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Sorption of Pharmaceuticals, Heavy Metals, and Herbicides to Biochar in the Presence of Biosolids

Daniel A. Bair, Fungai N. D. Mukome, Inna E. Popova, Temitope A. Ogunyoku, Allie Jefferson, Daoyuan Wang, Sarah C. Hafner, Thomas M. Young, and Sanjai J. Parikh*

Abstract

Agricultural practices are increasingly incorporating recycled waste materials, such as biosolids, to provide plant nutrients and enhance soil functions. Although biosolids provide benefits to soil, municipal wastewater treatment plants receive pharmaceuticals and heavy metals that can accumulate in biosolids, and land application of biosolids can transfer these contaminants to the soil. Environmental exposure of these contaminants may adversely affect wildlife, disrupt microbial communities, detrimentally affect human health through long-term exposure, and cause the proliferation of antibiotic-resistant bacteria. This study considers the use of biochar co-amendments as sorbents for contaminants from biosolids. The sorption of pharmaceuticals (ciprofloxacin, triclocarban, triclosan), and heavy metals (Cu, Cd, Ni, Pb) to biochars and biochar–biosolids–soil mixtures was examined. Phenylurea herbicide (monuron, diuron, linuron) sorption was also studied to determine the potential effect of biochar on soil-applied herbicides. A softwood (SW) biochar (510°C) and a walnut shell (WN) biochar (900°C) were used as contrasting biochars to highlight potential differences in biochar reactivity. Kaolinite and activated carbon served as mineral and organic controls. Greater sorption for almost all contaminants was observed with WN biochar over SW biochar. The addition of biosolids decreased sorption of herbicides to SW biochar, whereas there was no observable change with WN biochar. The WN biochar showed potential for reducing agrochemical and contaminant transport but may inhibit the efficacy of soil-applied herbicides. This study provides support for minimizing contaminant mobility from biosolids using biochar as a co-amendment and highlights the importance of tailoring biochars for specific characteristics through feedstock selection and pyrolysis–gasification conditions.

Core Ideas

- Common contaminants in biosolids demonstrate high sorption to selected biochars.
- Biochar has potential to decrease the efficacy of applied systemic herbicides.
- Biochar co-amendments may decrease contaminant bioavailability and transport.
- Biochar co-amendments should be selected for specific physiochemical characteristics.

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*Corresponding author (sjparikh@ucdavis.edu).

Land application of biosolids (treated sewage sludge) in agriculture has increased steadily over the last few decades due to their value as a source of nutrients and ability to improve soil health. Although largely beneficial, biosolids can also contain a variety of potentially harmful metals and organic chemicals, some of which are currently regulated and others that are relatively new contaminants of concern. The US federal regulations (USEPA, 2016) for agricultural land application of biosolids provide ceiling concentrations for pollutants, including lead (Pb; 840 mg kg^{-1}), copper (Cu; 4300 mg kg^{-1}), nickel (Ni; 420 mg kg^{-1}), and cadmium (Cd; 85 mg kg^{-1}) (USEPA, 2016). In a survey of biosolids from wastewater treatment plants across the United States conducted by the USEPA in 2009, heavy metals including Pb, Cu, Ni, and Cd were detected in all biosolids sampled at maximum concentrations of 450, 2580, 526, and 11.8 mg kg^{-1}, respectively. Although only Ni exceeded USEPA limits, additional regulations regarding pollutant loading rates can limit the use of biosolids on agricultural lands (USEPA, 2016). Organic chemicals were also commonly detected, with the pharmaceuticals ciprofloxacin, triclocarban, and triclosan found in at least 94% of the wastewater treatment plants with maximum concentrations of 47.5, 441, and 133 mg kg^{-1}, respectively (USEPA, 2009). At present, no national regulations are in place for pharmaceuticals. Release of these contaminants from biosolids and subsequent environmental exposure could lead to the disruption of microbial communities, possible negative human health effects from long-term exposure, and in the case of antibiotics and antibacterial agents, the potential proliferation of antibiotic-resistant bacteria (Halling-Sørensen et al., 1998; Kümmerer, 2009).

One possible approach for reducing the concentrations of harmful chemicals released from biosolids is to use a co-amendment with a high sorption capacity, such as biochar. Biochar is derived from the pyrolysis or gasification of biomass and is a by-product in a variety of industries. Biochar is typically hydrophobic and has a negative surface charge, high charge density, and high aromaticity (Kookana, 2010; Yang and Sheng, 2003).

D.A. Bair, I.E. Popova, A. Jefferson, D. Wang, S.C. Hafner, and S.J. Parikh, Dep. of Land, Air, and Water Resources, Univ. of California, Davis, CA; F.N.D. Mukome, Div. of Natural and Applied Sciences, William Jessup Univ., Rocklin, CA; T.A. Ogunyoku and T.M. Young, Dep. of Civil and Environmental Engineering, Univ. of California, Davis, CA. Assigned to Associate Editor Paul Williams.

Abbreviations: m/z, mass-to-charge ratio; RCF, relative centrifugal force; SW, softwood biochar; WN, walnut shell biochar.

