Dynamic of Polycyclic Aromatic Hydrocarbons in Soils Treated with Biochar

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Abstract In recent years the interest in pyrogenic carbon for agricultural use (biochar, i.e. carbonized biomass for agricultural use) has sharply increased. However biochar contain dangerous compounds such as Polycyclic Aromatic Hydrocarbons (PAHs), many of them potentially carcinogenic and mutagenic. They are organic compounds formed from incomplete combustion of organic materials and are persistent pollutants. Therefore, PAHs concentrations and their dynamic must be evaluated in soils amended with biochar. For this, soil samples were collected in three experimental areas in different years (1, 3, 5 or 6) after the application of 0 (control) or 16 Mg ha^{-1} of biochar. This is the first report of PAHs persistence up to six years in soil treated with biochar. The biochar application increased total PAHs concentrations up to five years after the application, however the levels have always been an order of magnitude lower the limits of prevention established by International Environmental Agencies for soils. Thus, under the evaluated conditions ,the use of biochar was safe concerning PAHs contamination, besides, after six years of the application, the levels found were similar to the control treatment, making it possible to define a safe frequency of application based on the persistence of PAHs in soil.

Introduction

Biochar is the stable, carbon-rich material produced by pyrolysis under low or no oxygen conditions. It has been applied in an agriculture in order to potentially improve soil fertility (Novotny et al., 2015). During pyrolysis of the biomass, Polyciclic Aromatic Hydrocarbons (PAHs) can be formed. Many of the PAHs are known as carcinogens, mutagens and teratogens and then the United States Environmental Protection Agency (US EPA) has classified 16 PAHs as priority pollutants (Takada et al., 1991; Fabbri et la., 2013). In this context, this work presents the evaluation of eighteen PAHs in soils treated with 16 Mg ha^{-1} of biochar and corresponding control treatment without biochar. The samples were collected in three different experimental areas in Brazil and in different years after the biochar application for evaluate the behavior of PAHs levels over time up to six years after the application.

Materials and methods

Soil samples were collected at 0-10 cm in three experimental areas (experiments I, II and III) where was applied 16 Mg ha^{-1} of biochar (eucalyptus charcoal) in a four randomized blocks design. Experiments (Exp) I and II are located in Nova Xavantina, MT, Brazil (14°34'50"S, 52º24'01"W). In the Exp I the soil samples were collected 3; 5 and 6 years after the biochar application and in Exp II only after 3 years of application. The Exp III is located in Santo Antônio de Goiás, GO, Brazil (49º16'54"S, 16º29'59"W) with collections after 1 and 3 years of the application. Sixteen priority PAHs, after US EPA; the benzo [e] pyrene and; perylene were determined by Gas chromatography–mass spectrometry (GC-MS) in a GC-MS 7890A / 5975C model (Agilent, USA) and separated using a chromatographic column DB17-MS (J & W Columns, USA). The samples were extracted with dichloromethane, which was evaporated and replaced by acetonitrile, with a final volume of 1 ml. Since this is a longitudinal study (observations in time are not independent) and the data is multivariate, for statistical analysis was chosen repeated measures Multivariate Analysis of Variance (MANOVA) approach. The model residues were evaluated for normality and homoscedasticity.

Results and Discussion

Considering all the experimental areas (Experiments I; II and; III), the total concentrations of PAHs (∑PAH) varied across the areas between 7.34 ± 0.83 ng g^{-1} and 26.3 ± 6.64 ng g^{-1} in the control soil samples and between 19.2 ± 0.49 and 39.4 ± 4.35 ng g^{-1} in the biochar amended soil samples. The predominant PAHs in all samples were naphthalene, phenanthrene, pyrene, fluoranthene, perylene and fluorene.

None of the PAHs concentrations, even in biochar amended soils, reached the permissible highest concentration according the Brazilian and European guidelines. In fact, the highest HPA concentration (Naphtalene: 36 ng g^{-1}) was one order of magnitude (28 times) lower than the maximum allowed of 1.00 µg g^{-1} for any of the 16 most important PAHs (Kuśmierz and Oleszczuk, 2014).

For all the experiments the application of biochar affected significantly ($P < 0.005$) the ∑PAH, and for the experiments sampled at different times from the application (Exp I and III), the interaction time x biochar was also statistically significant ($P < 0.005$).

