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Effect of composting and amendment with biochar and woodchips on the fate and leachability of pharmaceuticals in biosolids destined for land application

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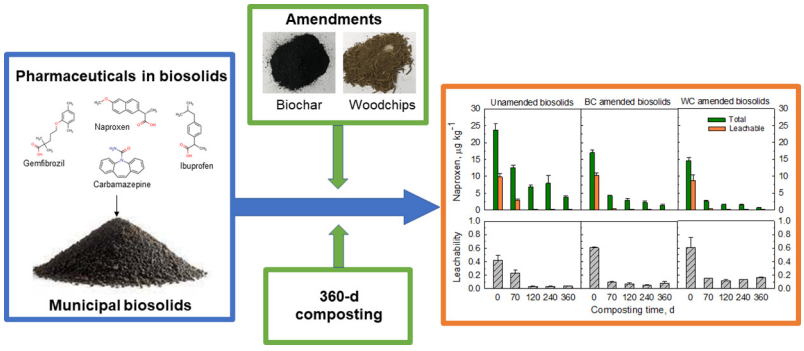
HIGHLIGHTS

- Composting enhanced removal of total and leachable pharmaceuticals in biosolids.
- BC and WC enhanced more rapid/greater removal of total/leachable pharmaceuticals.
- Half-lives of pharmaceuticals in biosolids during composting varied from 13 to 3053 d.
- BC and WC had positive or negative effect on pharmaceutical leachability.
- BC and WC effectively reduced leaching of pharmaceuticals from biosolids.

GRAPHICAL ABSTRACT



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ABSTRACT

Land application of biosolids can improve soil fertility and enhance crop production. However, the occurrence and persistence of pharmaceutical compounds in the biosolids may result in leaching of these contaminants to surface water and groundwater, causing environmental contamination. This study evaluated the effectiveness of two organic amendments [biochar (BC) and woodchips (WC)] for reducing the concentration and leachability (mobility) of four pharmaceuticals in biosolids derived from wastewater treatment plants in southern Ontario, Canada. The effect of 360-d composting on fate and leachabilities of target pharmaceuticals in biosolid mixtures was also investigated. Composting decreased total and leachable concentrations of pharmaceuticals in unamended and BC- and WC-amended biosolids to various degrees, from 10% up to 99% depending on the compound. Blending BC or WC into the biosolids greatly increased the removal rates of the target pharmaceuticals, while simultaneously decreasing their half-lives ($t_{0.5}$), compared to unamended biosolids. The $t_{0.5}$ of contaminants in this study followed the order: carbamazepine (304–3053 d) > gemfibrozil (42.3–92.4 d) > naproxen (15.3–104 d) > ibuprofen (12.5–19.0 d). Amendment with BC and(or) WC significantly reduced the leachability of carbamazepine, ibuprofen, and gemfibrozil to variable extents, but significantly enhanced the leachability of naproxen, compared to unamended biosolids ($P < 0.05$). Biochar and WC exhibited different (positive or negative) effects on the leachability of individual pharmaceuticals. Significantly lower concentrations of total and(or) leachable (mobile) pharmaceuticals were observed in amended biosolids than unamended biosolids ($P < 0.05$). Biochar and WC are effective amendments that can reduce the environmental impact of biosolid land applications with respect to pharmaceutical contamination.

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1. Introduction

Biosolids are nutrient-rich organic materials produced during wastewater treatment and are widely applied to agricultural lands to supply nutrients and improve soil quality. Land application of biosolids provides many agricultural and environmental benefits, including increased crop yields, reuse and recycling of organic matter and nutrients, and reduced chemical fertilizer usage and greenhouse gas emissions. Besides agriculture applications, biosolids are often used to reclaim other disturbed or degraded lands, such as forests, parks, and mine reclamation sites (Beauchemin et al., 2018; Lu et al., 2012; Sydnor and Redente, 2002). Biosolids have been successfully used to revegetate inactive mine tailings in Copper Cliff, Sudbury, ON, Canada (Northen Ontario Business, 2019). However, concerns about potential impacts, such as odors, release of pathogens, and eutrophication of waterbodies caused by excess loading of phosphorus, have hindered public acceptance of biosolids land application (Lu et al., 2012). Moreover, contamination caused by heavy metals and organic compounds in biosolids also draws great public attention; most biosolids destined for land application contain elevated concentrations of heavy metals (e.g., As, Cd, Cu, Pb, Hg, Mo, Ni, Se, and Zn) (Mortvedt, 1995) and organic compounds [e.g., polyaromatic hydrocarbons (PAHs), pesticides, herbicides, polychlorinated biphenyls (PCBs), dioxins, and pharmaceuticals] (Kinney et al., 2006).

Leaching of heavy metals and organic pollutants, especially pharmaceuticals and personal care products (PPCPs), to the environment during land application of biosolids has been reported (Marguí et al., 2016; Topp et al., 2008). Gottschall et al. (2012) detected more than 80 PPCPs in dewatered municipal biosolids (DMB) applied to an agricultural field in Ottawa, Ontario, Canada. The investigated PPCPs were detected in DMB aggregates incorporated into soil up to one-year post-application; some PPCPs, such as carbamazepine (CBZ), ibuprofen (IBU), acetaminophen, and triclosan, were also detected in tile drainage and groundwater (<2 m depth) in a concentration range from 5 to 74 ng L^{-1}. Topp et al. (2008) observed nine PPCPs, including atenolol, CBZ, cotinine, gemfibrozil (GEM), naproxen (NAP), sulfamethoxazole (SMX), and triclosan, in the runoff resulting from simulated precipitation on the day following broadcast application of biosolids, with concentrations ranging from 70 to 1477 ng L^{-1}; among these PPCPs, CBZ and triclosan were detected at low concentrations in a runoff event 266 days after application. The occurrence and persistence of PPCPs in biosolids may cause adverse environmental impacts and therefore improved management of contaminants before land application is required.

Carbonaceous materials such as biochar (BC) and woodchips (WC) are extensively used as organic amendments to improve soil fertility, increase crop yields, and restore degraded soil (Carlson et al., 2015). Biochar and WC are also widely used as reactive media to remove or stabilize different types of pollutants in soil and water. Studies have reported effective removals of nitrate and phosphate (Bock et al., 2015), heavy metals Cr, Hg, Cd, As, and Zn (Beesley and Marmiroli, 2011; Liu et al., 2020a; Liu et al., 2016), and organic contaminants naphthalene and p-nitrotoluene (Huang and Chen, 2010) from soil and water using BC and WC. In addition, these organic amendments have also been successfully used to remove emerging contaminants from water, including perchlorate, pharmaceutical compounds, artificial sweeteners, and perfluoroalkyl compounds (Dan et al., 2021; Keerthanan et al., 2021; Kim et al., 2016; Li et al., 2020; Liu et al., 2019; Liu et al., 2020b; Liu et al., 2014a; Ulrich et al., 2015).

Incorporation of organic amendments, such as BC, sawdust, and lignite in biosolids, to reduce the leaching of NO_3^--N, NH_4^+-N, total suspended solids, fecal coliforms, and heavy metals, has been extensively studied (Paramashivam et al., 2017; Williams and Edwards, 2017). However, very few studies have investigated the effectiveness of amendments with respect to reducing the leaching of emerging PPCP contaminants from biosolids. Wang et al. (2019) report the effects of inorganic amendments, including lime and mussel shells, on the fate of four PPCPs (CBZ, GEM, triclosan, and fluoxetine). However, there is a research gap with respect to the effect of organic amendments such as BC and WC on the fate and leachability (mobility) of PPCPs in biosolids during composting.

