Dissipation of bentazone, pyrimethanil and boscalid in biochar and digestate based soil mixtures for biopurification systems

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HIGHLIGHTS

- Biochar and digestate significantly affects the dissipation pattern of pesticides.
- Addition of digestate enhanced mineralization of studied pesticides.
- DT_{50} values decreased in the order pyrimethanil > boscalid > bentazone.
- Addition of biochar increased non-extractable residues formation for all pesticides.
- 5% biochar and 5% digestate mixture caused the rapid pesticide dissipation.

GRAPHICAL ABSTRACT
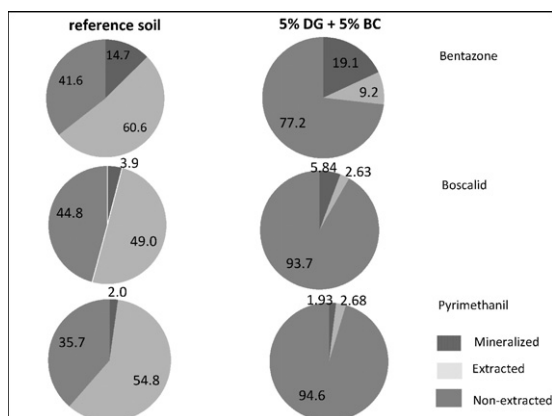
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ABSTRACT

Biopurification systems, such as biofilters, are biotechnological tools to prevent point sources of pesticide pollution stemming from on-farm operations. For the purification processes pesticide sorption and mineralization and/or dissipation are essential and both largely depend on the type of filling materials and the pesticide in use. In this paper the mineralization and dissipation of three contrasting ^{14}C-labeled pesticides (bentazone, boscalid, and pyrimethanil) were investigated in laboratory incubation experiments using sandy soil, biochar produced from Pine woodchips, and/or digestate obtained from anaerobic digestion process using maize silage, chicken manure, beef and pig urine as feedstock.

The results indicate that the addition of digestate increased pesticide mineralization, whereby the mineralization was not proportional to the digestate loads in the mixture, indicating a saturation effect in the turnover rate of pesticides. This effect was in correlation with the amount of water extractable DOC, obtained from the digestate based mixtures. Mixing biochar into the soil generally reduced total mineralization and led to larger sorption/sequestration of the pesticides, resulting in faster decrease of the extractable fraction. Also the addition of biochar to the soil/digestate mixtures reduced mineralization compared to the digestate alone mixture but mineralization rates were still higher as for the biochar/soil alone. In consequence, the addition of biochar to the soil generally decreased pesticide dissipation times and larger amounts of biochar led to high amounts of non-extractable

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residues of pesticide in the substrates. Among the mixtures tested, a mixture of digestate (5%) and biochar (5%) gave optimal results with respect to mineralization and simultaneous sorption for all three pesticides.

1. Introduction

Inappropriate use of pesticides can cause high concentrations in soils, ground and surface-waters with significant environmental consequences (Kolpin et al., 1995; Kolpin et al., 1998; Acevedo et al., 2011). In general, pesticide pollution of water stems either from diffuse source pollution caused e.g. by pesticide leaching to groundwater or by surface runoff from fields to water bodies (Carter, 2000). Pollution may also origin from point sources caused by the release of pesticide contaminated waters from e.g. washing of the spray equipment, pesticide handling (filling of spray equipment), or e.g. by illegal dumping of post-harvest pesticide treatment waters (Coppola et al., 2011b; Karanasios et al., 2010a). At the catchment scale, studies have elucidated that 40 to 90% of surface water contamination by pesticides can be due to point source pollution (Carter, 2000; Kreuger and Nilsson, 2001).

The fate of pesticides in the environment is closely connected to dissipation, of which mineralization is one key process, and soil sorption, which in combination mainly governs the leaching potential of the substances in soils (Boesten and Van der Linden, 1991). To assess the environmental fate of pesticides, standard laboratory experiments are performed to measure the mineralization (total breakdown of substance to CO_2) and dissipation (sum of mineralization, metabolization, and non-extractable residue formation, which is measured via extractable active ingredient) behavior and to determine appropriate end-points for pesticide registration. These end-points are the half-life values which express the time required for 50% of the initial mass to mineralize ($MinT_{50}$) or to dissipate (DT_{50}). Hereby the DT_{50}, or dissipation, does not differentiate between transfer processes (e.g., leaching or erosion), sequestration (e.g., non-extractable by organic solvents due to strong sorption), or degradation (biotic or abiotic transformation of the substance) processes (FOCUS, 2006).

