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An investigation into the mobility of heavy metals in soils amended with biosolids-derived biochar

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ABSTRACT. *A laboratory experiment that was conducted to gain an understanding of heavy metals dynamics in soils amended with biosolids (treated sewage sludge) and biochar produced from biosolids. The findings of this study, albeit limited in scope, go some way to inform the development of a scientific-based framework that supports practical and cost-effective management of biochar intended for land application. The risk of heavy metals (Zn, Cu, Cr) leaching in two soils of contrasting mineralogy and physico-chemical properties (Yellow Chromosol and Red Ferrosol) was quantified in a laboratory setup using leaching columns. Application of biosolids and biochar to soil increased pH of the leachate solution, and it increased with the rate of biosolids or biochar applied to soil. Differences in pH of leachate between biosolids and biochar-treated soil were not significant. Zinc (Zn) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol, but total Zn recovered after six leaching events was less than 20 mg* kg^{-1}*, and there was no clear effect of rate. There was a little more Zn recovered in leachate from biochar- compared with biosolids-treated soil. Copper (Cu) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol, but no Cu was recovered after the fourth leaching event, and in both soils Cu in leachate increased with the application rate. The amount of Cu recovered in leachate from biochar-treated soil was about one-third the amount recovered from biosolids-treated soil. Chromium (Cr) recovered in leachate was similar in both soils and recoveries were fairly consistent between-leaching events. In both soils, Cr recovered in leachate increased with the application rate. Total Cr recovered in leachate from biochar-treated soil was about eight times lower than from biosolids-treated soil. There is a need to extend the work reported here and to consider other soil types (e.g., Vertisols) that may respond differently from the physico-chemical and hydrological perspectives, and to capture the dynamics of other heavy metals as well as phosphorus, which were not part of this study. Based on the results of this work, there appears to be potential for future use of biochar in these two Queensland soils.*

Keywords. *Copper, Chromium, Land application of biosolids, Leaching, Potentially toxic elements, Sewage Sludge, Zinc.*

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Introduction

Biochar is a carbon-rich solid material produced by heating biomass in an oxygen-limited environment and can be applied to soil as a means to sequester carbon, improve soil condition and function (Joseph et al., 2010). The negative high surface charge density of biochar enables the retention of cationic nutrients via ion exchange, whereas the relatively extensive surface area, internal porosity, and polarizability facilitate anionic nutrient sorption via covalent bonds (Lu et al., 2020). The relatively high cation exchange capacity of some char materials, such as biosolids-derived biochar, have the ability to adsorb heavy metals and organic contaminants that may be present in the soil environment (Hill, 2005). There is limited information on the cycling and mobility through the soil of heavy metals present in biochar derived from sewage sludge. The risk of heavy metal contamination following application of waste to agricultural soils is a serious environmental concern (Jones and Johnston, 1989; Yeboah et al., 2017). Biochar derived from biosolids may carry an elevated level of heavy metals, and therefore, land application of such material may result in soil contamination and subsequent transfer of heavy metals to surface and underground waters through leaching and runoff (Clarke et al., 2016; Antille et al., 2017). There is also a risk of plant uptake in soil enriched with heavy metals, which may be then transferred to the food chain (Singh et al., 1984; Dudka and Miller, 1999). This risk can be higher in soils with acidic reaction (Kookana et al., 2011; Torri and Corrêa, 2012). The interaction between biochar, soil, microbes and plant roots are known to occur within a short period of time after application (Lehmann and Joseph, 2009) and are highly influenced by soil pH (Gorovtsov et al., 2020). Understanding the extent and implications of these interactions is necessary for effective assessment of risks associated with biochar use in agriculture and for improved use efficiency of such materials (Joseph et al., 2010; Agegnehu et al., 2015).

In Australia, commercially available biochar materials are marketed with limited or no analytical data disclosing their chemical composition (Singh et al., 2014). Such information is critical when these materials are used for land application together with the physico-chemical properties of the soil being treated with biochar; including, but not limited to: mineralogy, soil pH, and background level of heavy metals in soil (Verheijen et al., 2010; Oni et al., 2019).