These properties make biochar a favorable sorbent for both heavy metals and organic contaminants. Biochar made from broiler litter has been shown to enhance the immobilization of heavy metals in water and soil (Uchimiya et al., 2010a, 2010b), and a pine sawdust biochar (550°C) has been shown to be an effective sorbent for Cu in contaminated water (Lou et al., 2016). In another study, pine needle biochar increased sorption of polycyclic aromatic hydrocarbons in soil (Chen and Yuan, 2011). High temperature (700°C) *Pinus radiata* wood biochar demonstrated greater sorption of terbuthylazine herbicide than biosolids in New Zealand forest soils (Wang et al., 2010). Several other studies have demonstrated the applicability of hardwood green waste and woodchip biochars for sorption of three commonly used pesticides (atrazine, simazine, acetochlor) with sorption coefficients as high as 1400 L kg^{-1} (Spokas et al., 2009; Zheng et al., 2010). More recently, endocrine-disrupting compounds (bisphenol A, atrazine, 17α-ethinylestradiol) and pharmaceutically active compounds (sulfamethoxazole, carbamazepine, diclofenac, ibuprofen) were shown to have greater sorption to biochar containing more diverse polar functional groups (Jung et al., 2013).

The primary objective of this research was to provide baseline data to evaluate the potential of biochar co-amendments to sequester common contaminants found in biosolids and agrochemicals in the soil. The sorption behavior of heavy metals (Cu, Cd, Ni, Pb), an antibiotic (ciprofloxacin), antibacterial agents (triclocarban, triclosan), and herbicides (monuron, diuron, linuron) in the presence of biosolids and biochar are reported. A soil co-amendment of biochar with biosolids could serve as a sink for contaminants from the biosolids, such as heavy metals and pharmaceuticals, although it might also reduce the efficacy of soil applied herbicides in agricultural soils.

Materials and Methods

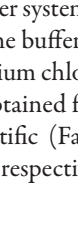
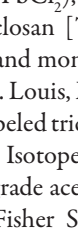
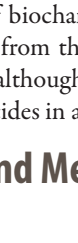
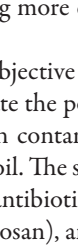
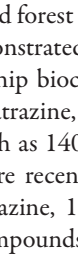
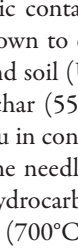
Chemicals

Heavy metals (cadmium, $CdCl_2$; copper, $CuCl_2$; nickel, $NiCl_2$; and lead, $PbCl_2$), pharmaceuticals (ciprofloxacin, triclocarban, and triclosan [Table 1]), and phenylurea herbicides (diuron, linuron, and monuron (Table 1]) were purchased from Sigma-Aldrich (St. Louis, MO). Deuterated triclocarban (TCC-d_7), and isotope labeled triclocarban (TCC-$^{13}C_6$) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Optima LC-MS grade acetone, methanol, and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA). Ultrapure water (18.2 MΩ cm, Barnstead Thermolyne NANOpure Diamond UV water system, Dubuque, IA), was used to make the buffer solution. The buffer solution also contained sodium azide (99% purity), calcium chloride dehydrate, and sodium bicarbonate, which were obtained from Acros Organics (N.V., Fair Lawn, NJ), Fisher Scientific (Fair Lawn, NJ), and EMD Chemicals (Gibbstown, NJ), respectively.

Sorbents

Biosolids were collected from a wastewater treatment plant that used anaerobic digestion. Biosolids were air-dried, homogenized with a mortar and pestle, and sieved to <2 mm. Yolo silt loam (fine-silty, mixed, superactive, nonacid, thermic Mollic Xerofluvents) soil was collected from the University of

Table 1. Chemical properties of herbicides and pharmaceuticals used in this study.† Phenylurea herbicides are nonionizable.

Compound	Herbicides			Pharmaceuticals		
	Monuron	Diuron	Linuron	Ciprofloxacin	Triclocarban	Triclosan
Chemical structure						
pK_a	–	–	–	6.18, 8.76	12.7	7.90
Log K_{OW}‡	1.80	2.85	3.00	0.28	4.90	4.76

† From Giudice and Young, 2011; Halling-Sørensen et al., 1998; Lozano et al., 2010; Uslu et al., 2008; and Yang et al., 2006.

‡ K_{ow}, octanol/water coefficient.

California, Davis, Campbell Tract field site (http://remote.ucdavis.edu/campbell_location.asp) from the top 20 cm of soil after removal of large debris. The soil was composed of 35% sand, 43% silt, and 22% clay (v/v), with a pH of 6.7 and an organic nitrogen and carbon content of 0.07 and 1.0%, respectively. Soil was air-dried and sieved to <2 mm. Two types of biochar from different feedstocks were used in the sorption experiments. A biochar made from a popular softwood (SW) feedstock at typical production temperature and a biochar produced as a by-product of bioenergy production utilizing walnut shells (WN) as a feedstock at a high temperature were selected to enable the comparison of biochars representing a large span of the biochar continuum. The SW biochar was made from pine wood residue (primarily *Pseudotsuga menziesii* with some *Abies concolor*) collected in Oregon, which was pyrolyzed at 510°C for 25 min with 50 psi of steam at the end of the process. The WN biochar (Dixon Ridge Farm, Winters, CA) was pyrolyzed at a temperature of 900°C. The biochars were sieved to <2 mm and analyzed for key physical and chemical characteristics (Table 2). A detailed discussion of the biochar characteristics can be found in Mukome et al. (2013a, 2013b). Activated carbon (highly sorbing organic reference material; 50–200 mesh, steam activated charcoal) was purchased from Fisher Scientific, and kaolinite (mineral reference material) was purchased from Fluka Analytical.

Batch Sorption Experimental Setup

Heavy metal, herbicide, and pharmaceutical batch sorption isotherms were prepared using optimal conditions for each class of contaminant to evaluate affinity for the various sorbents.

