Science of the Total Environment 565 (2016) 339–345

Contents lists available at ScienceDirect

Science of the Total Environment

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

The effects and mode of action of biochar on the degradation of methyl isothiocyanate in soil

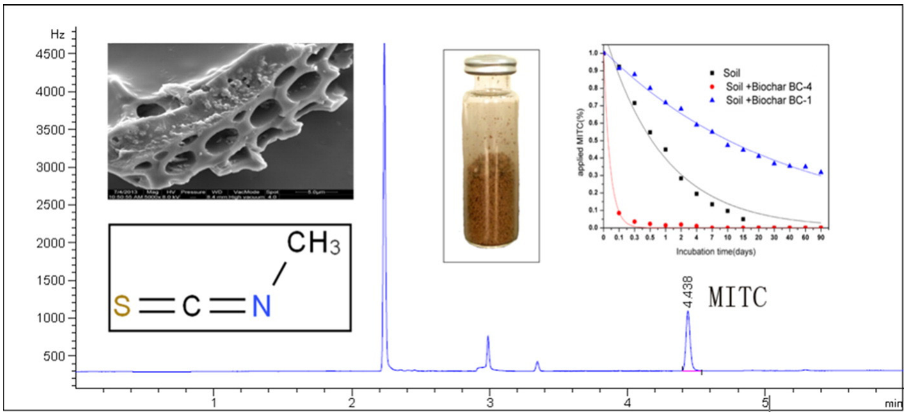
Wensheng Fang, Qiuxia Wang *, Dawei Han, Pengfei Liu, Bin Huang, Dongdong Yan, Canbin Ouyang, Yuan Li, Aocheng Cao *

Plant Protection Institute of Chinese Academy of Agricultural Sciences, State key Laboratory for Biology of Plant Disease and Insect Pests, Beijing 100193, China

HIGHLIGHTS

- Biochars can delay or decrease the persistence of MITC in soil.
- MITC degradation be inferred from the H/C value, SSA, C content and pH of biochars.
- The acceleration or deceleration of MITC degradation by biochar amendment can be contribute to reduce MITC emissions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 January 2016
Received in revised form 17 April 2016
Accepted 23 April 2016
Available online xxxx

Editor: Ajit Sarmah

Keywords:
Fumigant
MITC
Abiotic degradation
Adsorption
Fertilizer

ABSTRACT

Biochar is used as a new type of fertilizer in agriculture; however, its effect on the fate of fumigants in soil is not fully understood. The objective of this study was to investigate the effects of biochar on methyl isothiocyanate (MITC) degradation in soil in laboratory incubation experiments, including the effects of biochar composition, amendment rate, moisture, temperature, soil sterilization and soil type. The dissipation pathways of MITC in biochars included adsorption and chemical degradation. The adsorption of MITC by biochars was positively correlated with the specific surface area (SSA) of the biochar. Biochar with a high SSA and low H/C value (such as biochar type BC-1) reduced MITC degradation in soil substantially; following BC-1 amendment, the degradation rate was 73.9% slower than in unamended soil. The degradation of MITC was positively correlated with the H/C value of biochar, and MITC degradation in soil increased 2.2–31.1 times following amendment with biochars with higher H/C values (e.g. biochar types BC-3–6). The biochar with the lowest organic matter and low H/C value did not affect the fate of MITC in soil. Biochars affect abiotic degradation processes more than biodegradation. When soil samples had a higher water content (>10%), higher temperature (40 °C), and lower organic matter, the addition of BC-1 biochar reduced MITC degradation substantially; and this did not change significantly when the amendment rate increased. However, BC-4 biochar accelerated MITC degradation with increasing amendment rate, increasing temperature, and decreasing soil water content. The differences in degradation rates due to soil type were minimized by amendment with BC-4, but significant differences in BC-1. The results showed that the rational use of biochar has the potential to reduce MITC emission by accelerated degradation and adsorption.