Heavy metals

Heavy metals are a group of elements with specific gravities of higher than 5 g cm^{-3} (Ross, 1994). At high concentration, some heavy metals; namely: cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn), are regarded as toxic and environmentally damaging (Johnston, 2008; Johnston and Jones, 1995), but Cu, Ni and Zn (transition metals) are also essential for plant metabolism (Antille et al., 2013; Yue et al., 2017). The availability of heavy metals in soils amended with biochar derived from biosolids is affected by the type and composition of biosolids used in their production, the pyrolysis temperature and soil properties, particularly soil pH (Yang et al., 2018; Figueiredo et al., 2019). The process of pyrolysis increases the concentration of heavy metals in biochar relative to that of the raw material (Phoungthong et al., 2018), but also reduces their bioavailability (Paz-Ferreiro et al., 2018; Figueiredo et al., 2020).

The risk of heavy metal leaching in soil amended with biochar is also reduced during the pyrolysis for which biosolids-derived biochar may be regarded as safe (Mendez et al., 2012). Hence, proposals have been put forward to consider limit values in the Australian regulations based on leachability of heavy metals instead of their concentration in biochar (e.g., Roberts et al., 2017; Yang et al., 2018). Such proposals also imply soil type and soil pH are considered when determining the risk of leaching. For example, a study by Hossain et al. (2011) in Australia applied 10 Mg ha^{-1} of biosolids-derived biochar, but recovery of heavy metals in tomatoes did not exceed the maximum allowable concentrations stated in the Food Standards Australia and New Zealand (https://www.foodstandards.gov.au/Pages/default.aspx), despite the fact that heavy metal concentrations (as total elements) in soil exceeded current guidelines (Edgerton and Buss, 2019).

Objectives

The work reported in this paper was conducted to quantify the risk of heavy metals (Zn, Cu, Cr) leaching in soils amended with biosolids-derived biochar. The study was conducted under controlled laboratory conditions using two different soil types from Queensland (Australia), which are commonly used for arable cropping. This preliminary study aims to inform the development of a scientific-based framework that supports practical and cost-effective management of biochar intended for land application.

Materials and Methods

Soils

Two soils from southern Queensland (Australia) were used in this laboratory study, namely: Red Ferrosol (Oxisol in the NRCS-USDA Soil Taxonomy) from Toowoomba and Yellow Chromosol (Alfisol in the NRCS-USDA Soil Taxonomy) from Gatton, respectively. The selection of these soils was mainly based on their contrasting mineralogy, texture, pH and carbon contents (Table 1). Soil samples were collected from the 0-200 mm depth interval, air-dried at 40°C and sieved to pass 2-mm.

Table 1. Physicochemical characterization of the soils used in the leaching experiment. 'BDL': below detection limit.

Description	Red Ferrosol	Yellow Chromosol
GPS Location	27°36'32.27" S, 151°55'52.96" E	27°35'44.9" S, 152°18'20.1" E
pH (1:5 soil/water), %	6.0	5.5
EC (1:5 soil/water), dS/m	0.03	0.01
Total C, % (w/w)	3.51	1.69
Total N, % (w/w)	0.27	0.16
Clay (<0.002 mm), % (w/w)	57	14
Silt (0.002–0.02 mm), % (w/w)	11	11
Sand (0.02–2 mm), % (w/w)	32	75
Total Zn, mg/kg	89.80	42.70
Soluble Zn, mg/kg	0.19	0.23
Total Cu, mg/kg	46.20	8.50
Soluble Cu, mg/kg	BDL	BDL
Total Cr, mg/kg	331.0	13.5
Soluble Cr, mg/kg	0.12	0.01
Dominant clay mineral	Kaolinite	Kaolinite, Montmorillonite

Biosolids and biochar

Both biosolids and biochar produced from the same biosolids material (henceforth referred to as biochar) were sourced from Pyrocal Pty Ltd. (Toowoomba, Queensland, https://www.pyrocal.com.au/). The biochar was industrially produced in a commercial thermal gasification system. Both materials were air-dried at 40°C and sieved to pass 2-mm. The physico-chemical properties of biochar and biosolids are presented in Table 2.

