
Al	20000	2070	11990	1110		
As	5.7	4.8	3.7	2.5	12	12
B	239	107	–	–		
Cd	< 0.03		0.4	0.1	1.4	2.2
Co	15.7	5.3	7.3	1.7	40	300
Cr	**156**	21	30	7.5	64	87
Cu	**388**	108	60	23	63	91
Mn	444	47	491	72		
Mo	**131**	81	**8.9**	20	5	40
Na	844	158	1050	250		
Ni	**1050**	229	26	7	45	89
Pb	32.1	4.4	32	12	70	600
Se	**495**	67	**170**	36	1	2.9
Zn	66.5	26.7	174	47	200	360

The mining company applied a cover of organic residuals over these low sulfur tailings in the fall and winter of 2011–2012. The organic cover was prepared from Greater Toronto municipal yard waste compost (> 95%) blended with composted wood and bark fiber from northeastern Ontario lumber operations (< 5%). They spread the organic residual by bulldozer in the spring of 2012 over an area of 225 m by 125 m, (~3 ha), producing a thickness gradient of organic residuals from ~70 cm along the eastern edge to < 10 cm along the western edge. After spreading, the organic cover had a circumneutral pH (7.4 ± 0.2), high organic matter content in the < 2 mm fraction (26.3 ± 2.6% dry content), and high CEC (27.1 ± 1.7 cmol (+) 100 g^{-1}; mean ± SD; $n = 10$; K. Nicholls, unpublished data). The composts had low total content of the elements of concern, except for total Mo which just surpassed the agricultural guideline and total Se which was much higher than the industrial guideline (Table 1).

A farmer prepared, seeded and fertilized the organic covers in 2012 and 2013. He prepared the substrate using a tiller-mulcher, followed by an S-tine cultivator with double rolling basket harrows to remove weeds and break up clods. In early July in both years, the farmer seeded canola (DEKALB® 73-75 RR; 0.1 M seeds ha^{-1}) or sunflower (Dupont Pioneer® 63A21; 1.6 M seeds ha^{-1}) onto the freshly cultivated organic residuals using a broadcaster in alternating 3 m wide strips, parallel to the thickness gradient of organic residuals, in an east-west direction. Each year, he applied fertilizer at seeding using a broadcaster, first with 10-20-20 NPK at a rate of 247 kg ha^{-1} and second with 34-0-0 NPK as ammonium nitrate, again at a rate of 247 kg ha^{-1}. He used a harrow and chains to lightly cover the seed and fertilizer. In mid-July 2013, he again applied ammonium nitrate (34-0-0 NPK) at a rate of 247 kg ha^{-1}.

On September 19, 2013, we sampled plants and substrates at 16 locations for each crop species, with eight locations per crop on the thicker organic covers and eight per crop on thinner covers, in alternate crop strips. At each location, we randomly selected an individual plant, measured the exact thickness of the organic residual cover, and collected a bulk sample of the organic residuals within the rooting zone. We carefully excavated roots to determine the maximum rooting depth and rooting width and then collected the aboveground parts of each plant. We also sampled the top 10–15 cm of underlying tailings from locations below the thick and thin organic residuals ($n = 7$).

We air-dried the organic residual and tailing samples, passed them through a 4 mm sieve, and selected 50–100 g subsamples for chemical analysis. We broke up aboveground plant parts, air-dried and then oven-dried them at 70 °C for 48 h prior to determination of dry biomass. We then subsampled stems and seeds with hulls, and ground them for subsequent chemical analyses.

We conducted plant and soil chemistry analyses at the Elliot Lake Research Field Station (ELRFS) laboratory in Sudbury, except for the C, N and S content in substrates, which were determined by Lucas Services in Thunder Bay using an Elementar Vario EL Cube® CNS analyzer. The ELRFS lab measured pH on 10 mg of dry substrate with a 1:1 ratio of deionized water for tailings and a 1:2 ratio for organic residuals (Carter, 1993). They determined plant-available elements using a $LiNO_3$ extraction (Abedin et al., 2012). Briefly, they mixed ~3 g tailings or organic residuals with 0.01 M $LiNO_3$ at a ratio of 1:10 of substrate to solution, shook them overnight in a shaker, centrifuged and filtered them with Whatman 44 paper, then quantified their elemental concentrations using a Varian Liberty II ICP-OES (Spiers et al., 1983). The ELRFS lab also determined total element content in the samples of stems and seeds/hulls by digesting 0.5 g (± 0.02 g) of dried material in 50 mL flat-bottomed centrifuged tubes with a mixture of trace metal grade hydrochloric acid (7.5 mL) and trace metal grade nitric acid (7.5 mL) to make a 50:50 aqua regia acid. Following overnight predigestion, the samples were heated in a digestion block for a total of 4 h at 112 °C. Once the samples cooled to room temperature, the lab added ultrapure water to dilute the samples to 50 mL and determined total element content using a Varian 810 ICP-MS.