The hypothesis of this study is that organic amendments BC and WC reduce leaching of PPCPs from biosolids during composting. Two organic amendments (BC and WC) were mixed with biosolids obtained from wastewater treatment plants in southern Ontario, Canada. The effect of two organic amendments and 360 days of composting on the fate and leachability of target pharmaceutical compounds in the biosolids was investigated. The leachability (mobility) of pharmaceuticals was calculated as the ratio of the leachable (soluble) mass/concentration to the total mass/concentration at a specific curing period in biosolids with/without amendment (Chefetz et al., 2008; Wang et al., 2018). The term removal in the following discussion is used in a generic way to refer to all mechanisms that result in a decrease of total or leachable concentrations (such as microbial degradation and retention on sorbing phases).

The target pharmaceuticals included CBZ, caffeine (CAF), SMX, IBU, GEM, and NAP. The target pharmaceuticals possess different environmental persistence (Bu et al., 2016; Glassmeyer et al., 2007; Yamamoto et al., 2009) and other characteristics [e.g., molecular structure, acid dissociation constant (pK_a), octanol-water partitioning coefficient ($\log K_{ow}$), and usages] (Table 1), and are often detected in wastewater and biosolids (Miao et al., 2005; Xia et al., 2005). The results of this study provide novel information on the fate and leachability of target pharmaceuticals in biosolids during 360-d composting. The results further fill the identified knowledge gap regarding the effectiveness of BC and WC to reduce pharmaceutical leaching from biosolids during composting. This information can be used to improve prediction and management of pharmaceutical contamination associated with biosolids land applications.

2. Materials and methods

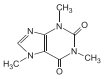
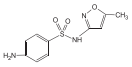
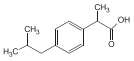
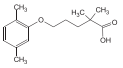
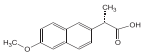
2.1. Materials

Municipal biosolids were collected from cities in southern Ontario, Canada and mixed to produce a blended material by Terrapure Organics Solutions (formerly Terratec Environmental Ltd., Niagara Falls, ON, Canada), a company that manages biosolids handling and spreading at Vale waste management facility at the Copper Cliff mine site, ON, Canada. The municipal biosolids result from anaerobic digestion [maximum count of 2×10^6 cfu (colony forming units) for *E. coli* (*Escherichia coli*)] and are considered a class B biosolid according to EPA 40 CFR Part 503 Standards (US EPA, 1993). The Airex 2 BC was obtained from fast pyrolysis of spruce sawdust at 425 °C, and cooling of the product by water atomization (Airex Énergie, Airex Industries Inc., Laval, Quebec, Canada). Based on dry sieving, 96 wt% of the BC was <2 mm and 82 wt% was <2 mm and >0.25 mm. Woodchips were obtained from Terrapure Organics Solutions and are used at the Copper Cliff site to cover the municipal biosolids pile for odor control. The coarse WC material was sieved to pass 2 mm before use. Acetonitrile and methanol (HPLC grade), sodium phosphate monohydrate (reagent grade), and phosphoric acid and hydrochloric acid (Instra-analyzed) were obtained from Fisher Scientific (Canada). Calcium chloride was purchased from BDH chemicals (VWR, Canada).

2.2. Incubation and batch experimental procedures

At the field site, the biosolids are generally mixed with approximatively 30% WC or yard wastes on a wet volume basis, and the mixture is then pre-composted for two months before being surface applied on tailings. Based on estimated bulk densities and dry matter contents, this input of WC or yard wastes represents approximately 26 dry wt% of biosolids. To simulate the impact of composting and organic amendment inputs (BC or WC) on the leachability of the targeted pharmaceuticals in

Table 1
Structures and characteristics of target pharmaceuticals.

Pharmaceutical (abbreviation)/ Use	Structure	Character (charge)	pK_a[a]	logK_{ow}[b]	logD_{ow}[c]
Carbamazepine (CBZ)/ Antidepressant		Base (N)	−3.8	2.77	2.77
Caffeine (CAF)/ Stimulate		Base (N)	−1.16	−0.55	−0.55
Sulfamethoxazole (SMX)/ Antibiotic		Acid/Base (−)	1.97, 6.16	0.79	−0.11
Ibuprofen (IBU)/ Anti-inflammatory drug		Acid (−)	4.85	3.84	0.85
Gemfibrozil (GEM)/ Anti-cholesterol		Acid (−)	4.42	4.39	1.14
Naproxen (NAP)/ Anti-inflammatory drug		Acid (−)	4.19	2.99	−0.36

Note: (N): Neutral; (−): Negatively charged. The values of pK_a, log K_{ow}, and log D_{ow} were obtained from Chemicalize.org by ChemAxon (http://www.chemicalize.org).
[a] pK_a is the acid dissociation constant. For bases (CBZ and CAF), the pK_a values are for their conjugate acids.
[b] log K_{ow} is the octanol-water partitioning coefficient for non-ionized (neutral) pharmaceutical.
[c] log D_{ow} (pH dependent log K_{ow}) is the octanol-water partitioning coefficient for ionized pharmaceutical. The log D_{ow} values reported in this study are for pH 8 (initial biosolid pH).

the biosolids, aerobic incubations were conducted in the laboratory using three treatments: 100% biosolids, WC-amended biosolids, and BC-amended biosolids. The 100% biosolids treatment was used as a control to determine the impact of incubation on pharmaceutical degradation over time. The other two treatments were prepared by adding the organic amendment (BC or WC) to the municipal biosolids at a rate of 20 wt% of biosolids (dry basis). At an application rate of 150 t ha^{-1} of biosolids as is often the case in the field, this rate represents an input of 30 t ha^{-1} of BC or WC. The concentrations of target pharmaceuticals (total and leachable) in BC- and WC-amended biosolids reported in this study have been corrected by the amendment ratio of 20 wt% of biosolids.

The experiment was designed as randomized complete blocks with two replicates. Five destructive batches (for five sampling dates: 0, 70, 120, 240, and 360 d) were prepared for each treatment. The unamended and BC- and WC-amended biosolids were placed in 1-L open Mason jars and incubated in a growth chamber in the dark at 25 ± 1 °C under a humid oxygenated atmosphere for up to 360 d. The moisture in the mixture was maintained at 30% (wt./wt.). Every two weeks, the biosolid samples were manually stirred to allow air penetration in the mixture, and the water content was re-adjusted if needed. At Day 0, and after 70, 120, 240, and 360 d of incubation, two replicate samples of each treatment were collected to determine the concentration of total pharmaceuticals (acetonitrile extractable) in the unamended/amended biosolids as well as the leachable pharmaceuticals ($CaCl_2$ extractable) over time. Biosolids samples were freeze-dried (Labconco FreeZone 2.5, Kansas City, MO, USA), homogenized with a mortar and pestle, sieved to <2 mm, and stored prior to extraction.

2.3. Extraction and analysis of target pharmaceuticals

Biosolid samples were spiked with an isotope-labelled internal standard (IS) of each target compound to track analyte recovery, instrument variability, and matrix suppression during sample preparation and analysis. The total pharmaceuticals in the biosolids were extracted using acetonitrile following the acidic extraction method described in EPA method 1694 (US EPA, 2007). The leachable pharmaceuticals in the biosolids were extracted using 0.01 M $CaCl_2$ solution (Casey et al., 2004; Durán-Álvarez et al., 2012). The acetonitrile and $CaCl_2$ extracts were purified and concentrated through a series of solid phase extraction (SPE) procedures. Details of the procedures are provided in the supplementary information (SI).