Table 2. Physicochemical characterization of biosolids and biochar used in the leaching experiment.

Description	Biosolids	Biochar
pH (1:5 soil/water)	5.6	9.5
EC (1:5 soil/water), dS/m	5.38	0.51
Total C, % (w/w)	40.59	34.55
Total N, % (w/w)	7.07	4.65
Total P, % (w/w)	4.99	7.89
Soluble P, g/kg	7.13	0.13
Total Zn, mg/kg	957.0	1517.4
Soluble Zn, mg/kg	1.43	0.20
Total Cu, mg/kg	580.1	692.3
Soluble Cu, mg/kg	0.05	0.02
Total Cr, mg/kg	53.0	98.7
Soluble Cr, mg/kg	0.31	0.01

Analytical methods

Standard analytical methods were used for determination of pH and EC (1:5 soil/water ratio) (Rayment and Lyons, 2011), and particle size distribution (Gee and Bauder, 1986). Total carbon (C) and total nitrogen (N) were measured by ignition with a LECO Elemental Analyser (LECO Australia, https://leco.com.au/). The chemical composition of soil, biochar and biosolids, and heavy metal content were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (ELAN 6000, Perkin Elmer, Switzerland) after digestion in *Aqua regia* (HNO_3:HCl, 3:1 ratio) in a microwave oven (Multiwave, 3000 Anton Paar, USA). X-ray diffraction (XRD) was used for clay (<2 µm) fraction analysis; this fraction was separated from the bulk soil through sedimentation (Jackson, 2005). The XRD patterns for randomly oriented air-dried samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer. XRD data were collected and displayed using the CSIRO software XPLOT for Windows (Raven, 1990).

Soil columns and leaching experiment

Soils were mixed with biosolids (BS) and biochar (BCh) at three different rates, expressed as % (by weight) as follows: 2.5, 5 and 10 referred to here as BS2.5, BS5, BS10, BCh2.5, BCh5 and BCh10, respectively. A control (zero-amendment) for each soil type was also used. All treatments were replicated three times ($n = 3$). The transport of Zn, Cu and Cr through the soil was evaluated under saturated/near-saturated soil conditions using vertically oriented Plexiglas columns (87 mm inner diameter by 200 mm long). Soil in columns was maintained between saturation and 90% saturation (corresponding to suctions between 0 and -50 cm; Ngo-Cong et al., 2021) over the entire experiment; this minimized the risk of by-pass flow between the soil matrix and the inner wall of the PVC tube. The soil columns were allowed to drain freely during the leaching events and there was never water ponding on the soil surface. Over time, the soils in the columns consolidated due to the effect of gravity and successive leaching events. A total of six leaching events were conducted at days 1, 3, 7, 14, 30 and 60, respectively after the experiment was established. Soil in columns (500 g each) was carefully packed to achieve uniform density within the PVC tube and in triplicates; this process was repeated with both soil types and for all treatments, including controls (Figure 1). The bottom of the soil columns was fitted with a nylon mesh screen and filter paper, and another filter paper placed on the top of the soil to reduce surface disturbance while pouring the leaching solution to the soil. To achieve uniform packing, the air-dried soil sample was carefully placed into the columns using a spatula and then gently vibrated. The columns were first wetted-up with a 0.01M $CaCl_2$ solution from the base of the column to reach saturation by capillary rise, which was achieved after about 48 hours.