We calculated bioconcentration factors (BCF) using the ratio of the total element content in a plant to the bioavailable concentration in the organic covers below the same plant. We conducted separate regression analyses of pH, CNS and bioavailable elements in the organic covers as a function of the thickness of the covers. We then conducted separate general linear model analyses of biomass, maximum rooting depth, rooting width and total elements in plant stems and seeds/hulls as a function of thickness of organic covers, crop and their interaction. We nested plant parts (stems and seeds/hulls) within the crop variable. We examined residuals of the statistical models for homogeneity of variance and normality and log-transformed the data where necessary. We performed these analyses with Statistica® version 10, using a type I error rate of 5%. We also explored for discontinuities in the shape of the regressions to identify breakpoints using segmented regression with the software SegReg (www.waterlog.info). Segmented regression models were only chosen if they were superior to the linear regression models, as determined from their type I error rate.

3. Results

3.1. Substrate content

The tailings had a median of pH 7.0, but the samples ranged from as low as pH 5.0 to pH 7.7 (Online Appendix A). The organic covers were also circumneutral, but the pH increased linearly with increasing cover thickness, from pH 7.0 in thin covers to pH 7.5 in thick covers ($P = 0.0008$; $r^2 = 0.35$). Carbon content of the tailings was less than 0.5%, but increased in the thin organic covers until a breakpoint at 17.4 cm cover thickness, beyond which carbon content remained constant at ~22% ($P = 0.0002$; Fig. 1), an observation suggesting that the tailings mixed with the thin organic covers. The total N and bioavailable P concentration in the substrates followed the carbon trend, with negligible content in the tailings and low content in the thinnest covers, but increasing until breakpoints at 18.1 cm for N and 15.2 cm for P ($P = 0.0067$ and $P < 0.0001$, respectively), then remaining constant in the thicker covers at 1.7% total N and 570 $\mu g\ g^{-1}$ bioavailable P (Fig. 1). The carbon to nitrogen ratio of the organic residuals remained at approximately 13:1 across the cover thickness gradient. Concentrations of bioavailable K were similar in both thin organic covers and tailings, but increased over an order of magnitude with increasing thickness of organic covers ($P < 0.0001$; Fig. 1). The median total S concentration in the tailings was 0.34% and slightly lower in the organic covers at 0.23%, but did not vary with cover thickness ($P = 0.33$; not illustrated). Bioavailable Ca was higher in the thin organic residuals than in the tailings, but declined gradually with increasing cover thickness ($P < 0.0001$; Online Appendix A), while bioavailable Mg concentrations were slightly higher in the thin organic covers than in the tailings, increasing exponentially to a breakpoint at 16.6 cover thickness, then gradually declining in thicker organic residuals ($P < 0.001$; Online Appendix A).

In contrast to the other nutrients, the concentration of bioavailable Fe was high in the tailings and in the thin organic covers and declined an order of magnitude as the thickness of organic covers increased to a breakpoint at 15.2 cm, beyond which it was constant ($P < 0.0001$; Fig. 1). Bioavailable Ni and Cu shared similar patterns to Fe (Fig. 1), with highest concentrations in tailings and thin organic covers, declining by an order of magnitude with increasing cover thickness up to common breakpoints at 15.2 cm, beyond which the bioavailable concentrations were constant for Ni and increased slightly for Cu (each $P \leq 0.0001$). Bioavailable Ni concentrations were often below the detection limit in the thicker organic covers. The bioavailable Ni and Cu concentrations in the organic residuals reached maxima in the 5 cm thick covers of 90 $\mu g\ g^{-1}$ and 36 $\mu g\ g^{-1}$, respectively. Cr acted similarly to Ni, with higher bioavailable concentrations in the tailings and thinner covers of organic residuals and reaching a maximum in the 5 cm thick covers at 3.1 $\mu g\ g^{-1}$, but was below the detection limit in organic residual covers greater than 15 cm thick ($P = 0.001$; Online Appendix A).