The concentrated pharmaceutical extracts from SPE were analyzed using high performance liquid chromatography (HPLC; Agilent 1100, Agilent Technologies) followed by electrospray tandem mass spectrometry (4000 Q TRAP, Applied Biosystems, Foster City, CA, USA). The detailed analytical method, quality assurance/quality control (QA/QC) results, and method detection limits of target pharmaceuticals are described in the SI. Besides target pharmaceuticals, pH, EC, dissolved organic carbon (DOC), and dissolved total carbon (DTC) of water extraction 1:15 (wt./wt.) from fresh biosolids mixtures were measured; the solid total organic carbon (TOC) and solid total carbon (TC) in each solid mixture were also analyzed. The bio-available nutrients (K, P, and N) were analyzed with the following extractions: 2 M KCl solution for extracting N (sum of NO_3-N and NH_4-N), 0.5 M $NaHCO_3$ solution for extracting P (PO_4-P), and 1 M NH_4OAc solution for extracting K (University of Guelph, Laboratory Services, ON, Canada). These results are reported in the SI, Figs. S1–S5.

2.4. Pharmaceutical recovery test

A pharmaceutical recovery test was conducted to validate the acetonitrile extraction method. Known amounts of target native pharmaceutical analytes and their isotope-labelled internal standards were spiked into the amendments (BC and WC only) and three treatments (unamended biosolids, BC- and WC-amended biosolids), on Day 0 (before composting) and Day 360 (after composting) (n = 2). Recovery of a pharmaceutical was calculated as the percentage ratio of the concentration difference between a spiked and non-spiked sample to the known spiked concentration. Results are summarized in Table S1.

2.5. Statistical analysis and removal rate calculation

Statistical analysis was performed using the two-way repeated measures analysis of variance (ANOVA), followed by the Holm-Sidak multiple comparison test (SigmaPlot 11.0) to compare the significance of differences of total, leachable, and leachabilities of the pharmaceuticals between composting time (0, 70, 120, 240, and 360 day) as well as the significance of differences between treatments (unamended vs. amended biosolids; one amended vs. the other amended biosolids). In addition, the interaction between the two factors (composting time and treatments) was also determined. When the normality and(or) equal variance test failed, ANOVA was conducted on ln transformed data to better comply with the assumptions of analysis of variance. Statistical analyses were conducted at a level of significance of $\alpha = 0.05$.

When the interaction between composting time and treatments was significant, the significances of one factor within another factor (e.g., significant differences between treatments at a given

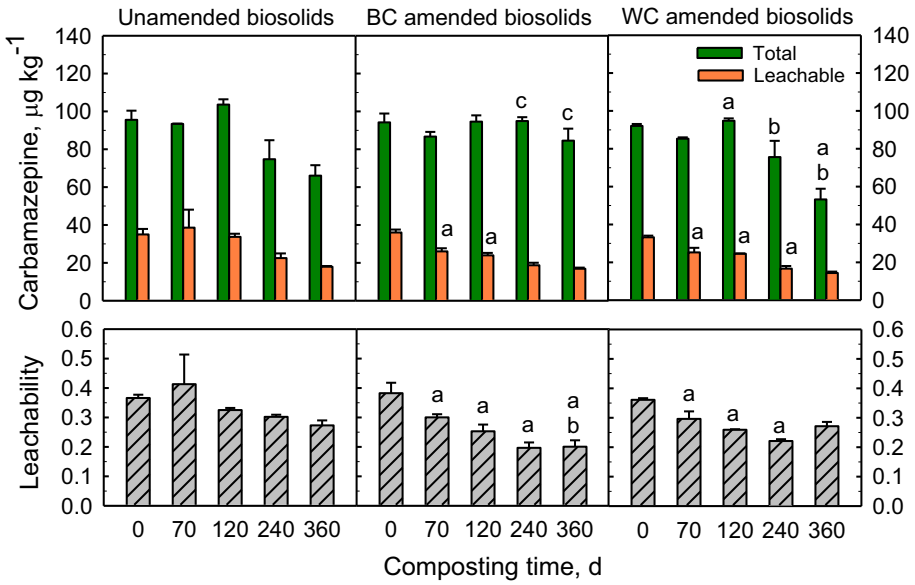


Fig. 1. Concentrations of total and leachable carbamazepine (CBZ) (top subplot) and leachability of CBZ (expressed as the ratio of leachable to total concentrations; bottom subplot) in the three treatments [unamended biosolids, biochar (BC)- and woodchips (WC)-amended biosolids] as a function of composting time. Error bars show standard error of the mean (n = 2). Letters a, b, and c denote statistically significant differences between treatments at a given composting time (interaction between treatment and time is significant, $P < 0.05$). Letter a denotes statistically significant lower concentration or leachability in amended biosolids than unamended biosolids at a given composting time. Letter b denotes statistically significant lower concentration or leachability in one amended biosolids compared to the other amended biosolids at a given composting time. Letter c denotes statistically significant higher concentration in amended biosolids than unamended biosolids at a given composting time. Results of statistically significant differences between composting time for a given treatment are summarized in the SI, Tables S2, S3, and S10.

composting time or significant differences between composting time for a given treatment) were reported. When the interaction between composting time and treatments was not significant, significances of each factor were reported separately. Detailed statistical results are summarized in the SI, Tables S2–S13, and the results of significances between treatments are also denoted in Figs. 1–4 using letters a, b, and c.

Least-squares regression [polynomial (for zero-order rate) or exponential decay (for first-order rate) regression equations] using SigmaPlot (11.0) was conducted to calculate the removal rate constants (k_{obs}) for target pharmaceuticals during composting. The removal rates and k_{obs} of target pharmaceuticals are reported in the SI (Tables S14–S17). Table 2 summarizes the half-lives ($t_{0.5}$) of each pharmaceutical (total and leachable) as affected by amendment inputs.

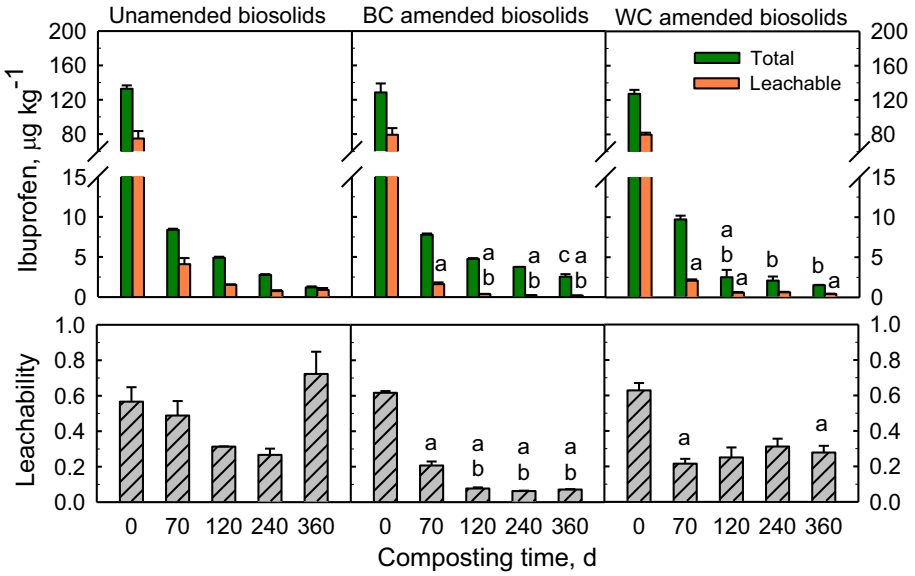


Fig. 2. Concentrations of total and leachable ibuprofen (IBU) (top subplot) and leachability of IBU (expressed as the ratio of leachable to total concentrations; bottom subplot) in the three treatments [unamended biosolids, biochar (BC)- and woodchips (WC)-amended biosolids] as a function of composting time. Error bars show standard error of the mean (n = 2). Letters a, b, and c denote statistically significant differences between treatments at a given composting time (interaction between treatment and time is significant, $P < 0.05$). Letter a denotes statistically significant lower concentration or leachability in amended biosolids than unamended biosolids at a given composting time. Letter b denotes statistically significant lower concentration or leachability in one amended biosolids compared to the other amended biosolids at a given composting time. Letter c denotes statistically significant higher concentration in amended biosolids than unamended biosolids at a given composting time. Results of statistically significant differences between composting time for a given treatment are summarized in the SI, Tables S4, S5, and S11.

