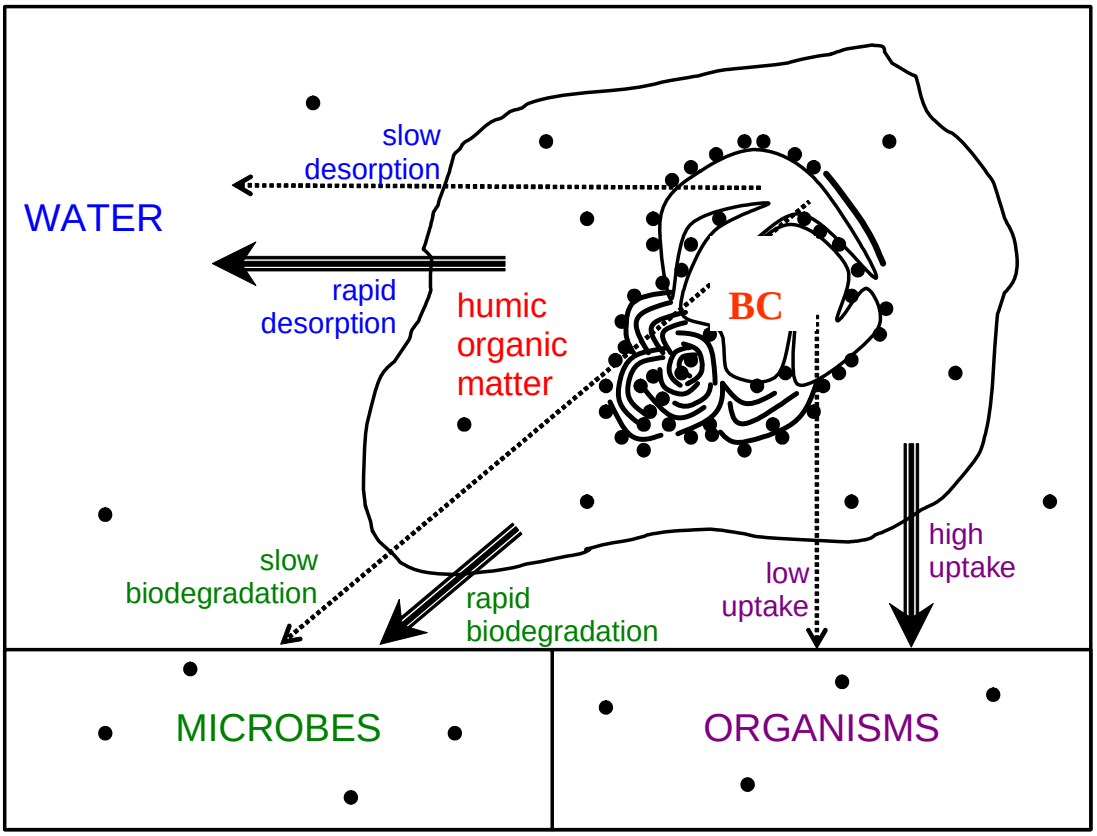
Polycyclic Aromatic Hydrocarbons (PAH) In Biochar: Total and Bioavailable Concentrations

By: Gerard Cornelissen, Sarah E. Hale, May 2015; for more information, please see www.biochar-international.org

PAHs and PCDD/F contaminants in biochar

Contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-dioxins and furans (PCDD/Fs) can be present in the biochar matrix and can exert a toxic effect if they are taken up by organisms. However, before these contaminants can exert such deleterious effects, they must be bioavailable. In order to be bioavailable, they need to be able to enter the water phase. This process is very limited as biochar, in accordance with all pyrogenic organic materials, binds PAHs and dioxins very strongly, lowering the bioavailable content to only 1-10% of total content[1].



The link between strong sorption of contaminants (the black dots) to biochar (BC), and slow desorption (release), slow biodegradation and low uptake (risk).[2]

Measurement of total contaminant concentrations in biochars using toluene extraction

If biochar is used as a soil amendment, it needs to be tested to ensure it meets safety standards—both the *IBI Biochar Standards* and the *European Biochar Certificate (EBC)* require testing for the concentration of PAHs and other toxicants. Extensive testing has shown that hot extraction with the solvent toluene in a Soxhlet, reflux or accelerated solvent extraction unit is the best method to extract these compounds from biochar[3,4].

Production conditions

A producer of biochar can minimize the concentration of resulting PAHs in the biochar during production by diverting and collecting pyrolysis gases separately. Poorly controlled pyrolysis production conditions, and especially flash pyrolysis, tend to yield a product with higher PAH content[1]. Other process parameters such as temperature, residence time or feedstock could have an effect on PAH formation, but clear trends have up to now not been found, even though PAH contents show a trend of going up with pyrolysis temperature for biochars not made by slow pyrolysis[1,5].

Measurement of bioavailable PAHs using passive samplers

Bioavailable PAHs and PCDD/Fs are best measured with *passive samplers*[6], which are simple sheets of plastic that are added to biochar-water slurry and shaken for about a month[1]. The best passive sampling materials are cheap and ubiquitous: polyoxymethylene, silicon and low-density polyethylene[7]. When the passive sampler is added to the biochar-water mixture, equilibrium (steady state) is reached between contaminant concentrations in the plastic passive sampler, the biochar and the water. With the help of pre-calibrated sampler-water distribution ratios, the freely dissolved contaminant concentration in water (in equilibrium with the biochar) can be determined. This freely dissolved concentration is the best measure for bioavailability, and can be directly compared to water quality criteria[6].



The passive sampler polyoxymethylene (POM)

Overall assessment

Overall, it is unlikely that the application of biochar to soils poses any substantial eco-toxicological risk to soil environments caused by the presence of native PAHs in the biochars. In the most extensive study where PAHs were measured in 60 biochars it was found that biochars would only release/leach 0.2-2 ng/L PAHs. This compares very favorably with the water quality criterion of 500 ng/L[8]. These ng/L concentrations are comparable to those in

relatively low-polluted coastal waters in many areas of the world[9].

Also polychlorinated dibenzo-p-dioxins and -furans (PCDD/F; "dioxin") can be formed during the pyrolysis of biomass, especially for feedstocks containing considerable amounts of chlorine (PVC, seawater, salt). However, even more so than for PAHs, it is unlikely that the possible presence of dioxins in biochars poses a toxicological risk to soil, since dioxins are even more strongly bound than PAHs[1] and thus almost not bioavailable. Avoiding feedstocks containing considerable amounts of chlorine certainly rules out the problem. In almost 60 biochars, even total dioxin concentrations were below 100 ng/g. Especially when mixed into soil at 1-10 weight-%, biochar would thus add dioxin contents in soil that are is far below most quality criteria for dioxins in soil (Sweden: "sensitive soil use" 250 ng/kg; UK: 8000 ng/kg for residential areas, 240 000 ng/kg for commercial property; Canada 1000 ng/kg for agricultural land, 100 000 ng/kg for residential areas[1]). Bioavailable dioxins were almost all below the detection limit (around 0.0001 pg/L) of the reputed dioxin lab in the world at Umeå.

To comply with current legislation which in most countries unfortunately is based on total PAH contents rather than bioavailable PAH contents[10], product quality via proper testing must be assured. Proper testing in this case is extraction of the biochars with toluene in order to measure total PAHs. Passive sampler extraction should also be done to perform a "reality check" and check the "actual risk" – the extent to which the contaminants can be taken up and so pose a risk to humans and ecosystems. Fortunately, some countries are already opening up for such bioavailability assessments in so-called tier-2 or tier-3 assessments.

Literature

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