In contrast, bioavailable Mo was below the detection limit in the tailings and thin organic covers, but increased gradually with organic cover thickness ($P = 0.004$; Online Appendix A), especially in covers more than 50 cm thick. Bioavailable Se concentrations were similar in tailings and in thin organic covers and did not vary with cover thickness ($P = 0.48$; Online Appendix A), although they exceeded the Canadian industrial guideline for soils of 2.9 $\mu g\ g^{-1}$ in a third of the samples of tailings and organic residuals. The level of bioavailable Na in the thin organic covers was similar to that in the tailings at near 250 $\mu g\ g^{-1}$, but increased 20-fold with increasing thickness of organic covers to greater than 5000 $\mu g\ g^{-1}$ ($P < 0.0001$; Fig. 1).

3.2. Plant content

The total concentration of P in the plants was an order of magnitude higher than what was bioavailable in the organic covers (mean BCF 11), but plant-P did not increase with increasing cover thickness ($P = 0.90$; Fig. 1), nor did it depend on crop species ($P = 0.93$), although plant parts differed ($P < 0.001$), with more P in the seeds. K was also much higher in plants than was available in the thinner organic covers (mean BCF 4), but plant-K only gradually increased in thicker covers ($P = 0.0003$; Fig. 1); K did not differ between crop species ($P = 0.93$), although plant parts again differed ($P < 0.0001$), but with more in the stems. The total plant concentrations of Ca and Mg had similar concentrations as available in the organic covers, but did not change with thicker organic covers ($P > 0.36$; Online Appendix A), although both Ca and Mg content depended on crop species and plant parts ($P < 0.002$).

Total Fe concentration in both crops was lower than the bioavailable Fe concentrations within the organic covers and increased with organic cover thickness ($P < 0.0001$; Fig. 1). There was, however, a significant difference in Fe content between plant parts of both crop species. Fe content of seeds did not change, but Fe in stems of both crops was below detectable limits of 1 $\mu g\ g^{-1}$ in covers less than ~30 cm thick, at least two to three orders of magnitude below what was bioavailable in the organic covers.

The total concentrations of Ni and Cu in the plants followed similar concentrations as were bioavailable in the organic covers (Fig. 1); Ni declined almost an order of magnitude and Cu declined slightly, but with no breakpoints (both $P < 0.0001$). Ni content did not depend on