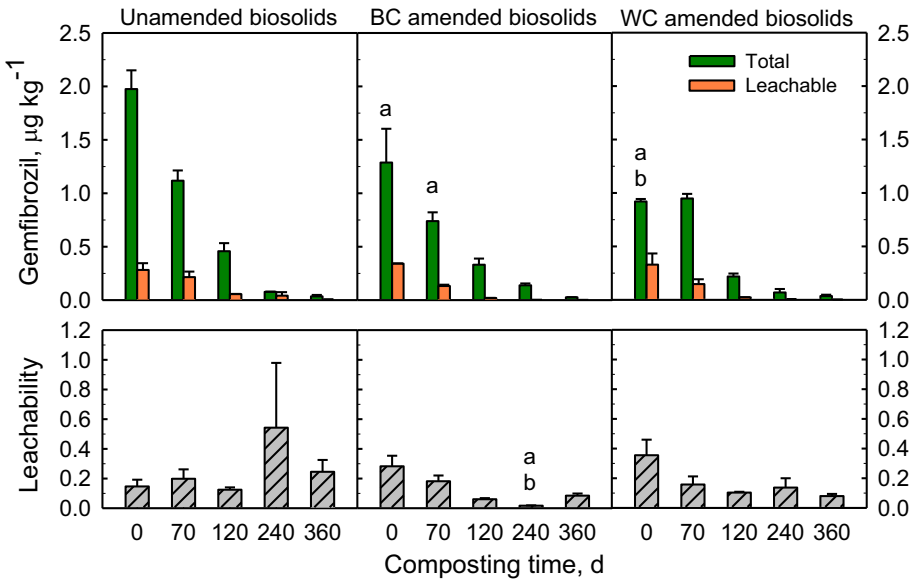


Fig. 3. Concentrations of total and leachable gemfibrozil (GEM) (top subplot) and leachability of GEM (expressed as the ratio of leachable to total concentrations; bottom subplot) in the three treatments [unamended biosolids, biochar (BC)- and woodchips (WC)-amended biosolids] as a function of composting time. Error bars show standard error of the mean (n = 2). Letters a and b denote statistically significant differences between treatments at a given composting time (interaction between treatment and time is significant, $P < 0.05$). Letter a denotes statistically significant lower concentration or leachability in amended biosolids than unamended biosolids at a given composting time. Letter b denotes statistically significant lower concentration or leachability in one amended biosolids compared to the other amended biosolids at a given composting time. Results of statistically significant differences between composting time (for a given treatment for total GEM and leachability of GEM) are summarized in the SI, Tables S6, S7, and S12.

3. Results and discussion

3.1. Ionization and hydrophobicity of target pharmaceuticals and characterization of amendments

Except for CBZ and CAF, the target pharmaceuticals evaluated in this study undergo ionization under the pH range of biosolids mixtures (7.4–8.3). Carbamazepine and CAF are basic compounds and occur primarily in their neutral forms within the pH range of the biosolids [pK_a (conjugate acids) < pH] (Table 1). Pharmaceuticals SMX, IBU, GEM, and NAP are acidic compounds and predominantly exist as anionic species (negatively charged, pK_a < pH) (Table 1). The ionization (dissociation) of pharmaceuticals has a direct impact on their environmental fate and hydrophobicity (Schwarzenbach et al., 2003; Wang et al., 2018).

The octanol-water partition coefficient ($\log K_{ow}$) is used to express the hydrophobicity of a non-ionized (neutral) pharmaceutical. A pharmaceutical is considered to be hydrophilic when $\log K_{ow}$ < 1,

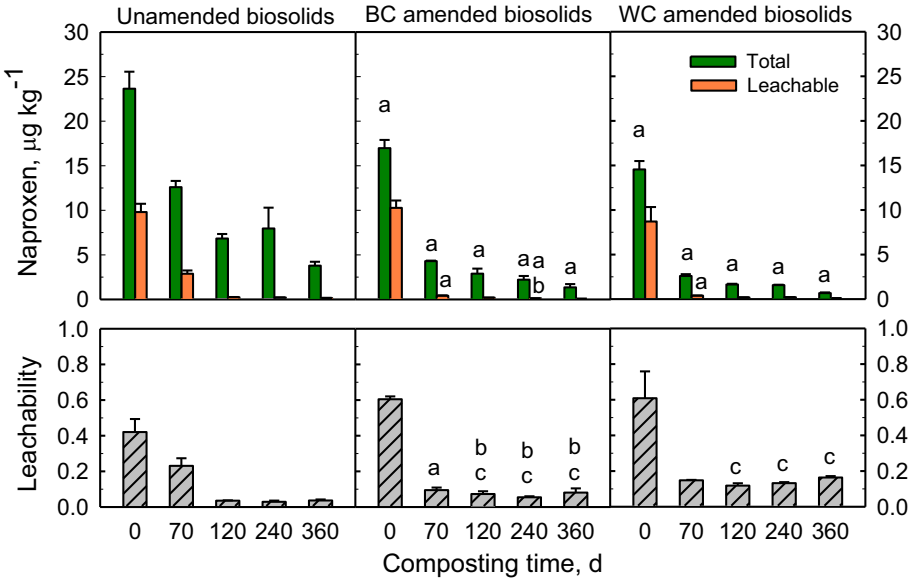


Fig. 4. Concentrations of total and leachable naproxen (NAP) (top subplot) and leachability of NAP (expressed as the ratio of leachable to total concentrations; bottom subplot) in the three treatments [unamended biosolids, biochar (BC)- and woodchips (WC)-amended biosolids] as a function of composting time. Error bars show standard error of the mean (n = 2). Letters a, b, and c denote statistically significant differences between treatments at a given composting time. The interaction for leachable NAP and leachability of NAP between treatment and time is significant, $P < 0.05$; the interaction of total NAP between treatment and time in not significant. Letter a denotes statistically significant lower concentration or leachability in amended biosolids than unamended biosolids at a given composting time. Letter b denotes statistically significant lower concentration or leachablity in one amended biosolids compared to the other amended biosolids at a given composting time. Letter c denotes statistically significant higher leachability in amended biosolids than unamended biosolids at a given composting time. Results of statistically significant differences between composting time (within treatments for leachable NAP and leachability of NAP) are summarized in the SI, Tables S8, S9, and S13.

Table 2
Half-lives ($t_{0.5}$, d) of total (Tot) and leachable (Lea) pharmaceuticals [carbamazepine (CBZ), ibuprofen (IBU), gemfibrozil (GEM), and naproxen (NAP)] in the three treatments [unamended biosolids, biochar (BC)- and woodchips (WC)-amended biosolids] during 360 d of composting.