Heavy Metals

Batch isotherm experiments with a mixture of Cd, Cu, Pb, and Ni were conducted with each of the following sorbents: biosolids, WN biochar, SW biochar, activated carbon, kaolinite, and 1:1 mixtures of each sorbent with biosolids. Kaolinite served as a mineral reference material representing low sorptive capacity, and activated carbon served as an organic reference material with high sorptive capacity. Heavy metals solutions were prepared at various concentrations (0–200 mg L^{-1}) with 5 mmol L^{-1} NaCl and adjusted to pH 7 with 0.025 mol L^{-1} NaOH. Samples were prepared by adding 0.48 g kaolinite, activated carbon, WN biochar, or SW biochar into 15-mL plastic centrifuge tubes. A NaCl solution (5 mmol L^{-1} NaCl) was then added, and the pH was adjusted to 7 with 1 mol L^{-1} HCl for activated carbon and WN biochar, 0.01 mol L^{-1} HCl for SW biochar, and 0.025 mol L^{-1} for kaolinite for a final volume of 12 mL (1:25 solid/solution ratio). Samples were reacted for 24 h at room temperature on an end-over-end shaker at 8 rpm. The solution was then centrifuged for 8 min at 8000 relative centrifugal force (RCF) and the supernatant filtered through 0.8-μm polycarbonate track-etch syringe filter membranes. Heavy metal concentrations were quantified using atomic absorbance spectrometry.

Table 2. Select properties of the activated carbon and biochar sorbents used in this study.

	Activated carbon	Walnut shell biochar	Softwood biochar
Label	AC	WN	SW
pH	8.8	9.7	7.3
Ash content (%)	1.5	46.4	3
H/Cr ratio	0.08	0.22	0.3
O/C ratio	0.03	0.02	0.18
(O+N)/C ratio	0.05	0.46	0.13
P (%)	0.01	0.64	0.02
Surface area ($m^2\ g^{-1}$)	1064	227.1	165.8
Cation exchange capacity (cmol g^{-1})	28.2	33.4	12
Acidity	0.65	n.d.†	0.27
Basicity	0.66	11.71	0.93

† n.d. = not determined due to high basicity of sample

Herbicides

Batch isotherms for monuron, diuron, and linuron were measured for the same sorbents as the heavy metals in 8-mL glass vials equipped with polytetrafluoroethylene-lined screw caps. The initial aqueous phase concentrations of each herbicide were 0.5, 1, 5, 25, and 50 mg L^{-1}. A buffer solution containing 200 mg L^{-1} $CaCl_2$, 5 mg L^{-1} $NaHCO_3$, and 200 mg L^{-1} sodium azide was used to maintain constant ionic strength and inhibit biological activity. A 5.2-mL aliquot of buffer solution was added to 0.12 g of each sorbent. Samples were pH adjusted to 7.0 using 0.05 mol L^{-1} HCl. The vials were then placed onto an end-over-end shaker for 48 h in the dark at 22 ± 1°C. The supernatants were filtered (0.45 μm, Millipore Corporation, NH), and filtrates were analyzed by high-pressure liquid chromatography–ultraviolet detection as described below.

Pharmaceuticals

Adsorption isotherms for pharmaceuticals were constructed following the Organization for Economic Cooperation and Development Guideline 106 method (OECD, 2000). A constant mass of sorbent was added to each pre-weighed centrifuge tube, followed by addition of a buffer solution. The buffer solutions contained 200 mg L^{-1} sodium azide, 0.01 mol L^{-1} $CaCl_2$, and 5 mg L^{-1} $NaHCO_3$ to inhibit microbial activity, maintain ionic strength, and buffer the solution at pH 6. Buffer solutions were also fortified with various concentrations of each pharmaceutical, 0.005 to 0.030 mg L^{-1} for triclosan, 0.075 to 1.2 mg L^{-1} for triclocarban, and 0.1 to 5 mg L^{-1} (individual sorbents) and 5 to 100 mg L^{-1} (soil–biochar–biosolids) for ciprofloxacin. To minimize pharmaceutical losses by adsorption to the reaction vessel, glass centrifuge tubes (50 mL) with silver-lined Teflon caps were used for triclocarban and triclosan, and 40-mL Teflon tubes and caps were used for ciprofloxacin. All samples were run in triplicate with controls containing no sorbent to correct for system losses. Samples were rotated end-over-end (8 rpm) at 23°C ± 1.5 in the dark for 48 h. At the conclusion of the specified contact period, tubes were centrifuged at 1280 RCF for 15 min, and an aliquot of the aqueous phase was filtered with 0.22-μm polyvinyl difluoride syringe filters. Filtrates were analyzed by high-pressure liquid chromatography–tandem mass spectrometry as described below. Quality control is addressed in the Supplemental Material.

Chemical Analysis

Atomic Absorbance Spectrometry

Graphite furnace atomic absorbance spectrometry (PerkinElmer AAnalyst 800) was used to determine the supernatant concentrations of heavy metals. Lamp wavelengths used for

each metal were 228.8, 324.8, 232.0, and 217.0 nm for Cd, Cu, Ni, and Pb, respectively. Calibration curves for each metal were made by serial dilution of 1000 ppm atomic absorption reference standard solutions (Fischer Scientific) with the background solution used in experimental samples.