---

* Corresponding authors at: Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing 100193, China.
E-mail addresses: qxwang@ippcaas.cn (Q. Wang), caoac@vip.sina.com (A. Cao).

http://dx.doi.org/10.1016/j.scitotenv.2016.04.166
0048-9697/© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Biochar (BC) is a carbonaceous material made from a variety of organic feedstocks, such as crop straw, farmland weeds or forest trees, at low temperature (<700 °C) and under limited oxygen conditions (Lehmann and Joseph, 2009). As a soil conditioner, biochar with high carbon content, rich pore structure, and stable physical and chemical properties (Chen and Meng, 2013) is widely used as a new type of fertilizer in agriculture. Many studies have shown that the application of biochar in agricultural soil can change the soil's physicochemical and biological properties, improve soil fertility, immobilize nutrient elements, and increase crop yield (Novak et al., 2009). The high stability and resistance of biochar to degradation, allow this material to mitigate climate change through direct carbon sequestration (Lehmann, 2007; Lehmann et al., 2011), as well as potentially reducing soil greenhouse gas emissions (i.e. N_2O) following amendment (Ippolito et al., 2012; Spokas et al., 2009). In addition, biochar can adsorb organic contaminants and heavy metals (Karami et al., 2011; Minori et al., 2010), affecting their fate in soil. Zhang et al. suggested that biochar can suppress the degradation of diuron in soil through adsorption (Yang et al., 2006; Zhang et al., 2004), and Nicolai David found that biochar accelerated the degradation of atrazine (Nicolai David et al., 2013). Therefore, through adsorption or degradation, biochar has the potential to increase or reduce the concentration of organic pollutants in soil, such as pesticides in soil. However, when biochar is applied to the soil as a fertilizer it may also affect the efficacy of pesticides in soil (Graber et al., 2011; Kookana, 2010), especially fumigants.

Methyl isothiocyanate (MITC), the principal breakdown product of metham-sodium and dazomet, is a viable alternative to methyl bromide which is being phased out because it depletes stratospheric ozone (Ruzo, 2006). MITC is generally used prior to seeding or transplanting to control soil insects, fungi, nematodes, and weed seeds (Frick et al., 1998). The recommended application dose of MITC is 250 kg/ha, which is two orders of magnitude greater than the dose of most conventional pesticides (Kiely et al., 2004; Saeed et al., 1997). Therefore, the effect of biochar on the fate of MITC in soil is expected to be greater than on other pesticides. Moreover, MITC has a relatively high vapor pressure (20.7 mm Hg at 20 °C) and is easily emitted to the air, and this loss of MITC gas may cause environmental and health problems due to its irritant, lachrymatory and toxic qualities (Kiely et al., 2004). Hence, it is necessary to develop strategies to minimize emissions. The application of organic amendments (e.g. manure) on the soil surface has been demonstrated to substantially reduce volatilization losses (Dungan et al., 2003; Gan et al., 1998), and may increase the soil's capacity to degrade MITC by abiotic and biotic mechanisms. Wang et al. demonstrated that biochar can reduce 1.3-dichloropropene emission by >92% by adsorption (Wang et al., 2014), and reduce chloropicrin losses by 85.7–97.7% by accelerated degradation (Wang et al., 2015). This clearly indicates that biochar has great potential in terms of reducing MITC emission.

When used as an organic amendment, biochar's strong adsorption capacity may decrease MITC degradation and increase the fumigant's residence time in soil, however, in contrast, the vast amount of free radicals (Graber et al., 2011) in biochar may potentially accelerate MITC degradation via radical reaction (Lu et al., 2014). To date, the influence of biochar on MITC degradation in soil has not been well understood. Moreover, different types of biochars have different physical and chemical characteristics depending on the specific feedstock and production parameters (Lua et al., 2004), and this may also influence the fate of MITC in soil. The primary objectives of this study were to investigate the effects of biochars produced from different feedstocks on MITC degradation in soil, including the effects of biochar characteristics, amendment rate, moisture, temperature, soil sterilization and soil type, and to identify the mechanisms of biochar's interaction with MITC. Information obtained from this study will be useful for evaluating the effects of biochars on the bioavailability and efficacy of MITC, as well as identifying the potential for biochar to reduce MITC emissions in agriculture.

