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Effect of pesticides on microorganisms, enzymatic activity and plant in biochar-amended soil

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ABSTRACT

The objective of the study was the determination of the effect of biochar and pesticides (2,4-D and dicamba) on the enzymatic activity and ecotoxicity of soils. The study was realized within the framework of a field experiment in which biochar was applied to soil at two doses, 30 t/ha and 45 t/ha. Soil samples for analyses were taken 17 months after the application of biochar to the soils. In the soil samples the basic physicochemical properties, enzymatic activity and the ecotoxicological properties were analysed. Biochar stimulated the activity of enzymes in almost all experimental treatments. In addition, it also reduced the negative effect of pesticides on the enzymatic activity and on certain microorganisms in the Microbial Assay for Risk Assessment (MARA). More effective reduction of the negative effect was observed for dicamba than for 2,4-D. Depending on the matrix tested (elutaries or solid phase) varied impacts of the biochar and the pesticides on *Lepidium sativum* were observed. 2,4-D had an additive effect with the biochar, significantly increasing the phytotoxicity of the soil relative to the soil without any biochar content.

1. Introduction

Biochar improves many physical, chemical and biological properties of soils (Lehmann and Joseph, 2009) and moreover it has a beneficial effect on the development of soil organisms (Li et al., 2011). In conjunction with its positive effect on the climate, this causes that biochar more and more often finds common application as an additive to soils (Stavi and Lal, 2012). However, based on current information it is known that biochar may contain contaminants (e.g. heavy metals and polycyclic aromatic hydrocarbons) (Freddo et al., 2012; Hale et al., 2012; Hilber et al., 2012). The application of biochar containing those contaminants to soil can, therefore, cause a negative impact on the environment. Enzymatic tests (Gianfreda et al., 2005; Stotzky and Bollag, 2000) and ecotoxicological assays (Kuczyńska et al., 2005; Malara and Oleszczuk, 2012) are effective indicators of soil quality. The advantage of those tests is not only the possibility of estimation of the direct negative effect of various substances on the environment, but also the determination of the potential risk related with their mutual interactions. In addition, as a result of the application of biological tests we get information on potential risks in the context of soil properties. This is important, as the properties of soils may attenuate or intensify the negative impacts of contaminants (Oleszczuk et al., 2012). Soil enzymatic activities are often used for monitoring impacts of soil management, agricultural practices or contaminations on soil health (Gianfreda et al., 2005). Enzymatic activities in soil play an important role because (Gianfreda et al., 2005): (1) all biochemical transformations in soil are dependent on, or related to, the presence of enzymes, (2) enzyme activities are related to soil fertility and may influence soil productivity, and (3) the measurement of specific enzymatic activities may contribute to the understanding of the metabolic processes involved in the biogeochemical cycles of nutrients. In principle, it is assumed that high values of enzymatic activity are evidence of good quality of soil, while low values indicate an incorrect run of biological processes in the soil. Research shows that enzymatic tests can be an effective indicator of soil contamination with heavy metals, pesticides, or hydrocarbons (e.g. polycyclic aromatic hydrocarbons) (Baran et al., 2004; Gianfreda et al., 2005). In spite of the existing data which indicate biochar contamination with heavy metals and PAHs, which may result in the introduction of those contaminants to the soil, the literature does not provide information on how those impacts may affect the biological life. It is assumed that the contaminants occurring in biochar are strongly bound, not easily available for organisms, and thus potentially non-toxic. This is confirmed by the research of Hale et al. (2012) who found that the concentration of bioavailable PAHs in biochars varied from 0.17 ng/L to 10.0 ng/L, which is lower than concentrations reported for relatively clean urban sediments. Our recent study (Oleszczuk et al., 2013) showed, however, that biochars can exert a negative effect on

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microorganisms, crustaceans and plants, though that effect was dependent on the test organism and on the kind of biological assay used. It should be emphasised that the study was conducted on raw biochars (not mixed with soil). To eliminate the potential risk and to verify the safety of application of materials of this kind, additional research is necessary. In this context particularly important are long-term and field studies which permit the obtainment of results concerning the actual conditions. Moreover, studies of this kind take into account the role of the soil as an important factor affecting the ultimate toxicity of the materials studied. The existing publications in this area have been concerned primarily with research conducted under laboratory conditions and for relatively short periods of time (maximum 112 days). From the environmental point of view, longer periods of study, permitting the prediction of effects remote in time, are of extreme importance.

Another important issue that should be addressed in the context of biochar application to soils is the determination of its effect on the activity of pesticides. Although many of the research reports published so far indicate that an addition of biochar to soil affects the sorption of pesticides (Kookana, 2010; Sopeña and Bending, 2013; Tatarková et al., 2013) and their mobility (Kookana, 2010), there is a scarcity of information that would explain how pesticides added to soil containing biochar will impact the enzymatic activity and other ecotoxicological parameters of soils. Taking into account the sorptive properties of biochar, it can have a considerable impact on the fate of pesticides in soil, including inhibition of their effectiveness, increase of their persistence in soil, and an indirect effect on their mobility in the environment. All of those processes may affect the enzymatic activity and the ecotoxicological properties of soils. The infrequent studies addressing these issues are either concerned with a small number of enzymes or of the pesticides under analysis and, as mentioned before, are conducted within a short time-frame.