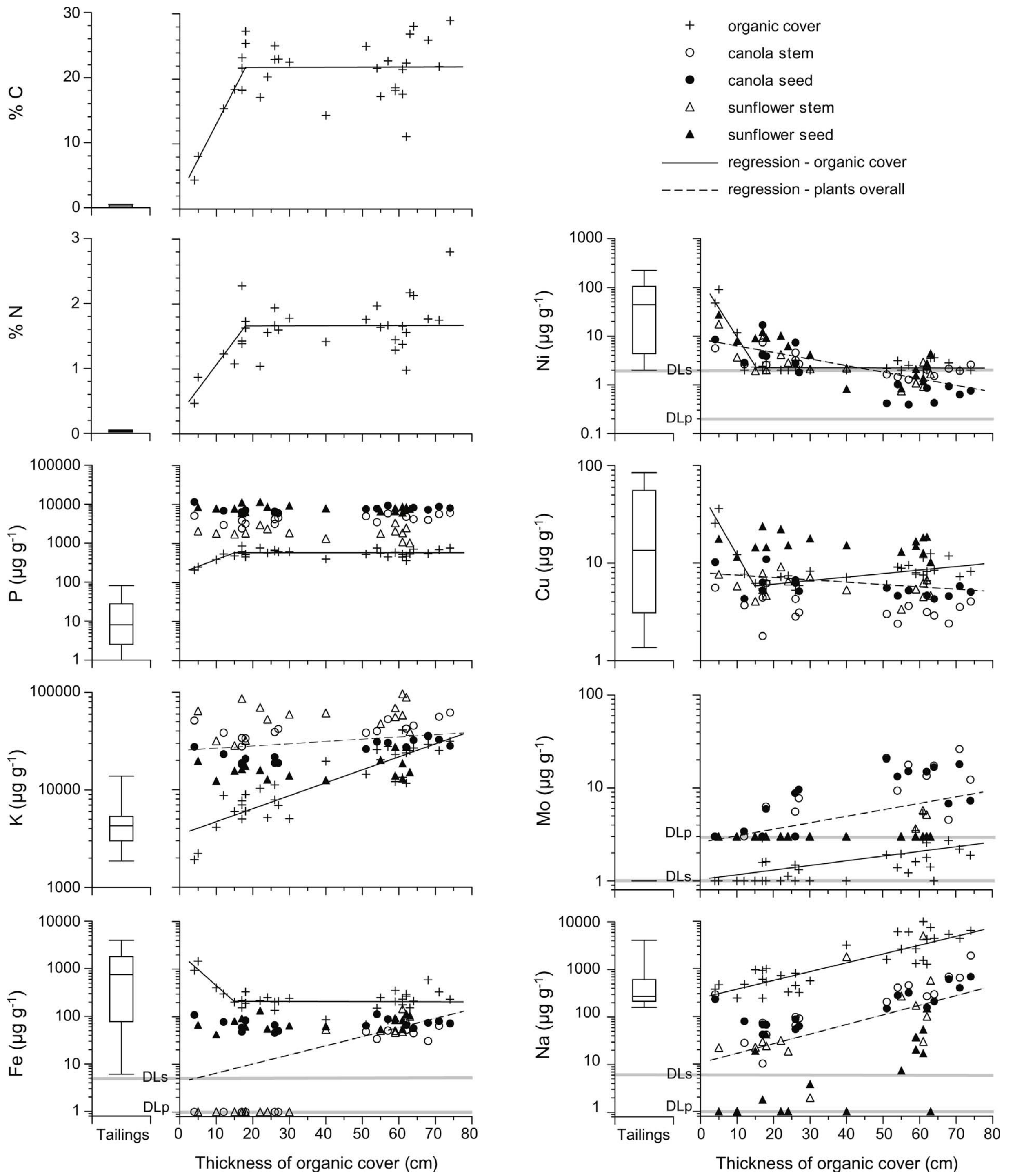

Fig. 1. Boxplots of total N and bioavailable P, K, Fe, Ni, Cu and Na in the mine tailings and along the thickness gradient of organic-rich covers, overlain with their total concentrations in stems and seeds of canola and sunflower along the cover thickness gradient. Solid regression lines show the significant trends of bioavailable elements as a function of organic-rich cover thickness, while dashed regressions lines show the significant trends for total elements across both crop species and plant parts as a function of cover thickness. Non-significant regressions lines are not shown. Horizontal gray lines show detection limits for the analyses of substrates (DLs) and plants (DLp).

crop species ($P = 0.17$), but Cu content in sunflower was over double that in canola ($P < 0.0001$). In both crops, seeds had only slightly more Ni content than stems ($P = 0.02$), but twice as much Cu ($P < 0.0001$). Mean BCFs for Ni were 1.2 and 0.6 for sunflowers and canola, respectively, across plant parts, while for Cu they were 1.4 and 0.6 for sunflowers and canola, respectively. The contents of Cr and Se in the plants were mostly below detection limits and did not show any pattern with the thickness of organic covers, crop species or plant parts (Online Appendix A). Mo was usually over an order of magnitude higher in canola plants than in the organic residuals (mean BCF: 7.3), but not in sunflowers (mean BCF 1.1). Mo increased in canola by at least an order of magnitude with increasing organic cover thickness ($P < 0.0001$; Fig. 1), with no difference between plant parts, but Mo remained below detection limits in sunflower. Finally, total plant content of Na also increased with cover thickness by over an order of magnitude ($P < 0.0001$; Fig. 1), but both species excluded Na, with mean BCFs of 0.06 and 0.16 for sunflower and canola, respectively, across plant parts.

