Science of the Total Environment 550 (2016) 504–513

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Properties of biochar-amended soils and their sorption of imidacloprid, isoproturon, and atrazine

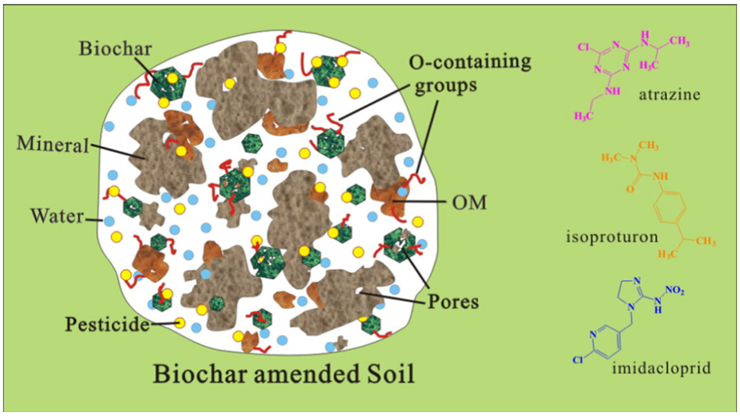
Jie Jin [a,c], Mingjie Kang [a], Ke Sun [a,*], Zezhen Pan [a], Fengchang Wu [b], Baoshan Xing [c]

[a] *State Key Laboratory of Water Simulation, School of Environment, Beijing Normal University, Beijing 100875, China*
[b] *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China*
[c] *Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA*

## HIGHLIGHTS

- Sorption of pesticides by biochar–soil mixtures was determined.
- Sorption of the mixtures increased as expected with biochar dose.
- The OC content and surface area of the mixtures could be lower than prediction.
- Intrinsic sorption by biochars could be either overpredicted or underestimated.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 27 October 2015
Received in revised form 19 January 2016
Accepted 19 January 2016
Available online xxxx

Editor: D. Barcelo

*Keywords:*
Biochar
Soil
Sorption
Pesticides
Herbicides
Insecticides

## ABSTRACT

Biochars produced from rice straw, wheat straw and swine manure at 300, 450 and 600 °C were added to soil at 1, 5, 10, or 20% levels to determine whether they would predictably reduce the pore water concentration of imidacloprid, isoproturon, and atrazine. The sorption capacity of the mixtures increased with increasing biochar amounts. The enhanced sorption capacity could be attributed to the increased organic carbon (OC) content and surface area (SA) as well as the decreased hydrophobicity. Biochar dominated the overall sorption when its content was above 5%. The OC contents of the mixtures with 10% and 20% biochar were generally lower than the predicted values. This implies possible interaction between soil components and biochar and/or the effect of biochar oxidation. For soils amended with biochars produced at 300 °C, the $N_2$ SA ($N_2$-SA) values were underestimated. The predicted $CO_2$ SA ($CO_2$-SA) values of the mixtures at the biochar content of 10% and 20% were generally higher than the experimental values. Sorption of imidacloprid to the soils amended with biochar at 10% and 20% levels, excluding the soils amended with rice (SR300) and wheat (SW300) straw-derived biochar produced at 300 °C, was lower than the predicted value. For SR300 and SW300, the intrinsic sorption capacity of biochar was enhanced by 1.3–5.6 times, depending on the biochar, solute concentration, and biochar dose. This study indicates that biochars would be helpful to stabilize the soil contaminated with imidacloprid, isoproturon, and atrazine, but the sorption capacity of the mixtures could exceed or fall short of predicted values without assuming a cross-effect between soil and biochar.

---

* Corresponding author.
*E-mail address:* sunke@bnu.edu.cn (K. Sun).

http://dx.doi.org/10.1016/j.scitotenv.2016.01.117
0048-9697/

## 1. Introduction

Biochar refers to carbonaceous residues of incomplete combustion of carbon-rich biomass under oxygen-limited conditions at relatively low temperatures (<700 °C) (Lehmann and Joseph, 2009). It has attracted more and more attention as a soil amendment at levels up to 5%–10% by weight (about 100 t/ha) to improve soil fertility and plant productivity and sequester carbon (Lehmann, 2007; Lehmann and Joseph, 2009; Woolf et al., 2010). Lately biochar is of interest as an effective sorbent for hydrophobic organic compounds (HOCs) in soil (Jones et al., 2011; Teixidó et al., 2013; Yang and Sheng, 2003). Related pyrogenic substances, known as environmental black carbon (BC), are widely present in soils and sediments, in fire-impacted soils comprising up to 30–45% of total organic carbon (OC) (Cornelissen et al., 2005). BC exhibited 10–1000 times stronger affinity with HOCs than natural organic matter (NOM) (Cornelissen and Gustafsson, 2005; Cornelissen et al., 2005; Yang and Sheng, 2003), so even a small amount of environmentally or artificially added BC in soil and sediment should dominate the overall sorption of organic contaminants. For instance, at content of 0.1%, the biochar produced from pine needle at 400 °C dominated the overall sorption of naphthalene (Chen and Yuan, 2011). Moreover, sorption in the biochar–soil mixtures was generally enhanced with increasing biochar dose compared to the soil alone (Chen and Yuan, 2011; Teixidó et al., 2013). The sorption ability of HOCs to biochar has been reported to be affected by many factors, such as heat treatment temperatures (HTTs) and feedstock sources (Chen et al., 2008; Sun et al., 2012; Sun et al., 2013a). However, previous studies about biochar amendment mainly focused on the biochar produced from plant residue (Chen and Yuan, 2011; Teixidó et al., 2013). The enhancement effect of animal waste-derived biochars on soil sorption needs further study.