Leaching with $CaCl_2$ solution

The effect of biosolids and biochar on heavy metal leaching was assessed by monitoring $CaCl_2$-extractable metal concentrations released from soil (control without amendment), soil-biosolids and soil-biochar mixtures during the experiment. The 0.01 M $CaCl_2$ extraction provides information about the soil solution and exchangeable metal pools, and it can be regarded as an indicator of metal solubility, bioavailability and mobility in soils (Houba et al., 2000; Pueyo et al., 2004; Kalis et al., 2007). At days 1, 3, 7, 14, 30 and 60 from the start of the experiment, columns were leached with approximately 150 mL of 0.01M $CaCl_2$ solution. Leaching was performed by slowly pouring the solution into the columns above the soil covered with filter paper. Columns were covered with plastic cups to minimize evaporation during the leaching events, and they were allowed drain into plastic containers at the bottom of stands. The receiving containers had a cap with a small hole drilled through it that allowed the drain tube to be inserted into the container to minimize evaporative losses. The amount of leachate collected at each leaching event was determined volumetrically. Leachate samples were filtered and analyzed for pH and EC, Zn, Cu and Cr concentration as indicated earlier.

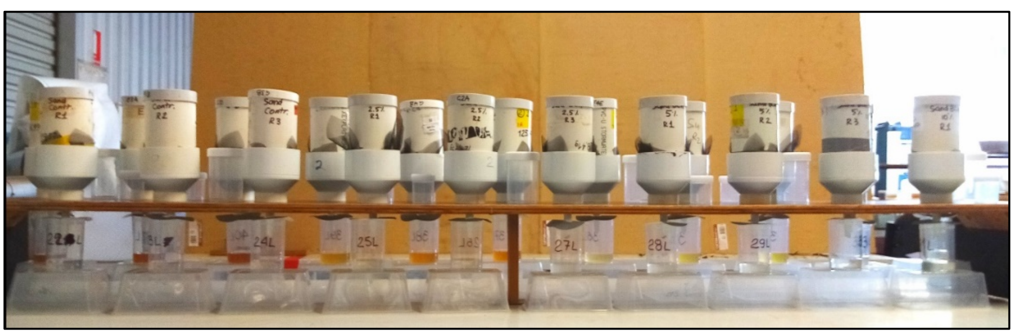

Figure 1. Overview of the leaching experiment conducted under controlled laboratory conditions.

Statistical analyses

The statistical package GenStat Release® 19th Edition (VSN International Ltd., 2020) was used to analyze heavy metal concentration and leachate pH data and involved repeated measurement of ANOVA. The least significant differences (LSD) were used to compare means with a probability level of 5%. Statistical analyses were graphically assessed by means of residual plots and normalization of data was not required.

Results and Discussion

pH of leachate

The addition of soil amendments tended to increase the pH in the leachate recovered; the maximum pH in leachate samples was recorded after the last leaching event (Table 3). The increase in leachate pH in the Yellow Chromosol was more significant than the Red Ferrosol, which was attributed to lower soil buffering capacity.

Table 3. Changes in pH of leachate observed during the experiment. Biochar (BCh) and biosolids (BS) applied to soil columns at rates of 2.5%, 5%, and 10% (w/w). Values shown are means (n =3) for each leaching event, P<0.001, LSD: 0.054 (Soil type), P<0.001, LSD: 0.077 (Control *vs*. Treatment), P>0.987, LSD: 0.082 (Amendment type), P<0.001, LSD: 0.087 (Amendment rate), P<0.001, LSD: 0.055 (Leaching events). LSD values were estimated using a 5% probability level.