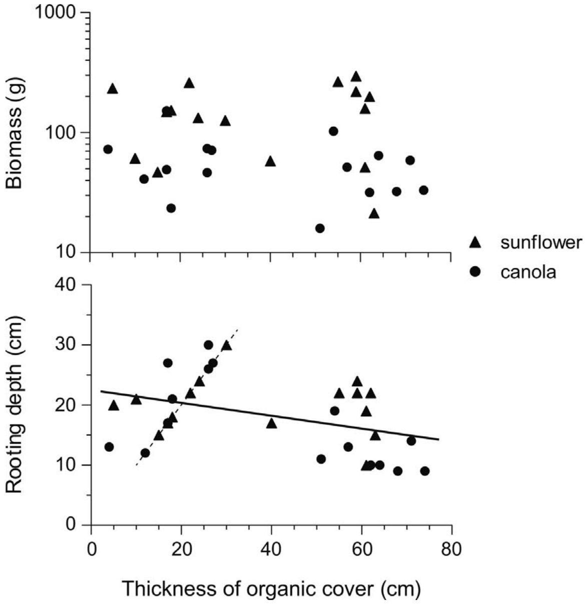

Fig. 2. Scatterplots of aboveground biomass production per plant and maximum rooting depth as a function of the thickness of organic-rich covers over Ni-Cu mine tailings. On the lower panel, roots of plants to the left of the dashed line penetrated the tailings.

3.3. Plant growth

Despite the changes in nutrient and contaminant availability in the thin organic covers, the aboveground biomass did not vary with cover thickness ($P = 0.54$; Fig. 2), with no difference between crop species ($P = 0.18$) and no interaction ($P = 0.66$). Biomass of both species was quite variable with compost thickness ($r^2 = 0.002$), and was spread across an order of magnitude. We did not notice any evident chlorosis in plants growing on thinner organic covers. In contrast, the few plants that germinated and survived on the fertilized tailings with no organic cover were extremely stunted and chlorotic. In the first growing season, the aboveground biomass for these crops was actually higher on the thinner organic residuals, although we measured aboveground biomass per unit area instead of per plant as we report here.

Both crop species rooted more deeply in the thin organic covers ($P = 0.039$; Fig. 2), again with no difference between the species ($P = 0.46$), but the relationship was quite variable ($r^2 = 0.15$). Several individuals of both species rooted 5–15 cm into the tailings when they were grown on thin organic covers, and roots of both species reached the cover-tailings interface even when grown in 30 cm thick organic covers. In covers 40 cm or more thick, roots did not reach the cover-tailings interface. Rooting width had a borderline relationship with the thickness of organic covers, with both species having wider roots in thicker covers ($P = 0.069$; figure not shown), and was also quite variable ($r^2 = 0.12$).

4. Discussion

The tailings had low total macronutrient concentrations (N, P, K, S) and high total concentrations of contaminants (Ni, Cu, Cr, Mo, Se), which far exceeded Canadian guidelines for industrial soils (CCME, 2016). Even the bioavailable concentrations of Ni, Cu and Se in tailings often exceeded these total guidelines. With the expected influence of the tailings, we had predicted that the thinner covers of organic residuals would have lower concentrations of nutrients and higher contaminants after the second growing season. Indeed, the concentrations of macronutrients were lowest in organic covers less than ~15 cm, despite our fertilization, and bioavailable Ni, Cu and Cr were also highest in thin covers, with even bioavailable Ni exceeding Canadian soil guidelines. However, not all contaminants increased in thin covers. Bioavailable Se showed no trend with cover thickness, although it exceeded soil guidelines about a third of the time. The low levels of bioavailable Mo actually increased with increasing cover thickness.

The decrease in macronutrients and the increase in bioavailable Fe, Ni, Cu and Cr in the thin organic covers were concomitant with a decrease in carbon content, strongly suggesting a physical mixing of the thin organic covers with the tailings during tillage. There was little evidence that Ni or Cu diffused from the tailings to the surface of organic covers. Ni content of plants remained elevated when growing in the 30 cm thick organic residuals, but the plant roots reached the cover-tailings interface, so this likely reflects root uptake from the tailings. The circumneutral to slightly alkaline conditions in the tailings and organic covers must limit the solubility and movement of Ni, Cu and Cr (Adriano, 2001; Bradl, 2004; Kabata-Pendias and Mukherjee, 2007). Organic matter also has a strong affinity to sorb Ni, Cu and Cr, especially under circumneutral to alkaline conditions (Adriano, 2001; Siebielec and Chaney, 2006), which must further limit availability and movement into the organic covers. Hargreaves et al. (2012) studied the use of thick covers of organic-rich pulp and paper sludge (pH 6.6) over oxidized Ni-Cu tailings (pH 2.2), and also reported only very minor increases in bioavailable trace metals within the sludge (Cu, Ni, Pb and Zn) near the sludge-tailings interface.