High-Pressure Liquid Chromatography–Tandem Mass Spectrometry

High-pressure liquid chromatography–tandem mass spectrometry was used for analysis of ciprofloxacin, triclosan, and triclocarban, using an Agilent Series 1200 HPLC with an Agilent 6320 ion trap mass spectrometer (Agilent Technologies, Palo Alto, CA). Chromatographic separation was performed on an Agilent Zorbax Eclipse Plus C18 column (2.1 mm by 100 mm, 3.5 μm), equipped with a guard column with the same stationary phase (4.6 by 12.5 mm, 5 μm; Agilent Technologies). The column temperature was 40°C, and the autosampler temperature was 4°C. The mobile phase consisted of 0.1% formic acid (v/v) (solvent A) and 0.1% formic acid (v/v) in methanol (solvent B). The compounds were separated at 0.5 mL min^{-1} using a gradient; solvent B was held at 20% for 2 min, increased to 95% by 5 min, and held until 7 min. The mass spectrometry data were collected in positive electrospray ionization–tandem mass spectrometry mode for ciprofloxacin, negative electrospray ionization–tandem mass spectrometry mode for triclocarban, and negative mass spectrometry mode for triclosan. The nebulizer temperature was 350°C, nebulizer pressure was 50 psi, and the drying gas flow rate was 10 L min^{-1}. Compounds were quantified using a mass-to-charge ratio (m/z) 289 for triclosan and the product ions of m/z 332→288 for ciprofloxacin and m/z 313→160 for triclocarban.

High-Pressure Liquid Chromatography–Ultraviolet Detection

Concentrations of monuron, diuron, and linuron were analyzed following prior methods (Wang et al., 2015) using an Agilent 1200 Series HPLC (Agilent Technologies) with a diode-array detector at 254 nm and an Agilent ZORBAX Eclipse Plus C18 column (4.6 mm by 250 mm, 5 μm) at a flow rate of 0.4 mL min^{-1} and an injection volume of 5 μL. Isocratic elution was used with 0.1% formic acid in water to 0.1% formic acid in methanol (40:60, v/v). Compounds were identified by comparing ultraviolet absorption spectra and retention times (2.2 min monuron, 3.7 min diuron, and 4.9 min linuron) with those of standards. Samples were quantified using an external calibration curve.

Data Analysis

Concentrations of contaminants sorbed by biochar, biosolids, or other sorbents were calculated as the difference between the initial and final corrected concentrations of the contaminant in the solutions and used to fit sorption isotherms. Single point distribution coefficients (K_d) were determined at initial contaminant concentrations of 100 mg kg^{-1} for metals and 25 mg kg^{-1} for herbicides (Table 3) using the equation

$$K_d = q_e / C_e$$

where q_e is the amount of adsorption and C_e is the aqueous concentration of the compounds at equilibrium.

Results and Discussion

Biochar

The high sorption capacities of biochar for a range of contaminants make it a promising co-amendment to attenuate undesirable compounds in biosolids; careful chemical and physical characterization of biochars is critical to guide selection of an appropriate material for this purpose. The WN biochar was produced at 900°C, a similar temperature to activated carbon but without activation, whereas the SW biochar was produced at 510°C. Due to these differences in production temperature, the WN biochar has low O/C and H/C ratios, similar to those for activated carbon, in comparison to SW biochar, suggesting greater aromaticity for WN biochar. This result is in agreement with published data demonstrating that biochar has both carbonized and noncarbonized regions (Chen et al., 2008; Verheihen et al., 2010), with higher pyrolysis temperature for a given feedstock typically resulting in a higher yield of carbonized biochar (Novak et al., 2009). Increased carbon content of biochars is typically associated with decreased H/C and O/C ratios (Krull et al., 2009; Spokas, 2010) and biochars that are more similar to activated carbon (Masiello, 2004). Surface area and ash content directly affect the sorption capacities and affinities and can also be significant factors when evaluating sorption. In the current study, the WN biochar has an almost fivefold smaller surface area and significantly higher ash content than activated carbon.

Table 3. Single point sorption coefficients (K_d) determined at initial contaminant concentrations of 100 mg kg^{-1} for metals and 25 mg kg^{-1} for herbicides.

Contaminant	K_d†							
	Without biosolids				Biosolids			
	SW	WN	KA	AC	SW	WN	KA	AC
	kg L^{-1}							
Cd	0	66	4	9	717	169	942	904
Cu	0	1991	19	12,138	117	598	182	2993
Ni	51	50	9	43	116	52	155	H
Pb	4	8748	H‡	H	719	723	1351	1350
Diuron	1374	H	H	H	39	H	24	H
Linuron	1947	H	H	H	40	4524	84	H
Monuron	1399	1340	11	H	2	H	7	H

† SW = softwood biochar; WN = walnut shell biochar; KA = kaolinite; AC = activated carbon.

‡ H indicates "high" sorption, as no analyte was detected in aqueous following sorption experiments.

Heavy Metals

The combined sorptive behavior of Pb, Cu, Ni, and Cd was investigated to determine competition for sorption sites where a mixture of multiple metals might be released from biosolids. Combining the metals allows for a more representative data set for describing such complex systems.

Based on K_d values for heavy metal sorption to sorbents without biosolids, activated carbon was overall the most effective sorbent of the metals (Table 3). Pb had the highest affinity for all sorbents studied except the SW biochar, which had greater sorption of Ni. Aside from the SW biochar, Ni and Cd consistently had lower K_d values than Pb and Cu, signifying lower binding affinity to the sorbents. The order of affinity of metals to kaolinite and activated carbon was similar (Pb > Cu > Ni > Cd), although the magnitude of K_d values was much higher for activated carbon, especially regarding Cu sorption. This order of affinity differed only slightly from the WN biochar (Pb >> Cu >> Cd > Ni) and SW biochar (Ni > Pb > Cu > Cd), although SW biochar had much lower affinity compared with the WN biochar for all metals except Ni, which had comparable affinity.

