P-26

Atrazine Sorption in Soil Treated with Biochar

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Keywords Pyrogenic carbon; biochar; pesticides; atrazine; sorption; high performance liquid chromatography

Abstract Biochar has been used worldwide as soil amendment. Due to the high sorption capacity of organic compounds by charcoal in general, the use of biochar can change the soil sorptive properties, that could result in a environmental protective strategy in one hand and/or in need of higher pesticides doses in another hand. However no data in the literature is available about the long term effect of biochar application in the sorptive properties of the soil, even studies about the sorptive properties of soil treated with biochar are scarce, the few available papers are with pure biochar. This unprecedented work, evaluating the sorption of atrazine in a clayed soil treated with biochar, under experimental field conditions, evaluated the sorption isotherms one and three years after the single biochar application (16 Mg ha^{-1} of biochar). One year after the biochar application the K_f was two times higher for the biochar amended soil than for the control one (without biochar). This effect decreases after three years from the application, but it is even significantly higher (50% higher) than the control treatment.

Introduction

Biochar has been used worldwide as soil amendment. Due to the high sorption capacity of organic compounds by charcoal in general, the use of biochar can change the soil sorptive properties (Jin et al., 2016; Zhou et al., 2016), that could result in a environmental protective strategy in one hand and/or in need of higher pesticides doses in another hand. Atrazine is one of the most widely used herbicides in the world and due to its persistency and high mobility in the soil there are special concerning about its environmental risks.

The Freundlich sorption coefficient (K_f) for biochar can be several orders of magnitude higher than for humic substances (Kleineidam et al., 1999) and presents nonlinear isotherms (Freundlich expoent, $n > 1$); and both Freundlich parameters are directly proportional to carbonization intensity (Chen et al., 2008). The sorption ability is related to the surface area, aromaticity and porosity (Beesley et al., 2011; Kookana et al., 2011).

However no data in the literature is available about the long term effect of biochar application in the sorptive properties of the soil, even studies about the sorptive properties of soil treated with biochar are scarce, the few available papers are with pure biochar. This unprecedented work, evaluating the sorption of atrazine in a clayed soil treated with biochar, under experimental field conditions, evaluated the sorption isotherms one and three years after the single biochar application (16 Mg ha^{-1} of biochar).

Materials and methods

Soil samples (clay: 550 g kg^{-1}; Total Organic Carbon: 16 g kg^{-1}) were collected at 0-10 cm in a field trial installed in Santo Antônio de Goiás, Brazil (49º16'54"S, 16º29'59"W). The treatments were: 0 (control) and 16 Mg ha^{-1} of eucalyptus charcoal in a 4 randomized blocks design. Soil samples were collected 1 and 3 years after the single biochar application.

The sorption study was performed using a batch equilibrium method (USEPA, 1992). Preliminarly, the soil/solution ratio was determined and 2 g of soil samples and 4 mL of $CaCl_2$ solution with atrazine were used. The adsorption equilibration time was 72 h and five test substance concentrations are used in the adsorption isotherms: 0.25; 0.5; 1; 2; 5 and 10 mg L^{-1}. Atrazine were determined by HPLC-UV Series 200 equipment (Perkin Elmer, USA) using a chromatographic column C-18 (5 µm, 250 x 4.6 mm) (NST, Brazil).

The data were treated by the linearized Freundlich equation: $\log(q) = \log(K_f) + n \log(C)$. Where q is the sorbed concentration of the studied compound in the solid phase (mg kg^{-1}), C is the solution concentration (mg L^{-1}) after a given contact time and K_f and n are empirical constants related to sorption.

Since this is a longitudinal study, the statistical analyses was performed by Repeated Measures Multivariate Analysis of Variance. Seeking to reduce the statistical residues, the total organic carbon contents before the biochar application was used as a covariate. When the effect was statistically significant ($p<0.05$), the means were compared by Tukey's Test ($p<0.05$).

Results and Discussion

All the determination coefficients (r^2) were higher than 0.98. Examples of adjusted atrazine isoterms is presented in Figure 1.

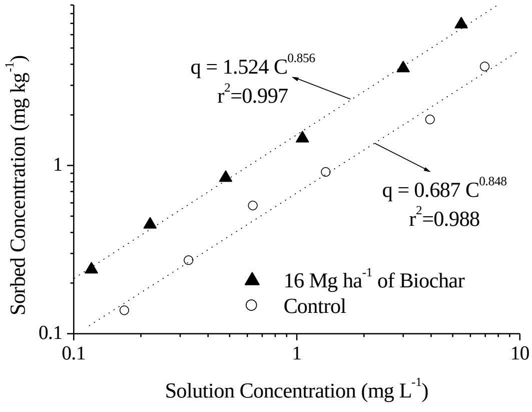

Fig. 1 Typical sorption isotherms of atrazine by soil. The sorption data were fitted with Freundlich sorption isotherm equation (logarithmic form).

Since the Freundlich exponents (n) were statistically equal for all isoterms, the K_f can be statistically compared (Spokas et al., 2009). One year after the biochar application the K_f was 2.22 times higher for the biochar amended soil (Figure 2) than for the control one (without biochar). This effect decreases after three years from the application, but it is even significantly higher (52% higher) than the control treatment.

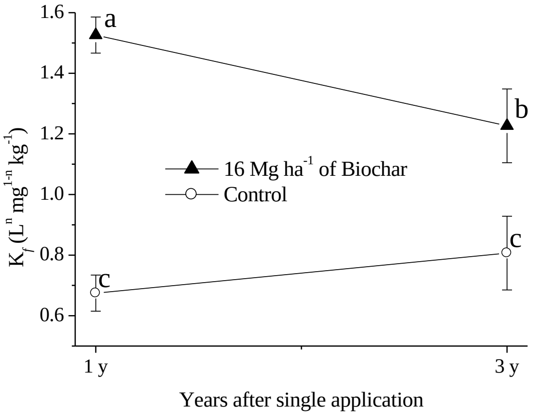

Fig. 2 Freundlich sorption coefficient (K_f) in function of biochar application and time after single biochar application. Vertical bars denote 0.95 confidence intervals. Symbols with different letters differs at 5% probably according Tukey's posthoc test.

The increase of the soil sorption capacity after biochar application has important environmental consequences, specially taking in account the high environmental contamination risk (e.g. ground and surface water contamination) of this persistent and mobile herbicide. Besides, the residual effect, detectable after 3 years of the single biochar application strengthens its use for environmental protection. However attention should be given to the risk of contamination by, for example, Polycyclic Aromatic Hydrocarbons after biochar application (see the abstract of Resende et al.). This decrease in the sorption capacity probably is due to the saturation and/or blocking of the sorptive sites and charcoal pores by colloidal particles such as clay and soil organic matter.

Acknowledgements

This work was supported by National Counsel of Technological and Scientific Development (CNPq) from Brazil. The first author is grateful for CNPq for the research fellowship.

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