2. Materials and methods

2.1. Soil, biochar and chemicals

Three soil samples (soil-1, soil-2 and soil-3) used in this experiment were collected in Beijing, Hunan province, and Shanxi province of China, respectively, at the depth of 0–20 cm. The physical and chemical characteristics of the soil are shown in Table 1. All soil samples were passed through a 2 mm sieve before use. The study tested six different types of biochar (BC-1 to BC-6), produced from oak, mixed hardwoods, macadamia, wood pellets, pine bark and wood chip feedstocks. Table 2 lists the feedstock and physical and chemical properties of the tested biochars. BC-1 was a commercial biochar, CoolTerra™ (purchased from Coolplanet company, America). The specific surface area (SSA) of the biochars was determined using V-Sorb 2800P surface area and pore distribution analyzer (Gold APP Instruments Corporation, China). The elemental composition was measured using a CHN element analyzer (vario PYRO cube, Elementar Analysensysteme GmbH, Germany). The biochar was sieved through a 2-mm screen before use. Analytical standard MITC (98.0% purity, Damas-beta, China) was used to make standard curves and degradation experiments. Ethyl acetate and sodium sulfate anhydrous (both analytical grade) were obtained from Beijing Chemical Works, China.

2.2. Degradation experiment

Laboratory incubation studies were conducted to determine the effects of biochar characteristics, soil sterilization, amendment rate, soil water content and temperature on the degradation of MITC in soil-1 (simplified as soil in the following paragraphs). The procedures were carried out as follows:

2.2.1. Biochar characteristics

The water content of soil samples was adjusted to 10% and 10.09% (w/w). Each tested biochar was added (at 1% rate) to a soil sample with 10.09% water content, generating a mixture of soil and biochar with 10% water content. 8 g (oven dry basis) soil, with or without biochar, was placed in a 20 ml clear headspace vial. 5 μl standard solution (ethyl acetate solution containing 48 mg ml^{-1} MITC) was added and the vials were immediately crimp-sealed with an aluminum cap and Teflon-faced butyl-rubber septum (Agilent Technologies, Inc., USA), giving an initial MITC concentration of 30 μg g^{-1} soil. The vials were inverted and placed in an incubator settled at 30 °C. Each treatment was repeated three times.

The degradation rate of MITC was also determined in each of the test biochars without the addition of soil. The preparation method was the same as the degradation experiment in soil, except that 0.2 g biochar was placed in each vial instead of the soil/biochar mixture. BC-1 was a commercial biochar (wood feedstock) which had a high SSA (348.84 m^2 g^{-1}) and low H/C value (0.07). BC-4 also had

Table 1
Physical and chemical properties of tested soils.

Site[a]	Silt(%)	Clay(%)	Sand(%)	pH	OM[b](g kg^{-1})	Soil type[c]
Soil-1	5.83	20.93	73.24	7.1	9.12	Sandy
Soil-2	16.45	50.22	33.35	8.04	7.19	Clay-loam
Soil-3	11.69	55.28	23.03	7.55	19.05	Clay

[a] Soil-1 = Beijing soil, from Shunyi District, Beijing, China (116.33W, 39.73N); Soil-2 = Hunan soil, from Yongzhou, Hunan Province, China (111.63W, 26.22N); and Soil-3 = Shanxi soil, from Xi'an, Shanxi Province, China (108.95W, 34.22N).

[b] OM = organic matter(g kg^{-1}) determined by $K_2Cr_2O_7$ titration.

[c] Soil particle size measured by Mastersizer particle size analyzer and classified by the international soil texture classification standard.