The presence of biosolids affected the total amount of metals sorbed, the sorption affinity of each metal, and the order of their relative sorption to each sorbent. The 1:1 sorbent/biosolids mixtures contained twice the total sorbent mass, and therefore increased sorption of metals from solution was expected. Since sorption (q_e) is calculated on a per mass basis (mg kg^{-1}), total metal sorption is discussed as mass (mg) of metal removed from solution. There is not a substantial difference in total sorption (mg sorbed) to kaolinite with the addition of biosolids, which suggests that biosolids are not significantly sorbing these metals (Fig. 1). Due to the relatively low cation exchange capacity of kaolinites, 2 to 15 cmol kg^{-1} (Sparks, 2003), sorption capacity for these contaminants is expected to be low. Softwood biochar, with a similar cation exchange capacity (12 cmol kg^{-1}) to kaolinite, generally has even lower sorption capacity with the exception of Ni. The SW biochar exhibits greater sorption for all metals when biosolids are added, except for Ni, which maintains a similar sorption affinity. Activated carbon and WN biochar sorption affinity for Cu and Pb did not change significantly with the addition of biosolids but increased for Cd. However, Ni sorption increased for activated carbon but did not change significantly for WN biochar. The increase in metal sorption to SW biochar resulted in both biochars having a similar magnitude of sorption for all heavy metals after addition of biosolids.

The overall order of sorption affinity based on K_d values changed with the addition of biosolids, resulting in notably decreased Pb sorption to WN biochar, kaolinite, and activated carbon: WN (Pb > Cu > Cd > Ni), SW (Ni > Pb > Cu > Cd), kaolinite (Pb > Cu > Ni > Cd), and activated carbon (Pb > Cu > Ni > Cd) (Table 3). The differences in sorption capacities between the biochars can be attributed to differences in the degree of aromaticity, as evidenced by differing H/C ratios and surface areas (Table 2; kaolinite surface area: 7.15 $m^2\ g^{-1}$).

The extent of heavy metal sorption to biochar has also been shown to be greatly affected by specific biochar characteristics, such as pH and phosphorus (P) content. Potential influence of pH on sorption is discussed in more detail in the Supplemental Material. The binding sequence could be attributed to sorption of divalent metal ions by phosphorus-containing functional groups of the biochar, as the sorption sequences of the metal ions on biochars is consistent with their affinity for orthophosphate ester ligands (Uchimiya et al., 2010a; Uchimiya et al., 2010b). Corroborating this, WN biochar, which has higher P content than SW biochar (0.64% vs. 0.02%, respectively) also exhibited higher sorption of all metals, particularly Pb. Furthermore, mineral impurities present in the ash and basic nitrogen groups of the biochars can serve as additional adsorption sites (Uchimiya et al., 2010b), both of which are much greater in the WN biochar than in the SW biochar (Table 2).

Herbicides

The order of sorption of diuron and linuron to the sorbents without biosolids was activated carbon ≈ WN ≈ kaolinite > SW, although K_d values for activated carbon, WN biochar, and kaolinite could not be calculated as the final aqueous concentrations were below detection limits (Fig. 2). The order of sorption for monuron differed in that activated carbon > SW ≈ WN > kaolinite. The WN biochar exhibited a high binding affinity for the phenylureas, comparable to activated carbon. Comparison of K_d values for the 25 mg kg^{-1} concentration demonstrated a similarly high sorption capacity for diuron and linuron to the four sorbents (Table 3). Kaolinite completely sorbed diuron and linuron but showed limited sorption (K_d = 11) with monuron. The sequence of herbicide sorption affinity (K_d) for SW was linuron > monuron ≈ diuron (Table 3). Sorption efficiency of WN biochar remained 100% for all initial concentrations (0.5–50 mg L^{-1}) of diuron and linuron and >95% for monuron.

The presence of biosolids did not change the order of herbicide sorption to WN biochar, kaolinite, or activated carbon but did change it for SW biochar (diuron ≈ linuron > monuron) (Table 3). The K_d values of SW biochar with biosolids decreased significantly when compared to the values without biosolids. Both WN biochar and activated carbon demonstrated complete sorption of all herbicides, with the exception of linuron to WN biochar. The sequence of herbicide sorption was linuron > diuron > monuron for both SW biochar and kaolinite.

Structurally similar phenylureas were selected to investigate the effect of the different substituents on binding affinity. It has been demonstrated that the sorption of phenylureas to soil increases with an increasing number of substituted halogens on the phenyl ring, with monuron (one Cl) having less affinity than diuron (two Cl) (Das and Mukherjee, 2012; Langeron et al., 2014). Further, the substitution of a methyl group (diuron) with a methoxy group (linuron) also resulted in increased sorption (Langeron et al., 2014). Both the methyl and methoxy groups are electro-donating groups that activate the aromatic ring. However, the mesomeric effects associated with the methoxy group are greater than inductive effects associated with the methyl group (Hammett, 1937). This leads to greater surface interaction and results in higher sorption, which is similar to the order seen in the present study with biochars. The order of sorption of the herbicides was also consistent with octanol/water (K_{ow}) partitioning coefficients of the herbicides. It is therefore proposed that hydrophobic interactions and van der Waals forces are important mechanisms for binding of these herbicides, which increases in the presence of biosolids (Lagaly, 2001). Both partitioning and