On the other hand, the sorption ability of biochar was known to depend strongly on its physicochemical properties, such as surface area, bulk or surface polarity, and mineral content (Chen et al., 2008; Sun et al., 2012; Sun et al., 2013a). With addition of biochar to soil, the physicochemical properties of biochar are expected to be changed, due to the possible interactions of biochar with soil components, such as abundant minerals or dissolved organic carbon (DOC). The components could block pore surfaces or compete for binding sites of biochar, making biochar surface less available for HOCs (Chen and Yuan, 2011; Cornelissen and Gustafsson, 2005). In addition, a reduction of the surface area (SA) of biochars was observed with increasing DOC contents (Garcia-Jaramillo et al., 2015). Thus, most of studies observed sorption attenuation of biochars coexisted with soil, compared to the pristine biochar (Chen and Yuan, 2011; Teixidó et al., 2013). However, a recent study found that alumina and montmorillonite exhibited a pore-expanding effect on biochar, which resulted in higher sorption of herbicides to the mineral-treated biochars than to the untreated biochars (Li et al., 2015). The conflicting conclusions may result from the different contents of minerals in the mixtures. Further research is still needed to sort out the effects of soil constituents (e.g., minerals and OC) on the properties and sorption capacity of biochars.

Consequently, the primary objective of this study is to investigate physicochemical properties (e.g., C%, surface or bulk polarity, and SA) of soil mixtures containing various biochars. At the same time, the effects of these biochars on sorption capacity of biochar-amended agriculture soil were also evaluated. The pesticides selected for this study were: atrazine and isoproturon, toxic herbicides that have been widely used around the world to control annual grasses and broadleaf weeds in agriculture; imidacloprid, an insecticide applied to control sucking and soil insects including plant hoppers, aphids, termites and other harmful pest species (Lewis et al., 2015). All these compounds along with their metabolites are frequently detected in surface and ground waters as a result of their high leachability, which leads to a potential long-term threat to the environment because of their persistence in the environment (Barbash et al., 2001; Garrido-Herrera et al., 2006). It is hypothesized that the effect of soil minerals on the SA of biochar is dependent on the application rate of biochar, i.e., the mineral contents in the mixtures. Also, due to the mixing of biochar with soil, the intrinsic sorption capacity of biochar would be different in mixtures with different biochar contents.

## 2. Materials and methods

### 2.1. Soil, pure biochars and biochar-amended soils

The soil used in the study was collected from the 0–20 cm horizon of an agricultural field in Tongzhou District, Beijing, China. Its pH in water was 8.6. It was a silt loam soil with 8.7% sand, 76.1% silt, and 15.2% clay. The soil minerals were mainly composed of illite and montmorillonite. Also, various kinds of herbicide and pesticide are widely used in this area (Sun et al., 2013). Thus, it is of interest to investigate the impacts of biochar addition on sorption of the chemicals by soil. The soil was air-dried at room temperature and the plant residues were removed before use.

The pure biochars were produced from rice, wheat straw and swine manure biomass; the details on biochar production were described elsewhere (Sun et al., 2013a). Briefly, all these air-dried feedstocks were ground to pass through a 1.5 mm mesh, and then charred for 1 h in a closed container under oxygen-limited conditions in a muffle furnace. Next, the HTTs were raised to target temperature, that is, 300, 450, and 600 °C, at a ramp rate of 10 °C/min. The obtained biochars were washed with 0.1 M HCl followed by ionized water flushing till neutral pH (Azargohar and Dalai, 2006), then were oven dried at 105 °C. According to the feedstock source (rice and wheat straw, swine manure), the pure biochars produced at 300 °C, 450 °C and 600 °C were referred as R300, R450, R600; W300, W450, W600; S300, S450, S600. The biochar amended soils used in the experiment were prepared by mixing the soil and pure biochars at different ratios. The percentages of each biochar material in the soil were 1%, 5%, 10% and 20% (w/w). To guarantee uniformity, both the soil and the biochar samples were passed through a 0.25 mm sieve prior to use in the study. The soil and biochar were mixed by hand first. Then, they were thoroughly mixed on a rotary shaker for 7 d as sorbents for sorption experiment. The biochar–soil mixtures were named as 1%SR300, 5%SR300, 10%SR300, 20%SR300; 1%SR450, 5%SR450, 10%SR450, 20%SR450; 1%SR600, 5%SR600, 10%SR600, 20%SR600; 1%SW300, 5%SW300, 10%SW300, 20%SW300; 1%SW450, 5%SW450, 10%SW450, 20%SW450; 1%SW600, 5%SW600, 10%SW600, 20%SW600; 1%SS300, 5%SS300, 10%SS300, 20%SS300; 1%SS450, 5%SS450, 10%SS450, 20%SS450; 1%SS600, 5%SS600, 10%SS600, and 20%SS600. The first capital "S" represents soil, and the second capitals stand for pure biochars (i.e., R—rice, W—wheat and S—swine).

### 2.2. Sorbates

Imidacloprid (1-[(6-chloro-3-pyridinyl) methyl]-*N*-nitro-2 imidazolidinimine, purity > 98%) and isoproturon (3-(4-isopropylphenyl)-1, 1-dimethylurea, purity > 99%) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan) with a reported purity of >97%. The selected properties of these pesticides are given in Table S2.

### 2.3. Characterization of sorbents

The bulk C, H, O and N content of the pure biochars, soil and biochar-amended soils were measured by Elementar Vario ELIII elemental analyzer through complete combustion. Ash content was determined by heating samples at 750 °C for 4 h. The solid-state cross-polarization magic-angle-spinning $^{13}$C nuclear magnetic resonance ($^{13}$C NMR) spectra data of pure biochars were obtained with Bruker Avance 300 NMR spectrometer (Karlsruhe, Germany). The detailed NMR running