Soil type	Red Ferrosol						Yellow Chromosol					
Treatment, leaching event	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**	**5**	**6**
Control	6.0	6.1	6.4	6.3	6.3	6.5	6.5	6.4	6.4	6.6	6.4	7.1
BCh2.5	6.1	6.4	6.6	6.7	6.9	7.2	6.6	6.7	6.9	7.2	7.2	7.8
BCh5	6.2	6.5	6.7	6.8	6.8	6.9	6.9	7.1	7.3	7.4	7.5	8.0
BCh10	6.7	6.9	7.3	7.4	7.5	7.8	7.3	7.6	7.9	8.0	8.1	8.2
BS2.5	6.2	6.7	7.2	7.2	7.5	7.4	6.1	6.9	7.5	7.6	7.7	7.6
BS5	5.9	6.7	7.3	7.3	7.8	7.7	6.0	6.8	7.4	7.6	7.5	7.8
BS10	5.8	6.8	7.2	7.4	7.7	7.7	5.7	6.6	7.4	7.6	7.9	8.3

Zinc

The concentrations of Zn recovered in leachate are shown in Figure 2. Overall, there were no differences in Zn concentration in leachate between control and treatments, which was observed in both soil types (P >0.05). There were significant differences between amendment types (P <0.01), but there was no amendment rate effect on Zn recovered in leachate (P >0.05). Total recovery of Zn across all leaching events was fairly low, ranging from 10.2 to 19.6 mg kg^{-1} in the Red Ferrosol and from 8.4 to 14.8 mg kg^{-1} in the Yellow Chromosol. These differences between soil types were significant (P <0.001). Differences between amendment types were mainly due to the effect of biochar applied to the Red Ferrosol, which yielded consistently higher recoveries than the same soil amended with biosolids. For the Yellow Chromosol, Zn recoveries in leachate were similar with both amendments. Approximately, 96% (biochar-treated soil) and 85% (biosolids-treated soil) of the Zn recovered in leachate were measured in the first four leaching events.

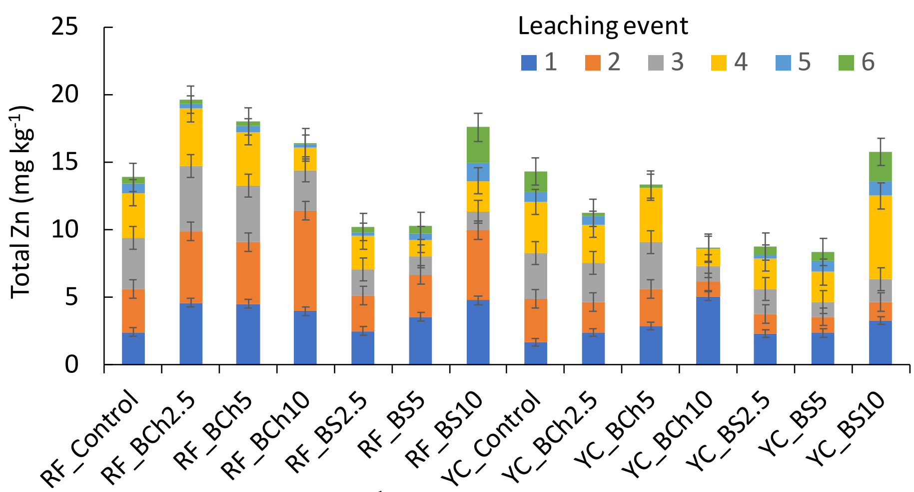

Figure 2. Zinc (Zn) recovered in leachate (as total Zn, mg kg^{-1}) over six leaching events. Note that after the fourth leaching event, the amount of Cu recovered in leachate was below detection limits. Notation: RF, Red Ferrosol; YC, Yellow Chromosol; BCh, Biochar; BS, Biosolids; the number that follows BCh and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, P<0.001, LSD: 0.317 (Soil type), P>0.05, LSD: 0.453 (Control *vs*. Treatment), P<0.011, LSD: 0.484 (Amendment type), P>0.05, LSD: 0.513 (Amendment rate), P<0.001, LSD: 0.388 (Leaching events). LSD values were estimated using a 5% probability level.