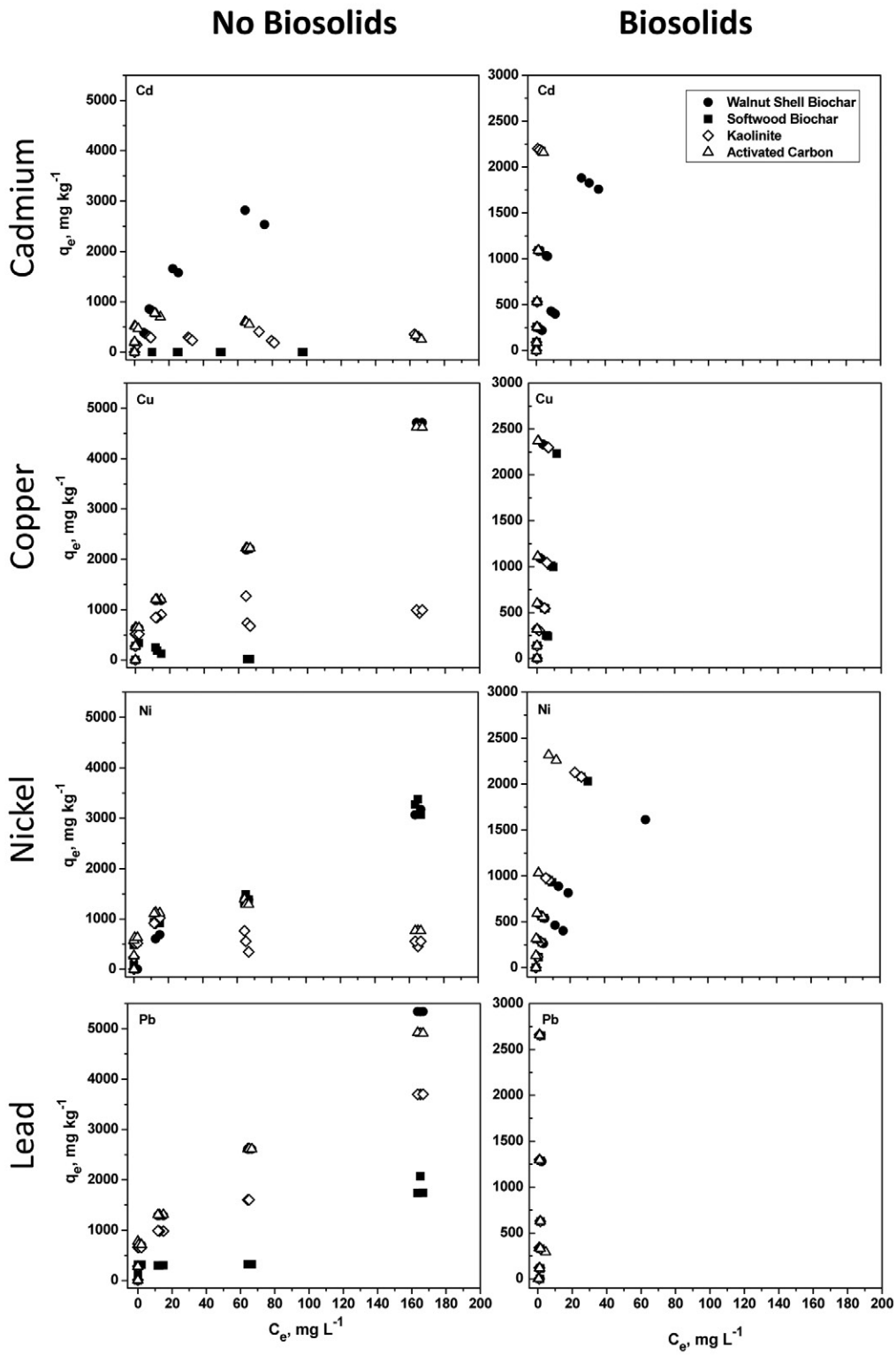


Fig. 1. Sorption isotherms characterizing the retention of Cd, Cu, Ni, and Pb to sorbents with and without biosolids (q_e) vs. aqueous concentration of the compounds at equilibrium (C_e). Figure scales vary between treatments of biosolids but are consistent within treatment category.

adsorption mechanisms have also been suggested for atrazine and simazine sorption to biochar (Zheng et al., 2010).

Monuron, diuron, and linuron each demonstrated higher sorption on WN biochar than on SW biochar or kaolinite. The application of WN biochar in an agricultural setting as a soil amendment would therefore likely limit the bioavailability and reduce the effectiveness of these herbicides when applied. It remains unknown, however, what effect SW biochar would have on the sorption of the herbicides at an average application rate of biochar. Yang et al. (2006), with wheat straw biochar, demonstrated that diuron efficacy could be completely lost when soil char content was 0.5% or higher.