The increases of bioavailable K, Na and Mo in thicker organic covers are less clearly explained. Plant uptake may be partially responsible for the declines in bioavailable K in the thin organic residuals. Cation exchange dynamics within the organic residuals may also be involved, since the monovalent cations of K and Na are more readily displaced through cation exchange than divalent cations of Ca, Mg and many trace metals (Bradl, 2004). Once in solution, K^+ and Na^+ may have migrated toward the surface of the organic cover by capillary movement and concentrated there. Mo is quite mobile under circumneutral to alkaline conditions, and readily co-precipitates with organic matter, $CaCO_3$ and Fe (Kabata-Pendias and Mukherjee, 2007), so the pH of the tailings and covers would have favoured Mo dissolution in the tailings and migration to the surface. The thicker organic residuals should also have produced more dissolved organic matter (DOM; Schwab et al., 2007), which may have complexed the Mo anion and potentially facilitated migration to the surface of the organic covers. Se also is mobile at circumneutral to alkaline pH in presence of high levels of organic matter, but can also volatilize to the atmosphere (Kabata-Pendias and Mukherjee, 2007), which may explain the uneven distribution of Se along our thickness gradient of organic covers.

Fewer trends were found in the plants in terms of nutrient or contaminant content along the organic cover thickness gradient. The plants concentrated P and K in their tissues, as expected, but there were no changes along the organic cover thickness gradient. The plants also had similar contents of Ca and Mg to those bioavailable in the substrates, but with no trend reflecting organic cover thickness. The plants appear to be successful in obtaining sufficient nutrients for growth, even over thin organic covers.

Plant Fe was below detectable limits (1 $\mu g\ g^{-1}$) in the stems of both plants growing on organic covers less than 30 cm thick, despite having bioavailable Fe concentrations two to three orders of magnitude higher in the organic residuals. Fe is a key micronutrient for plants, but trace metals are known to interfere with Fe root uptake, transport and utilization in the leaves (Fodor, 2006). The concurrent elevated Ni concentrations in plants grown on the organic residual covers less than 30 cm thick suggests that Ni is interacting with plant Fe nutrition. Similar negative relationships between Fe and Ni have been shown for canola and sunflowers when grown on Ni-contaminated substrates (Mohammadzadeh et al., 2014; Tsadilas and Shaheen, 2013). Although we did not see any evident chlorosis in plants, special attention to Fe nutrition when growing agricultural crops on thin organic covers over metal mine tailings may be necessary.

Many of the phytotoxic trace elements in the mine tailings (Ni, Cu, Cr, Mo and Se) are also micronutrients required by plants (Kabata-

Pendias and Mukherjee, 2007). In dose-response studies, the effective soil concentration for 10% growth reduction of barley roots in circumneutral to alkaline pH soils ranged between 26 and 120 μg g^{-1} of added Cu (Rooney et al., 2006), and above 100 of added Ni (Li et al., 2011; Rooney et al., 2007). However, we only observed maxima of 36 μg g^{-1} bioavailable Cu and 90 μg g^{-1} bioavailable Ni in our thinnest organic covers, so perhaps the thin covers contained insufficient bioavailable Ni and Cu to be phytotoxic. Sunflowers and canola are also reported to be tolerant to elevated trace metals. Rivelli et al. (2012) found that plant Cu concentrations in sunflower stems only reached ~7 μg g^{-1}, similar to our study, when 400 μg g^{-1} of Cu was added to soils, with their study only documenting ~20% reduction in aboveground biomass when multiple trace metals were added. For canola, Mohammadzadeh et al. (2014) only found impacts on shoot growth above 300 μg g^{-1} of added Ni, again far above our bioavailable Ni levels in the thin organic covers, although they did find effects on photosynthetic pigments at lower Ni levels. Our mean BCFs for Ni and Cu were 1.2-1.4 for sunflower and 0.6 for canola, slightly lower than in other studies (Marchiol et al., 2004; Shaheen and Rinklebe, 2015; Tsadilas and Shaheen, 2013), which indicates that sunflower and, to a lesser extent, canola tolerated slightly elevated Ni and Cu in their tissues, but neither species hyper-accumulated them. Mo does not reach phytotoxic levels below 100 μg g^{-1} in plants (Adriano, 2001), so the maximum levels of 26 μg g^{-1} found in canola stems grown on thick organic covers should not affect plant growth. Similarly, although plant Na increased in thicker covers of organic residuals, both canola and sunflowers are moderately salt-tolerant (Ashraf and McNeilly, 2004; Francois, 1996), so the elevated Na at the surface of the thick covers of organic residuals should not impact these species.