Treatment	CBZ		IBU		GEM		NAP	
	Tot	Lea	Tot	Lea	Tot	Lea	Tot	Lea
Unamended biosolids	534	333	18.2	17.0	65.4	80.6	104	35.0
BC-amended biosolids	3053	331	18.0	12.5	71.5	42.3	41.3	15.3
WC-amended biosolids	455	304	19.0	13.4	92.4	46.8	31.2	15.9

moderately hydrophobic (transphilic) when $1 < \log K_{ow} < 3$, and hydrophobic when $\log K_{ow} > 3$ (Verliefde et al., 2008). However, ionization of pharmaceuticals may result in a decrease in hydrophobicity. In this case, $\log D_{ow}$ (pH dependent $\log K_{ow}$) is used as an alternative to $\log K_{ow}$ to indicate the hydrophobicity of a pharmaceutical, which accounts for the ionization of both neutral and ionic species (Schwarzenbach et al., 2003). The values of $\log D_{ow}$ for target pharmaceuticals are summarized in Table 1. Under the pH range of biosolids mixtures in this study, the hydrophobicity of target pharmaceuticals followed the order CBZ > GEM > IBU > SMX > NAP > CAF. Carbamazepine ($\log D_{ow} = 2.77$) is the most hydrophobic pharmaceutical; CAF is the most hydrophilic compounds with the lowest $\log D_{ow}$ value (−0.55) within the pH range of this study.

The BC and WC had been previously characterized (Clemente et al., 2017, 2018). Results of solid-state ^{13}C direct polarization magic angle spinning-nuclear magnetic resonance (DPMASNMR) and diffuse reflectance-Fourier transform infrared (DR-FTIR) spectroscopy showed that Airex 2 BC is enriched in condensed aromatic structure, and contains aromatic, carboxyl, carbonyl, phenolic, and O-alkyl functional groups (Clemente et al., 2017). The Airex 2 BC contains ~80% TOC, with a low ash content of 1.4% and a high TOC/N of 362 (Clemente et al., 2018). The WC used in this study contains ~36% TOC and ~1.2% protein with a TOC/N ratio of 188.

3.2. Pharmaceutical recovery results

Results of recovery test show that CBZ had the highest recoveries (89–98%) among the target pharmaceuticals in both amendments (BC and WC) and three biosolid treatments using the acetonitrile extraction method (Table S1). This is likely due to the greater hydrophobicity of CBZ than other pharmaceuticals, which enhanced a more thorough extraction by the hydrophobic acetonitrile. Compared to CBZ, relatively lower recoveries were observed for GEM (78–96%), NAP (81–92%), and IBU (71–97%) (Table S1). Similar to this study, satisfactory recoveries of CBZ and GEM using the same EPA method 1694 (US EPA, 2007) have been reported by Walters et al. (2010). Lower to moderate recovery (21–46%) was observed for SMX; the lowest recovery (2–7%) among the investigated pharmaceuticals was CAF. The low recovery of CAF is likely due to its low hydrophobicity which limits effective extraction using hydrophobic acetonitrile. Due to the low recovery of CAF, further comparison of its removal is not included in the following discussion.

3.3. Occurrence of pharmaceuticals in unamended biosolids

Concentrations of CBZ, IBU, GEM, and NAP in the unamended biosolids used in this study varied greatly, ranging from 2 to ~140 μg kg^{-1} (Figs. 1–4). Several studies have reported a widespread occurrence of SMX (at ng L^{-1} levels) in wastewater (Liu et al., 2014b; Metcalfe et al., 2010; Van Nuijs et al., 2011) and biosolids destined for land application (Topp et al., 2008). However, SMX was not detected in the biosolids used in this study. The undetectable concentration of SMX in the biosolids can be attributed to its (bio)degradation and(or) low consumption in the regions serviced by the wastewater plants (Göbel et al., 2005; Zhou et al., 2013).

The highest concentration of pharmaceutical observed in the unamended biosolids (at Day 0) was IBU (~140 μg kg^{-1}), followed by CBZ (~100 μg kg^{-1}), NAP (~25 μg kg^{-1}), and GEM (~2 μg kg^{-1}) (Figs. 1–4). The variation in pharmaceutical concentration in the biosolids may result from variations in wastewater sources, wastewater treatment processes, sludge treatment, and production processes. The concentrations of target pharmaceuticals in the biosolids derived from the southern Ontario cities in this study are generally consistent with previous studies. Miao et al. (2005) report 70 to 258 μg kg^{-1} of CBZ and 7.6 to 166 μg kg^{-1} of CAF in untreated and raw biosolids from Peterborough, Ontario, Canada. Edwards et al. (2009) report variable concentrations of CBZ (9 μg kg^{-1}), IBU (750 μg kg^{-1}), GEM (24 μg kg^{-1}), and NAP (470 μg kg^{-1}) in biosolids from eastern Ontario, Canada.

3.4. Effect of composting on fate of pharmaceuticals in biosolids

The effect of composting on the fate of total and leachable pharmaceuticals in the biosolids was interpreted by comparing the factor (composting time) within the other factor (treatment) from the two-way repeated measures ANOVA (Tables S2-S9), except for leachable GEM and total NAP. Detailed interpretation for the ANOVA results is provided in the SI. Overall, composting enhanced the degradation of both total and leachable pharmaceuticals in the unamended and amended biosolids. Concentrations of target pharmaceuticals (total and leachable) in both unamended and amended biosolids significantly decreased from Day 0 to Day 360, with a lesser extent for CBZ (Figs. 1–4).

Carbamazepine is the most recalcitrant pharmaceutical in this study, with the lowest removals compared to other compounds. Statistically significant concentration reductions for both total and leachable CBZ within all three treatments (unamended biosolids, BC- and WC-amended biosolids) were observed, comparing the early stage (Day 0 and/or Day 70) to the late stage (Day 240 and/or Day 360) of the experiment ($P < 0.01$; Tables S2 and S3 in the SI). After 360 d of composting, total CBZ significantly decreased from an initial concentration of 96 to 66 μg kg^{-1} in unamended biosolids (31% removal), from 94 to 85 μg kg^{-1} in BC-amended biosolids (10% removal), and from 92 to 53 μg kg^{-1} in WC-amended biosolids (42% removal) ($P < 0.01$; Fig. 1).

Concentrations of leachable CBZ also significantly decreased from ~35 μg kg^{-1} on Day 0 to 14–18 μg kg^{-1} on Day 360, with removals of 49% in unamended biosolids, 53% in BC-amended biosolids, and 57% in WC-amended biosolids ($P < 0.008$). Temporal increases in concentrations of total CBZ (up to 104 μg kg^{-1}), compared to initial concentration (Day 0) were observed during the middle stage (Day 120) of the experiment in all three treatments (only statistically significant in unamended biosolids, $P < 0.01$; Table S2 in the SI), which is likely due to microbial transformation of conjugated metabolites to its free form (Miao et al., 2005). Similarly, a statistically significant increase in leachable CBZ was observed in unamended biosolids on Day 70, compared to Day 0 ($P = 0.04$; Table S3 in the SI). However, this temporal increase in leachable CBZ concentration was not observed in both BC- and WC-amended biosolids, indicating retention of leachable CBZ by the amendments.

