

The effect of freshly added and aged biochar on pesticide degradation and adsorption in soil and the effect of long-term exposure to biochar on selected key taxonomic and functional community composition of soil microbial communities

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Use of pesticides and other organic contaminants is only sustainable over the long-term if risk levels are acceptable. This ambition requires that concentrations of these substances in surface and ground waters are low, which can be obtained if contamination from point and diffuse sources are eliminated. This could be achieved by incorporation of biochar into or on vulnerable soil profiles, which would substantially increase sorption of the pollutants and thereby decrease their transport and leaching. Biochar incorporation will however probably also affect the degradation rate of the substances. In this work, degradation of pesticides with different sorption mechanisms (hydrophilic MCPA and diuron, lipophilic chlorpyrifos and glyphosate that binds to AL/Fe-hydroxides) is studied in two main experiments, where the effect of freshly added and aged biochar on degradation is studied. The effect of the aged biochar on adsorption of these pesticides was also studied.

The effects of biochar on soil biota have received much less attention than its effects on soil chemical properties, even though soil microorganisms are vital for soil functioning as they drive the major biogeochemical cycles and carry out a multitude of other process. Biochar can induce changes in microbial community composition, but if effects differ between ecologically or functionally different groups of soil microorganisms and if effects can be found when the biochar has aged for many years in soil is not known. Therefore, we also studied the effects of long-term exposure to biochar on selected key taxonomic and functional community composition of soil microbial communities.

Main physical and chemical characteristics of the four pesticides used are shown in Table 1.

Table 1. Some characteristics of the pesticides studied

Pesticide	Molecular mass (g mol ⁻¹)	Water solubility (mg L ⁻¹)	Log(<i>K_{ow}</i>) ^a
Glyphosate	168.07	10500	-3.2
Diuron	233.09	35.6	2.87
MCPA	200.62	29390	-0.81
Chlorpyrifos	350.89	1.05	4.7

^a *K_{ow}*: oil/water distribution coefficient

Degradation of pesticides in a soil without and with added biochar and with biochar in a layer in contact with the soil

A top-soil (0-20 cm) with 1.9% organic carbon was used. For the degradation studies, the pesticide was mixed into 5 g of soil (sieved to < 4 mm) to give an initial concentration of 10 µg per g dw. Skogens kol biochar was sieved to < 1 mm and was mixed in one treatment into the soil to give a dose corresponding to 10 tonnes/ha. In the other treatment, a layer with the same amount of biochar was placed below the pesticide-amended soil in the incubation tubes. The soil moisture was adjusted to 60% of WHC and the tubes were incubated at 20°C.

Biochar mixed into the soil corresponding to a dose of 10 tonnes/ha did not have any significant influence on pesticide degradation. Adding the same amount of pesticide to the

same amount of biochar, but now placed as a layer in contact with the same amount of soil, increased degradation half-lives from 84 to 156 days for diuron; from 5-6 to 15 days for MCPA and from 24-30 to 74 days for chlorpyrifos. The half-life of 10-13 days for glyphosate degradation was not affected by the biochar addition in any of the treatments.

Adsorption and degradation of pesticides in a soil with and without aged biochar

The effect of aging and clogging of pores by soil organic matter on pesticide sorption and degradation was compared between a control soil without biochar and the same soil with biochar that had been in contact with the soil for at least 70 years. The presence of aged charcoal in the soil resulted in an increase of organic carbon content to 21.6% compared to 5.6% in the control soil and pH increasing to 6.66 from 5.21.

The presence of biochar for more than 70 years in the soil had no effect on the adsorption of MCPA and chlorpyrifos compared to their adsorption in the control soil without biochar. There was a significant decrease in adsorption of glyphosate and a significant increase in the adsorption of diuron.

The presence of biochar for more than 70 years in the soil had no effect on the degradation rates of diuron, MCPA and chlorpyrifos compared to the rates in the control soil without biochar. There was a remarkable increased degradation rate of glyphosate in the soil with biochar, probably due to the lower adsorption in this soil compared to the control soil without biochar.

The effect of long-term exposure to biochar on selected key taxonomic and functional community composition of soil microbial communities

DNA was extracted from soil samples with and without aged biochar. Total bacterial abundances and abundances of key functional marker genes in the nitrogen biogeochemical cycle were determined using real-time quantitative PCR (qPCR).

The size of the total bacterial community was significantly higher in the soil with aged biochar compared to the control without biochar and higher abundance in the biochar soil was also the case for denitrifiers and ammonia oxidizing bacteria. This pattern remained when gene numbers were normalized to the total bacterial community size, demonstrating that the fraction of the bacterial community involved in nitrogen cycling increased more than bacteria in general. Interestingly, the relative proportion of nitrous oxide reductases to nitrite reductases was higher in the biochar soil than in the control soil ($p=0.020$), indicating an overall higher potential for reduction of nitrous oxide (N_2O) either via complete denitrification or by N_2O reduction by non-denitrifiers.



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