In the experiment I, the longest evaluated (up to 6 years after the single application of 16 Mg ha^{-1} of biochar), after three and five years of application, ∑PAH were statistically significant higher in biochar amended soil sample than in the control (Figure 1), then exhibiting a decrease, and with six years after application of biochar no difference between control and biochar amended soil was observed.

In experiment III, the trend is the same of the experiment I because higher PAHs concentration was found in the biochar amended soil (Figure 1). Also this concentration decreases with time, being smaller after three years than after one year, but still higher than the level observed in control samples. Finally, in the experiment II, sampled only three years after the biochar application, higher PAHs concentration was found in the soil amended with biochar.

These results indicates that biochar is a source of PAHs, however in the evaluated dose and conditions, the PAHs amount is not enough to surpass the national and international limits acceptable. It was expected that PAHs has been formed during the production of charcoal by pyrolysis (Fabbri et al., 2013; Oleszczuk et al., 2013). Besides, after six years of application the PAHs level was similar between the biochar treated and untreated samples, indicating that successive application of 16 Mg ha^{-1} each at least six year should not result in PAHs accumulation in the soil. Furthermore, the diminution in PAHs concentration with the time is more intense at the beginning.

The possible reasons for the ∑PAH decreases with time are microbial degradation of HPA (five- and six-ring PAHs), and volatilization of the remaining HPA (two- to four-ring PAHs) (Nicollini et al., 2015).

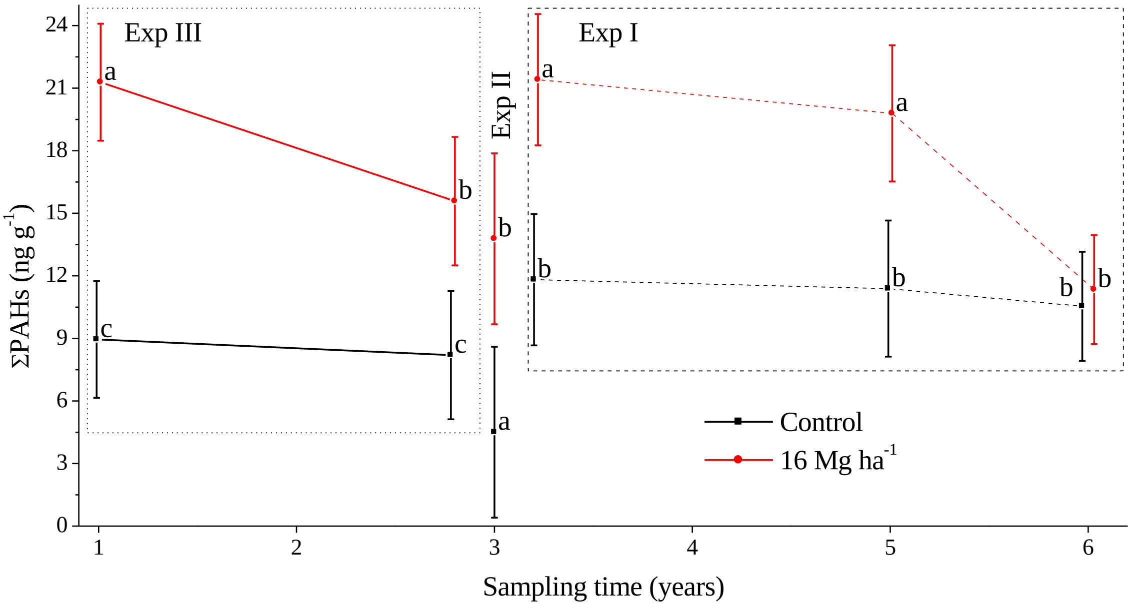

Fig. 1 Total concentrations of PAHs (∑PAH) as a function of time after biochar application(16 Mg ha^{-1}). Means followed by the same letter within each experiment, do not differ statistically at 5% probability by Duncan test. Vertical bars denote a 0.95 confidence interval.

Conclusions

Higher ∑PAH were observed in the soil treated with biochar than in control samples in experiments I, II and III. However the PAHs concentrations found in all the samples were below maximum permissible levels established in Brazil and in some European countries. The findings observed in the experiment I provide that the ∑PAH decreasing with time and after six years of biochar application in the soil there were no difference statistically significant between amended and control samples. The results obtained under field conditions of this study indicate that, under the evaluated conditions, there is no environmental risk if 16 M g ha^{-1} of biochar is used as soil conditioners in agricultural management. They also suggested that in a period of six years there is no risk of PAHs accumulation in the soil.

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