Similar to CBZ, composting statistically significantly decreased total and leachable concentrations of IBU, GEM, and NAP in both unamended and amended biosolids from the early stage (Days 0–70) to the late stage (Days 240–360) of the experiment ($P < 0.04$; Figs. 2–4; Tables S4–S9 in the SI). Almost complete removal (>98%) of initial IBU (total: ~140 μg kg^{-1}; leachable: ~80 μg kg^{-1}) and GEM (total: 0.9–2.0 μg kg^{-1}; leachable: ~0.3 μg kg^{-1}) was observed in both unamended and amended biosolids after 360 d of composting. About 84 to 95% of initial total NAP (15–24 μg kg^{-1}) was removed in all three biosolid treatments after 360 d of composting, with greater removal (92–95%) of NAP observed in the amended biosolids. Over 99% removal

of initial leachable NAP (~10 μg kg^{-1}) was observed in all three biosolid treatments.

Degradation of the pharmaceuticals targeted in this study in biosolids during composting has not been previously evaluated. However, composting has been reported to be an effective technique for degradation of pesticides and herbicides in biosolids (Büyüksönmez et al., 1999; Rao et al., 1995; Xia et al., 2005). Studies have also reported the degradation of PPCPs during composting in matrices similar to biosolids (Iranzo et al., 2018; Jonidi-Jafari et al., 2020; Lin et al., 2021). Kakimoto and Onoda (2018) report the fate of 17 PPCPs in a composting toilet, with a decomposition rate of ~62% for CBZ [greater than (10–42%) in this study] and ~73% for IBU [lower than (>98%) in this study] after a 336-d composting. Likewise, Thomas et al. (2020) reported an effective degradation of CBZ (66–83% removed from 5 mg kg^{-1}) during in-vessel co-composting of septage and mixed organic wastes.

3.5. Removal mechanisms for pharmaceuticals in biosolids during composting

Composting is the aerobic decomposition of organic materials in biosolids to the humus-like materials (biomass; compost) through biological degradation (Chia et al., 2020; Shammas and Wang, 2007). Composting of biosolids enhances the degradation of organic contaminants, likely as a result of greater microbial diversity and activities, associated with abundant nutrients, higher temperature, and successive transitions from anaerobic to aerobic conditions (Xia et al., 2005). Removal of target pharmaceuticals and other organic contaminants in biosolids during composting can occur through microbial degradation and sorption (hydrophobic and electrostatic interactions and hydrogen bonding) (Mejías et al., 2021; Min et al., 2018; Pan et al., 2009; Semblante et al., 2015).

Microbial degradation of target pharmaceuticals in biosolids alone during composting has not been reported, whereas biodegradation of PPCPs in similar matrices (such as raw sewage sludge and soil) during composting has been investigated. Biel-Maeso et al. (2019) report biodegradation for nine pharmaceuticals in soil during composting, with no removal for CBZ and >99% removals for SMX, IBU, and GEM; the high removals of IBU and GEM were similar to this study. Much lower removals of GEM (11–25%) through biodegradation are observed in soil during aerobic incubation (Fang et al., 2012). Iranzo et al. (2018) identified 11 strains of microorganisms that metabolize high concentrations of pharmaceuticals IBU, azithromycin, and irbesartan in sludge during composting, with IBU and azithromycin serving as a C source and irbesartan as a N source. Pharmaceuticals CAF, NAP, IBU, and metoprolol can also serve as a sole C source to support microbial degradation, with a preferential order: CAF > metoprolol > NAP > IBU (He et al., 2018).

Hydrophobic interaction is the predominant mechanism accounting for sorption of pharmaceuticals to organic matter in biosolids (Semblante et al., 2015). Hydrophobic interaction occurs between the hydrophobic moieties of target pharmaceuticals and hydrophobic organic carbon in biosolids. Stevens-Garmon et al. (2011) reported increasing sorption potential for neutral and negatively charged compounds with increasing logD_{ow} (hydrophobicity). CBZ (neutral, with the highest logD_{ow} value in this study; Table 1) exhibited relatively stronger hydrophobic interaction to organic carbon in biosolids, compared to other target pharmaceuticals. The hydrophilic pharmaceuticals such as CAF, SMX and NAP (with low logD_{ow} values) can sorb to biosolids through other mechanisms, such as electrostatic interaction (likely limited in this study) and(or) hydrogen bonding.

The biosolids used in this study likely have a net negative charge, because the pH (7.4–8.1) was greater than the reported isoelectric point (1–3) for biosolids (Citeau et al., 2011; Forster, 1982; Mejías et al., 2021; Navab-Daneshmand et al., 2015). Electrostatic interactions between the target pharmaceuticals (neutral or negatively charged) and negatively charged biosolids are likely limited in this study. However, for positively charged compounds, electrostatic interaction may be the dominating removal mechanism, compared to hydrophobic interaction (Stevens-Garmon et al., 2011). In other cases, the effect of electrostatic forces is less significant than hydrophobic interaction (Calace et al., 2002).

Hydrogen bonding can also contribute to removal of pharmaceuticals in biosolids during composting. Biosolids contain a variety of functional groups and species, including hydroxyl (–OH) containing groups and species (e.g., carboxylic groups, phenols, alcohol, polysaccharides, and saturated aliphatic species), C═O containing ketones, aldehydes, and carboxylic acid derivatives, and C—N and N—H containing amides in proteins, C═C containing aromatic and quinone groups, and many others (del Rocío Medina-Herrera et al., 2020; Torrecillas et al., 2013). The –OH, C═O, and N—H containing groups in biosolids and target pharmaceuticals can interact through hydrogen bonding.

3.6. Effect of BC and WC amendments on fate of pharmaceuticals during composting

The effect of amendments on the fate of pharmaceuticals during 360-d composting was interpreted by comparing the factor (treatment) within the other factor (composting time) from the two-way repeated measures ANOVA (Tables S2–S9). In addition, removal rates (Tables S14–S17) and half-lives ($t_{0.5}$) of target pharmaceuticals in the three treatments (Table 2) were also compared to indicate the effect of amendments on pharmaceutical removals. Overall, amendments exhibited different effects (enhancement or diminution, depending on the compound) on removals of target (total and leachable) pharmaceuticals during composting.

Amendments enhanced removals of total and(or) leachable CBZ after Day 70 to variable extents, compared to unamended biosolids. Concentrations of total CBZ in WC-amended biosolids were statistically significantly lower than both unamended and BC-amended biosolids during the middle and late stages of the experiment ($P < 0.001$; Fig. 1 and Table S2). However, concentrations of total CBZ were significantly higher in BC-amended biosolids than unamended biosolids after Day 240 ($P < 0.001$), consistent with the possible conversion of CBZ metabolites to their parent compound (Miao et al., 2005). Compared to unamended biosolids, both amendments BC and WC reduced the concentrations of leachable CBZ during composting, and this effect was significant for BC on Days 70 and 120 and for WC on Days 70–240 ($P \le 0.011$; Table S3 in the SI).

Removals of CBZ (total and leachable) in all three treatments followed a zero-order rate model ($R^2 > 0.79$, except for total CBZ in BC-amended biosolids with $R^2 = 0.57$) (Tables 2 and S14). Woodchips were more effective in enhancing removals of total and leachable CBZ, compared to unamended and BC-amended biosolids. The enhanced removals of total and leachable CBZ by WC were illustrated by their greater removal rates and shorter $t_{0.5}$, compared to unamended and BC-amended biosolids (Tables 2 and S14).