Despite having lower substrate nutrients, slightly elevated plant Ni and Cu and low stem Fe in thinner covers of organic residuals, the aboveground biomass production was not affected even on thin covers of organic residuals. Only a cover of organic residuals ~5 cm thick was needed to maintain biomass production at similar levels as on thicker covers. A comparison with our anecdotal observation of the few stunted and chlorotic plants growing on the bare fertilized tailings without organic covers demonstrate the importance of having even thin organic covers over the tailings to support crop growth. Thick organic covers, as used by Hargreaves et al. (2012) and Lock et al. (2010) to a provide hydraulic barrier with the underlying tailings, do not appear to be needed to grow these biofuel crops.

Paradoxically, both crops rooted deeper over the thin organic covers and even extended roots up to 15 cm into pure tailings, which suggests that some nutritional resources or water within these circumneutral tailings may be beneficial for plant growth. Given that the thin organic covers actually mixed with the tailings, but did not have reduced production and limited contaminant uptake, further research should go into testing whether mixes of circumneutral tailings with organic residual produce comparable crop biomass, without increased environmental risk. Other studies have evaluated mixes of tailings and organic amendments (Alvarenga et al., 2009; Forsberg et al., 2008; Gardner et al., 2010; Madejon et al., 2010; Verdugo et al., 2011), but they have not aimed for high biomass agricultural production with fertilization, as we have here.

5. Conclusion

Hargreaves et al. (2012) and Lock et al. (2010) previously demonstrated that biofuel crops, including oilseeds, could be grown on thick organic-rich covers over metal mine tailings > 40 cm thick. Our results demonstrate that fertilized organic covers less than 15 cm over circumneutral Ni-Cu tailings do not diminish oilseed crop production. Given the high concentration of Ni and Cu in the tailings but their low bioavailability in the organic covers and the low uptake of metals by sunflower and canola, organic covers as thin as 15 cm over Ni-Cu tailings also do not seem to pose significant environmental risks, at least over the short term. Managers should continue to monitor for longer-term crop yields and risks and should pay close attention to surface pH to limit the bioavailability of trace metals, but these results are encouraging. Spreading thin covers of organic residual waste covers over metal mine tailings will allow for more economical conversion of circumneutral Ni-Cu tailing facilities to oilseed cropland for biofuel production. Close environmental monitoring of drainage chemistry will be required, but this monitoring would be required in any event for these tailings facilities as part of the mine's long-term environmental compliance.

Metal mine deposits have variable mineralogical composition, even within sulfidic deposits (Kwong, 1993), and the composition of their tailings varies. As such, we acknowledge that the results in this case study may not be universally applicable to other metal mine tailings. However, organic amendments in metal-contaminated soils reduce the bioavailability of many trace metals and metalloids, often through pH-dependent processes (Park et al., 2011). This suggests that the approach may be more broadly applicable, especially over circumneutral tailings. Despite this being a site-specific case study, we believe it has strong value. It further demonstrates to both mining companies and to governing environmental agencies that the conversion of metal mine tailings facilities to biofuel croplands is at least worth consideration in regions with climates suitable for biofuel farming. It also demonstrates that organic covers < 15 cm thick may only be required. Further research should assess how growing biofuel crops over thin organic covers affects contaminant availability, crop uptake and crop yields across a diversity of metal mine tailings sites. If accompanied by tight environmental controls, this approach would allow for the transformation of some metal mine tailings facilities, which are considered as wastelands with liabilities, into croplands with value.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecoleng.2017.08.019.

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