Copper

The concentrations of Cu recovered in leachate are shown in Figure 3. After six leaching events, the concentration of Cu in leachate increased in the following order: control soil < biochar amended soil < < biosolids amended soil. Overall, there were significant differences between control and treatments (P <0.001), amendment types and rates (P-values <0.001). Differences in Cu recovered between-leaching events were significant (P <0.001). Total recovery of Cu across all leaching events was also fairly low, ranging from 0.4 to 4.7 mg kg^{-1} in the Red Ferrosol and from 0.3 to 2.2 mg kg^{-1} in the Yellow Chromosol. Differences between soil types were significant (P = 0.004).

The amount of Cu recovered in leachate tended to increase between the first and the fourth leaching events, which was observed in both soils, and recoveries were proportional to the application rate. There was no Cu recovered in leaching events 5 and 6 (below detection limits). Overall, application of biochar reduced the amount of Cu recovered in leachate, particularly in the Red Ferrosol.

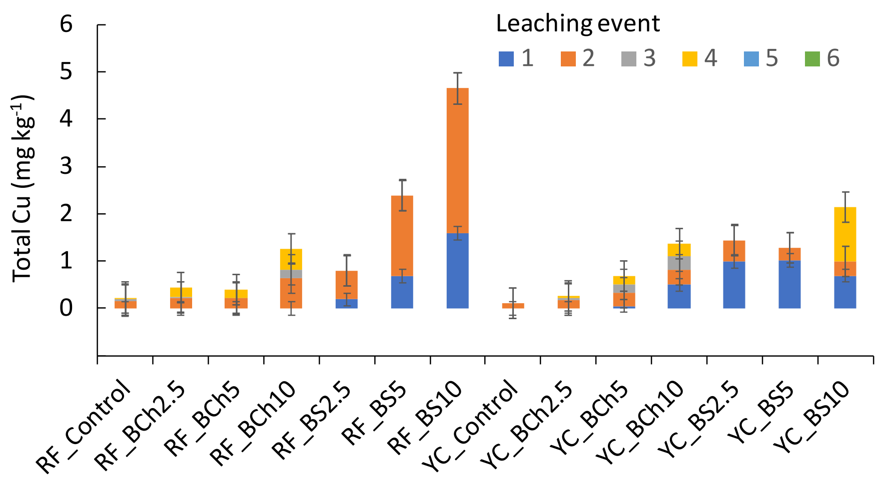

Figure 3. Copper (Cu) recovered in leachate (as total Cu, mg kg^{-1}). Note that after the fourth leaching event, the amount of Cu recovered in leachate was below detection limits. Notation: RF, Red Ferrosol; YC, Yellow Chromosol; BCh, Biochar; BS, Biosolids; the number that follows BCh and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, P=0.004, LSD: 0.044 (Soil type), P>0.001, LSD: 0.0636 (Control *vs*. Treatment), P<0.001, LSD: 0.068 (Amendment type), P>0.001, LSD: 0.072 (Amendment rate), P<0.001, LSD: 0.067 (Leaching events). LSD values were estimated using a 5% probability level.

Chromium

The concentrations of Cr recovered in leachate are shown in Figure 4. Overall, there were significant differences between control and treatments, amendment types and rates (P-values <0.001). Differences in Cr recovered between-leaching events were significant (P <0.001). Total recovery of Cr across all leaching events ranged from 0.3 to 3.0 mg kg^{-1} in the Red Ferrosol and from 0.5 to 3.4 mg kg^{-1} in the Yellow Chromosol, but differences between soil types were not significant (P>0.05). In biochar-treated soil, between 74% (Yellow Chromosol) and 91% (Red Ferrosol) of the Cr was recovered in the first four leaching events. In biosolids-treated soil, between 66% (Yellow Chromosol) and 82% (Red Ferrosol) of the Cr was recovered in the first four leaching events. As observed for Zn and Cu, Cr recoveries were proportional to the application rate.