Compared to CBZ, removal rates for total and leachable IBU, GEM, and NAP in all three treatments during composting were greater and followed a first-order rate model with $R^2 > 0.89$ (Tables S15–S17). Amendments did not enhance the removals of total IBU in amended biosolids, compared to unamended biosolids, with similar removal rates and $t_{0.5}$ (18–19 d) observed in three treatments. However, BC and WC significantly decreased the concentrations of leachable IBU from Day 70 to Day 360 ($P \le 0.005$, Table S5; Fig. 2), with shorter $t_{0.5}$ (~13 d) observed in both amended biosolids than unamended biosolids (17 d) (Table 2). In addition, the concentrations of leachable IBU were significantly lower in BC-amended biosolids than in WC-amended biosolids during the late stage of the experiment (Fig. 2). These results indicate a greater efficiency of BC in decreasing leachable IBU than WC, which is also reflected by the shorter $t_{0.5}$ of 12.5 d calculated for BC-amended vs. 13.4 d for WC-amended biosolids (Table 2).

Different from CBZ and IBU, statistically significant concentration reductions of total GEM and NAP in both amended biosolids were observed immediately after blending amendments with biosolids (on Day 0), compared to unamended biosolids ($P < 0.001$, Tables S6 and S8 in the SI; Figs. 3, 4). The concentrations of total GEM on Day 0 significantly decreased by 35–53% in both amended biosolids compared to unamended biosolids, with significantly greater concentration reductions by WC than by BC ($P < 0.005$; Fig. 3). In addition, a significant concentration reduction of total GEM was also observed in BC-amended biosolids on Day 70, compared to unamended biosolids ($P = 0.003$). Both amendments seemed to enhance the removals of leachable GEM during composting, but not total GEM, with greater removal rates and shorter $t_{0.5}$ observed in both amended biosolids ($t_{0.5}$: 40–50 d) than unamended biosolids ($t_{0.5}$: 81 d) (Tables 2 and S16).

Both BC and WC amendments exhibited statistically significant concentration reductions for total NAP throughout 360-d composting, compared to unamended biosolids ($P < 0.001$; Table S8 in the SI). Similar to GEM, on Day 0, immediate concentration reduction of total NAP was observed in BC-amended (28%) and WC-amended (39%) biosolids, compared to unamended biosolids ($P < 0.001$, Table S8; Fig. 4). Amendments also enhanced the removals of leachable NAP compared to unamended biosolids, but the effect was only significant on Days 70 and(or) 240 ($P \le 0.024$, Table S9 in the SI; Fig. 4). Both amendments exhibited the greatest enhancement on the removal rates of both total and leachable NAP among the pharmaceuticals investigated (Table S17). The $t_{0.5}$ of total and leachable NAP in both amended biosolids was shorter by 54–70% than that in unamended biosolids (Table 2).

Overall, BC and(or) WC amendments increased the removals of target pharmaceuticals (total and/or leachable); but the extent of removal was variable. Based on the reduction in concentration and the calculated $t_{0.5}$, the enhanced removals followed the order: NAP ≫ GEM > IBU ≫ CBZ. The limited enhancement of CBZ removal is likely due to its strong recalcitrance which has been extensively reported (Biel-Maeso et al., 2019; Topp et al., 2008). Enhanced removals of target pharmaceuticals during composting as a result of addition of BC or WC to biosolids have not been previously reported. However, BC and WC have been extensively used for removing pharmaceuticals from contaminated water and solid matrices (Czech et al., 2021; Liu et al., 2019; Min et al., 2018; Tseng et al., 2020).

3.7. Mechanisms for enhanced removals of pharmaceuticals by BC and WC during composting

Amending biosolids with BC or WC provided additional reactivity that further enhanced the removal efficiency (Figs. 1–4) and led to shorter $t_{0.5}$ (Table 2) of target pharmaceuticals, compared to unamended biosolids (except for total CBZ in BC-amended biosolids; Fig. 1 and Table 2). The Airex 2 BC used in this study contains many functional groups, including aromatic, carboxyl, carbonyl, phenolic, and O-alkyl functional groups (Clemente et al., 2017). The enhanced removals of target pharmaceuticals by BC compared to unamended biosolids can occur through a variety of mechanisms between the functional groups in BC and pharmaceuticals, including hydrophobic interactions, π-π electron donor-acceptor (EDA) interactions, π-π electron coupling interactions, electrostatic interactions, pore fillings, Van der Waals forces, and hydrogen bondings (Chen et al., 2017; Inyang and Dickenson, 2015; Liu et al., 2019; Oba et al., 2021; Ocampo-Perez et al., 2019). Compared to unamended biosolids, the addition of BC to biosolids improved air penetration and provided an additional source of available C (Fig. S1). Both factors may have enhanced microbial activity in the mixture.

Hydrophobic interactions likely occur between the hydrophobic aromatic rings in CBZ, GEM, and IBU and hydrophobic condensed-aromatic structures in BC. The aromatic rings in the target pharmaceuticals (CBZ, IBU, GEM, and NAP) can also interact with the aromatic structures in BC through π-π interactions. Chen et al. (2017) reported that hydrophobic and π-π interactions are the predominant adsorption mechanisms of CBZ on a peanut shell-derived biochar. The high adsorption efficiency (99% removal) of CBZ on BC was also illustrated by Dalahmeh et al. (2018).

The N, $-NH_2$, C═O, —O—, heterocyclic rings, and carboxyl groups in the target pharmaceuticals are electron withdrawing functional groups; they can thus interact with BC (π-electron rich aromatic structures) through π-π electron-donor-acceptor (EDA) interactions. Czech et al. (2021) reported the strong π-π EDA interactions for adsorption of NAP on BC, which follows pseudo-second order models with an adsorption capacity of 127 mg g^{-1}. π-π EDA interactions can also occur between the carboxyl, carbonyl, and phenolic groups on carbonaceous sorbents and aromatic ring of IBU (Delgado et al., 2015; Oba et al., 2021).

The target pharmaceuticals are either neutral (CBZ) or negatively charged (IBU, GEM, and NAP) (Table 1). Electrostatic interactions between neutral/negatively charged pharmaceuticals and negatively charged BC are negligible and not considered as a removal mechanism of the target pharmaceuticals by BC in this study. Hydrogen bonding occurs between H donors (such as –NH–, $-NH_2$, –OH) and H acceptors (such as C═O and –OH) in the BC and pharmaceuticals.

Compared to unamended biosolids, enhanced removals of target pharmaceuticals as a result of amendment WC to biosolids are likely through the improved microbial degradation and sorption of target pharmaceuticals by WC (Li et al., 2015; Tseng et al., 2020). WC can provide initial additional sources of available C for microbial degradation of the target pharmaceuticals (SI, Fig. S1). WC also contain lignin that breaks down more slowly than other forms of organic matter during composting. Lignin not only allows better air penetration within biosolids, which promotes the aerobic degradation of pharmaceuticals, but also enhances the bioavailability of the contaminants to microbes (Chen et al., 2004).

Tseng et al. (2020) investigated the biodegradation and sorption of CAF, CBZ, IBU, and other four emerging contaminants in a WC reactor, and reported removals ranging from ≤15% to ≥80%. Incorporation of fungi to wood has been used to enhance contaminant removals. Torán et al. (2017) observed high removals (75–90%) of IBU, NAP, and ketoprofen in a fluidized bed-reactor packed with immobilized polypore mushrooms (*T. versicolor*) on wood pellets. Removals of NAP and CBZ were improved by 4% and 30%, respectively, through addition of WC with an immobilized white fungus (*Phanerochaete chrysosporium*) to water (Li et al., 2015). In addition, combining BC and WC can also enhance removals of organic contaminants from water (Ashoori et al., 2019).