To evaluate the potential for loss of diuron based on the current study, an estimate was developed for typical field conditions. In a corn field with an average soil density (1.4 g cm^{-3}) and a biochar application rate of 10 t ha^{-1} to a depth of one furrow slice (0.4% application rate), and a typical diuron application rate of 900 g ha^{-1} (diuron 80 WDG weed killer, USEPA Reg. No. 34704-648), the results indicate that all diuron would be completely sorbed. Based on information given in Fig. 2, the

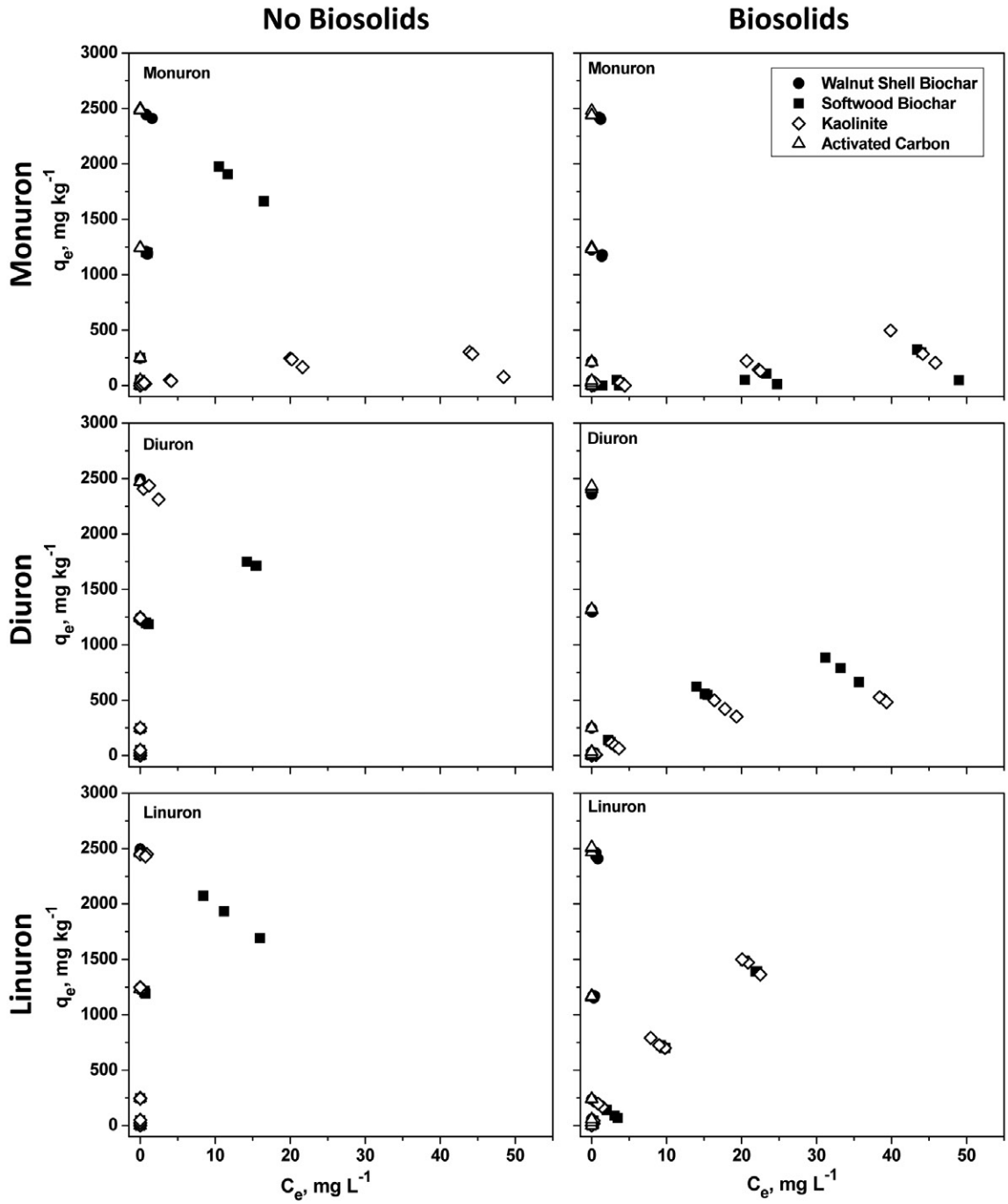


Fig. 2. Sorption isotherms characterizing the retention of monuron, diuron, and linuron to sorbents with and without biosolids (q_e) vs. aqueous concentration of the compounds at equilibrium (C_e).

maximum sorption of diuron to SW biochar alone is approximately 16,000 g ha^{-1} at 10 t ha^{-1} biochar application rate. Even when an equal amount of biosolids is added, the sorption of diuron would reach 13,600 g ha^{-1}, which far exceeds the 900 g ha^{-1} diuron application rate. Given that these calculations are based on the SW biochar, which sorbs significantly less than the WN biochar, the application of either of these biochars would likely greatly limit the efficacy of the herbicides.

Pharmaceuticals

The sorption of the pharmaceuticals was first evaluated to sorbents without biosolids. The WN biochar and activated carbon both completely sorbed ciprofloxacin, while comparatively low sorption was observed with SW biochar and kaolinite (Fig. 3). The sorption order for ciprofloxacin was activated carbon ≈ WN > kaolinite > SW. This sorption trend is similar to the sorption trend in herbicides. As anticipated, further experiments of ciprofloxacin sorption to soil amended with both WN biochar and biosolids demonstrated higher sorption affinity than soils amended with biosolids alone (Fig. 4).