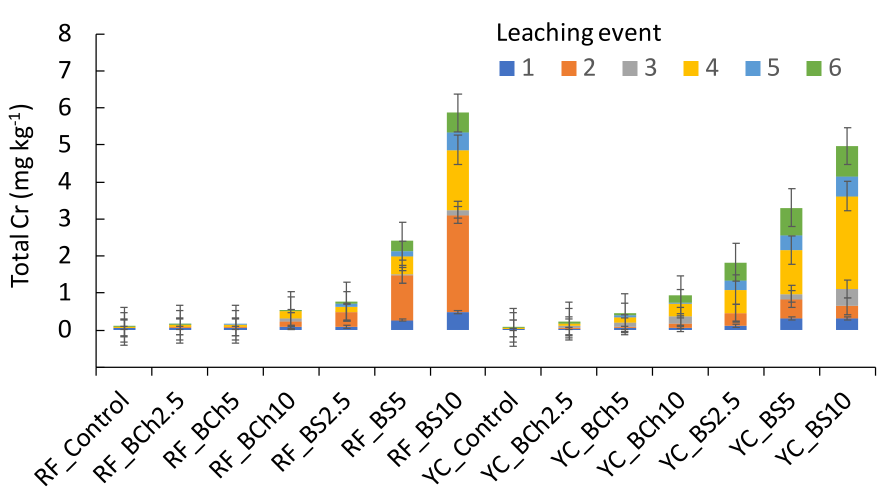

Figure 4. Chromium (Cr) recovered in leachate (as total Cr, mg kg^{-1}). Notation: RF, Red Ferrosol; YC, Yellow Chromosol; BCh, Biochar; BS, Biosolids; the number that follows BCh and BS denotes the application rate of the amendment expressed in % (by weight). Error bars on mean values (n = 3) denote the standard deviation, P>0.065, LSD: 0.045 (Soil type), P<0.001, LSD: 0.064 (Control *vs*. Treatment), P<0.001, LSD: 0.069 (Amendment type), P<0.001, LSD: 0.073 (Amendment rate), P<0.001, LSD: 0.066 (Leaching event). LSD values were estimated using a 5% probability level.

Summary

This paper presented preliminary results of a laboratory experiment that was conducted to gain an understanding of heavy metals dynamics in soils amended with biosolids (treated sewage sludge) and biochar produced from biosolids. The findings of this study, albeit limited in scope, will go some way to inform the development of a scientific-based framework that supports practical and cost-effective management of biochar intended for land application. The risk of heavy metals (Zn, Cu, Cr) leaching in soils of contrasting mineralogy and physico-chemical properties was quantified in a laboratory setup using leaching columns. The main results from this work are summarized here below:

- Application of biosolids and biochar to soil increased the pH of the leachate solution, and it increased with the rate of biosolids or biochar applied to soil. The pH of the leachate solution was consistently higher in the Yellow Chromosol compared with the Red Ferrosol (by about 0.5 pH units on average across treatments). Differences in pH of leachate between biosolids and biochar-treated soil were not significant.
- The amount of zinc (Zn) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol (by about 30%), but total Zn recovered after six leaching events was less than 20 mg kg^{-1}, and there was no clear effect of rate. Overall, there was a little more Zn recovered in leachate from biochar- compared with biosolids-treated soil.
- The amount of copper (Cu) recovered in leachate was higher in the Red Ferrosol than the Yellow Chromosol (by about 30%), but no Cu was recovered after the fourth leaching, and in both soils Cu in leachate increased with the application rate. On average, the amount of Cu recovered in leachate from biochar-treated soil was about one-third the amount of Cu recovered from biosolids-treated soil.
- The amount of chromium (Cr) recovered in leachate was similar in both soils and recoveries were fairly consistent between-leaching events. In both soils Cr recovered in leachate increased with the application rate. Overall, total Cr recovered in leachate from biochar-treated soil was about eight times lower than from biosolids-treated soil.

There is a need to expand the work reported here to other soil types used for cropping in Queensland (e.g., Vertisols), which will likely respond differently from the physico-chemical and hydrological perspectives, and to capture the dynamics of other heavy metals as well as phosphorus, which were not considered as part of this study. Based on the results of this work, there appears to be potential for future use of biochar in these two Queensland soils.

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