These enhanced removals of contaminants by addition of BC and(or) WC are consistent with this study. However, in this study, neither removal efficiency nor $t_{0.5}$ of total CBZ was improved by amendment BC, with higher total concentration and much longer $t_{0.5}$ compared to unamended biosolids (Table 2 and Fig. 1). This is likely due to either possible conversion of CBZ metabolites to their parent compound (Miao et al., 2005) that was more pronounced in BC-amended biosolids or the strong sorption of CBZ by BC (Dalahmeh et al., 2018), or the combination of both. The reasons behind this result are unclear and require further study. Similar to this study, positive, negative, or neutral enhancement on removals of 10 organic contaminants in lime- and WC-amended biosolids during composting has been reported (Lozano et al., 2014).

3.8. Effect of BC and WC amendments on leachability (mobility) of pharmaceuticals in biosolids

The leachability of a pharmaceutical is a function (ratio) of leachable and total concentration at a specific curing time. The interactions between two factors treatment and composting time for the leachabilities of all target pharmaceuticals were significant. Therefore, the effects of treatments on the leachability of a target pharmaceutical were compared at a given composting time (Tables S10–S13 in the SI). Overall, amendments BC and WC exhibited different (positive or negative)

impacts on the leachability of target pharmaceuticals over composting (Figs. 1–4).

Carbamazepine is the most recalcitrant pharmaceutical in this study. Its leachability in all three treatments exhibited an overall decreasing trend over composting period, but was only statistically significant in BC-amended biosolids between Days 0–70 and Days 240–360 ($P \le 0.005$; Table S10) and in WC-amended biosolids between Day 0 and Day 240 ($P = 0.002$). Statistical analysis indicated that BC and WC significantly decreased the leachability of CBZ from Days 70 to 360, compared to unamended biosolids ($P \le 0.016$, Table S10 in the SI; except for WC-amended biosolids on Day 360). Biochar seemed to be more effective in reducing the leachability of CBZ than WC, but only significantly on Day 360 ($P = 0.002$; Fig. 1).

The leachability of IBU in unamended and WC-amended biosolids followed an overall decreasing trend during the early stage of the experiment (significantly in WC-amended biosolids, $P < 0.001$), followed by an increasing trend during the late stage of the experiment (significantly in unamended biosolids, $P < 0.001$; Table S11 in the SI; Fig. 2). However, the leachability of IBU in BC-amended biosolids showed a significant decrease over 360-d composting by up to 89% ($P < 0.001$; Fig. 2). Both amendments, especially BC, significantly decreased the leachabilities of IBU, compared to unamended biosolids. In addition, BC was more effective in reducing IBU leachability than WC; statistically significantly lower leachability of IBU was observed in BC-amended biosolids, compared to unamended and WC-amended biosolids ($P \le 0.019$, Table S11 and Fig. 2).

Erratically temporal trends of the leachability of GEM were observed in the three treatments, with the exception of a significant leachability reduction between Days 0–70 and Day 240 in BC-amended biosolids ($P \le 0.002$, Table S12 in the SI and Fig. 3). Both amendments decreased the leachability of GEM during the late stage of the experiment, compared to unamended biosolids; however, a significant difference was only observed on Day 240 in BC-amended biosolids ($P < 0.001$; Fig. 3).

Statistically significant decreases of the leachability of NAP between the early stage and late stage of the experiment were observed in all treatments ($P < 0.001$ in Table S13 and Fig. 4), with leachability reduction of 90% in unamended biosolids, 87% in BC-amended biosolids, and 74% in WC-amended biosolids. However, statistically significant enhancement in NAP leachability by BC and WC were observed in both amended biosolids during the middle and late stage of the experiment ($P \le 0.01$). Moreover, WC were statistically more effective in enhancing the leachability of NAP than BC during Days 120–360 ($P \le 0.028$).

Effect of organic amendments (BC and WC) on the leachability of pharmaceuticals investigated in this study during composting has not been previously reported. Wang et al. (2018) reported similar reduced mobility of CBZ and enhanced mobility of NAP over a 63-d of curing by an inorganic lime amendment. In addition, Wang et al. (2019) noted the enhanced leaching of mobile fractions of pharmaceuticals (GEM, fluoxetine, and triclosan) with lime addition over 42-d curing, but reduced leaching of these mobile pharmaceuticals by a mixed amendment of lime and mussel shell. Although BC and WC have different effects on the leachability of target pharmaceuticals in this study, relatively lower total and/or leachable masses of target pharmaceuticals were observed in the amended biosolids compared to the unamended materials (Figs. 1–4), indicating their retention and/or enhancement of degradation of target pharmaceuticals.

3.9. pH, EC, DOC, DTC, TOC, and TC of biosolids during composting

Overall, composting reduced the pH of both unamended and amended biosolids from initial values of ~8.1 to final values of ~7.4 after 360 d of incubation; BC and WC did not alter the pH of amended biosolids compared to the unamended biosolids (SI, Fig. S2). Composting reduced the electrical conductivity (EC) of unamended biosolids, from 3.2 to 2.0 mS cm^{-1}, over the entire incubation time; however, relatively higher EC was observed in the BC- and WC-amended biosolids (SI, Fig. S3). Composting not only enhanced the degradation of the target pharmaceuticals in the biosolids, but also greatly reduced the DOC and DTC in both unamended and amended biosolids, with concentrations decreasing from > 6000 to < 1000 mg kg^{-1} after 360 d of composting (SI, Fig. S1). Similarly, a marked decrease in DOC concentration during biosolids composting has also been previously reported (Wang et al., 2013). Mass percentages of solid TC and TOC (accounted for >87% of TC) in all three treatments also decreased during composting, with reductions of 2–7% (SI, Fig. S4). Concentrations of bio-available K, P, and N in unamended biosolids were similar to WC-amended biosolids; BC provided additional bio-available N to the biosolids during the late stage of the experiment (SI, Fig. S5).

4. Conclusions

Biosolids, derived from cities in southern Ontario, Canada, contained variable concentrations of target pharmaceuticals CBZ, IBU, GEM, and NAP (2–140 μg kg^{-1}), with the highest concentration for IBU. Composting enhanced removals of total and leachable pharmaceuticals in both unamended and BC- and WC-amended biosolids, with the extent of removal specific to the properties of each pharmaceutical. Amending biosolids with BC or WC significantly enhanced the degradation and/or retention (sorption) of target total and(or) leachable pharmaceuticals CBZ, IBU, GEM, and NAP, especially GEM and NAP, compared to unamended biosolids, with shorter contaminant half-lives in amended biosolids. Amendments exhibited different effects (positive or negative) on the leachability (mobility) of the target pharmaceuticals; however, BC and(or) WC generally reduced total and(or) leachable (mobile) amounts of the target pharmaceuticals over the composting time compared to unamended biosolids.

Results of this study indicate that composting is an effective treatment technology for removing pharmaceuticals in biosolids. Pretreatment of biosolids by composting should be considered before field applications to reduce the amount of total and leachable pharmaceuticals in biosolids. In addition, BC and WC are effective amendments for biosolids to minimize leaching of target pharmaceuticals; they demonstrate potential for practicable use as amendments to reduce pharmaceutical contamination from biosolids. When applicable, amending biosolids with BC or WC prior to composting may represent an even more effective method for prevention, control, and mitigation of pharmaceutical contamination from land applications of biosolids.

CRediT authorship contribution statement

YingYing Liu: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Carol J. Ptacek:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Suzanne Beauchemin:** Conceptualization, Methodology, Investigation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Ted MacKinnon:** Investigation, Writing – review & editing. **David W. Blowes:** Resources, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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