Enzymatic activity is an indicator that can provide information on soil quality. Whereas, the inclusion of ecotoxicological assays will permit to acquire information on possible threats that may result both from the application of biochar itself as well as of pesticides. The objective of the study was the estimation of the ecotoxicity (Microtox® with *Vibrio fischeri*, MARA with 11 microorganisms, phytotoxicity with plant — *Lepidium sativum*) and of the enzymatic activity (dehydrogenases, urease, acidic and alkaline phosphatase, protease) of soil in the context of application of two different herbicides (2,4-D and dicamba) in 17 months after the application of biochar to the soil, at two different doses (30 and 45 t/ha).

2. Materials and methods

2.1. Characteristic of biochar and soil

Biochar applied to soil was obtained from commercial manufacturer and was produced by pyrolysis where the feedstock is thermochemically decomposed at a temperature range from 350 °C (start of combustion) to 650 °C (max. combustion temperature) in an oxygen-poor atmosphere (1–2% O_2). Biochar was produced of wheat straw and was provided by Mostostal Sp. z o.o. (Wrocław, Poland). The SEM pictures of biochar are presented in Fig. 1.

The chemical properties of biochar, soil and biochar-amended soil were determined by standard methods. The pH was measured potentiometrically in 1 M KCl after 24 h in the liquid/soil ratio of 10. The cation exchange capacity (CEC) and available potassium, phosphorus and magnesium were determined according to procedures for soil analysis (van Reeuwijk, 1992). Total organic carbon (TOC) was determined by TOC-VCSH (SHIMADZU) with Solid Sample Module SSM-5000. The total nitrogen (N_t) was determined by the Kjeldahl's method without the application of Dewarda's alloy (Cu–Al–Zn alloy-reducer of nitrites and nitrates) (van Reeuwijk, 1992).

To analyse the textural characteristics of biochar, low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2405 N adsorption analyzer. The specific surface area SBET was calculated according to the standard BET method. Carbon, hydrogen, and nitrogen contents of the biochars were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalysed combustion followed by infrared detection of resulting CO_2, H_2 and NO_2 gases. SEM studies were conducted on a Tesla BS-301 microscope Quanta 3D FEG operating at 15.0 keV. FT-IR/PAS spectrum of the biochar sample was recorded by means of the Bio-Rad Excalibur 3000 MX spectrometer equipped with photoacoustic detector MTEC300 (in the helium atmosphere in a detector) at RT over the 4000–400 cm^{-1} range at the resolution of 4 cm^{-1} and maximum source aperture. The spectrum was normalized by computing the ratio of a sample spectrum to the spectrum of a MTEC carbon black standard. A stainless steel cup (diameter 10 mm) was filled with biochar sample

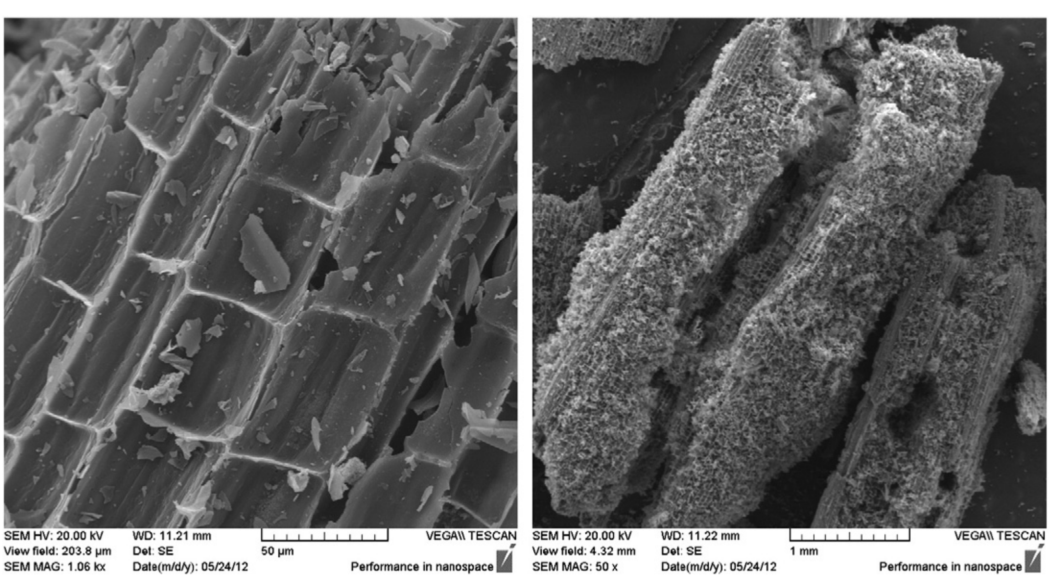

Fig. 1. SEM pictures of biochar used in the field experiment.