Batch sorption of triclocarban and triclosan were only evaluated on SW biochar. Batch experiments of triclocarban and triclosan to kaolinite, WN biochar, and activated carbon were not conducted due to complete sorption of triclocarban and high sorption of triclosan to the SW biochar, which typically has a lower sorption capacity than the other sorbents evaluated. The

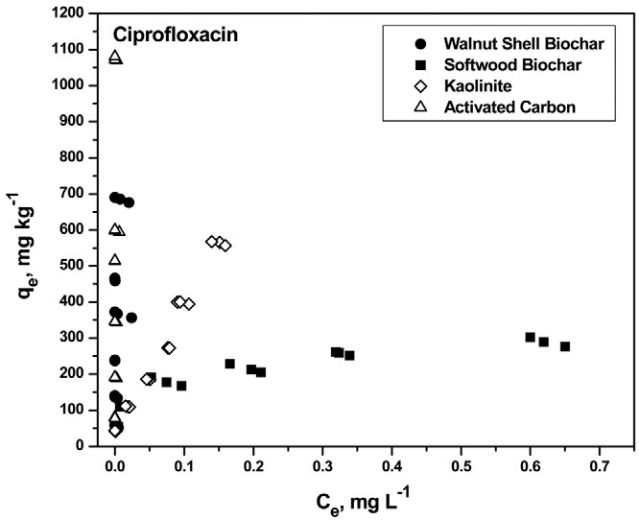


Fig. 3. Sorption isotherms characterizing the retention of ciprofloxacin to activated carbon, kaolinite, softwood biochar, and walnut shell biochar (q_e) vs. aqueous concentration of the compounds at equilibrium (C_e).

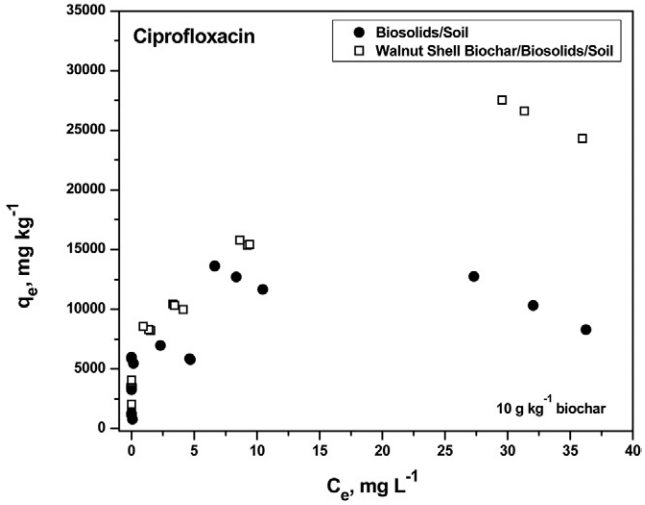


Fig. 4. Sorption isotherms characterizing the retention of ciprofloxacin to biosolids-amended soil, with and with without walnut shell biochar additions (q_e) vs. aqueous concentration of the compounds at equilibrium (C_e).

overall order of sorption affinity for all pharmaceuticals on SW biochar was triclocarban > triclosan > ciprofloxacin, with triclosan and triclocarban exhibiting a much higher affinity than ciprofloxacin (Supplemental Fig. S1). This order of sorption is consistent with the octanol/water coefficients (K_{ow}) of the three compounds, as triclocarban and triclosan have similar log K_{ow} values, whereas that for ciprofloxacin is much lower (Table 1).

Since ciprofloxacin is completely bound by WN biochar and has limited sorption to SW biochar, this class of contaminants appears to have increased affinity to biochars with higher carbon content. This is consistent with results from Mitchell et al. (2015), who demonstrated that biochars produced under higher temperatures that contain higher organic carbon content and lower O/C ratio enhanced antibiotic sorption.

The SW biochar, with 72% organic carbon, contains more than 30 times more organic carbon than the biosolids-amended soil, and normalization to organic carbon content produced a similar sorption affinity of ciprofloxacin to each sorbent, indicating that organic partitioning is a dominant influence in sorption of ciprofloxacin to biochar and the biosolids-amended soil (Chiou et al., 1983; Kile et al., 1995; Xia and Ball, 1999). The addition of biochar to the biosolids/soil system caused an increase in sorption affinity for ciprofloxacin. This result was anticipated given that sorption to biochar has been shown to exceed that of soil organic matter 10- to 1000-fold (Bucheli and Gustafsson, 2000; Chiou and Kile, 1998). In the case of ciprofloxacin, the addition of WN biochar to biosolids-amended soil appreciably increased sorption, supporting the suggestion that contaminant immobilization can be increased with biochar co-amendments.

Conclusions

Pharmaceuticals and heavy metals commonly found in significant concentrations in biosolids from wastewater treatment plants demonstrate high sorption to biochar, suggesting that co-amending biosolids with biochar may reduce environmental exposure to these contaminants. The current results indicate the potential efficacy of biochar for this purpose. There was greater sorption to WN biochar over SW biochar for almost all contaminants. The addition of biosolids caused a decrease in sorption of herbicides (monuron, diuron, linuron) to SW biochar, although there was no observable change in the high sorption to WN biochar. This suggests that while WN biochar may be effective in reducing agrochemical and contaminant transport, it may not be appropriate when soil-applied herbicides are used. Sorption of antibiotics and antimicrobials (ciprofloxacin, triclocarban, triclosan) to soils amended with biochar–biosolids was higher than to soils amended with biosolids alone. Overall, the results of this study demonstrate the potential efficacy for selected biochars to be used as sorbents to sequester contaminants present in biosolids. The data highlight the different sorptive properties of WN and SW biochars and provide baseline data for tailoring biochars to bind biosolids-borne contaminants by adjusting pyrolysis conditions and biomass feedstocks.

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