Dissipation and mineralization of pesticides are not only influenced by the chemical properties of the substances but they also depend on physico-chemical properties of the soil (such as pH value, soil organic carbon content (SOC), or soil texture), biological properties (activity and distribution of microorganisms), as well as environmental conditions controlling the chemical and biological processes (mainly soil temperature and soil water content). As a consequence, the dissipation (DT_{50}) and mineralization ($MinT_{50}$) half-life times have to be determined for each pesticide and soil combination individually.

Biopurification systems, like the biobed concept developed in Northern Europe (Castillo et al., 2008), biofilter system in Belgium (De Wilde et al., 2007), biobac or phytobac system in France (Guyot and Chenivesse, 2006), or biomassbed in Italy (Coppola et al., 2007) aim to reduce point pollution from farmyards by collecting all pesticide contaminated waters (e.g., from cleaning spray equipment) and to purify this waste water in a simple treatment system. The basic idea of these biofilter systems is that the pesticides will be degraded or sorbed/sequestered during the passage (drainage) of the water through suitable media (Castillo et al., 2000 and Castillo et al., 2008; Coppola et al., 2011a), whereby systems with a balance between sorption/sequestration, and mineralization/degradation are the most promising purification approach. Typically, different media are in use for such purpose depending on the location of the biopurification system and the availability of substrates such as mixtures of soil, straw, peat, but also residues from agricultural product processing or wastes (e.g., citrus peels, vine branches, coconut byproducts) have been reported (Coppola et al., 2007; De Roffignac et al., 2008; Karanasios et al., 2010a). The addition of fresh organic matter to the biofilter matrix in these setups is an essential component for pesticide purification because it enhances the microbial activity, and therefore, also the microbial turnover of the pesticides (Perucci et al., 2000; Walker, 1975; Nair and Schnoor, 1994). Not all substrates are locally available or can be sustainably sourced (e.g., peat). On the other hand, byproducts or wastes from bioenergy production (e.g., digestate from biogas production or biochar) become more and more available and might be suitable to substitute more traditional substrates in the biopurification systems.

The addition of biochar to soils and its influence on pesticide mineralization is currently controversially discussed. Biochar is characterized as a highly recalcitrant pyrolysis product (i.e. charcoal), showing high organic C content and a high specific surface area (Lehmann et al., 2011). Some authors reported an increase of pesticide mineralization as a result of the microbial stimulation in the system, whereas other studies report reduced mineralization, due to a lower pesticide bioavailability to microorganisms because of the increase in sorption/sequestration of pesticides at biochar surfaces. A higher sorption or sequestration on soils amended with biochar (made from wood pellets) has been reported for a range of pesticides (e.g. Cabrera et al., 2014; Si et al., 2011). However, for anionic pesticides or pesticide metabolites, beech wood biochar (fresh and composted) amendments did not show enhanced sorption in soils (Dechene et al., 2014). Regarding biochar influence on pesticide degradation, Loganathan et al. (2009) reported a decrease in atrazine mineralization in soils amended with 1% (w/w) wheat char and they hypothesized that this reduction is associated with the increase in sorption of the herbicide to the char surface. On the other hand, Guo et al. (1991) suggested that atrazine and alachlor degradation could be inhibited in presence of activated carbon, and stimulated by other uncharred amendments, such as municipal sewage sludge and manure. An increase in atrazine mineralization by the addition of organic amendments to a sandy loam soil was also reported by Mukherjee (2009).

In general, there is an increasing trend towards biogas production in most industrial countries because biogas is an important form of renewable energy (Makádi et al., 2008). Digestate is the solid and residual byproduct of the biogas industry following the anaerobic digestion process (Möller et al., 2008; Mukherjee et al., 2015). On the other hand, it is a good source of easily available carbon and lignin rich material which generally enhances microbial activity by increasing the microbial growth and respiration as shown by e.g. Makádi et al. (2008); Odlare et al. (2008), and Kirchmann (1991). To our knowledge, no investigation has been done yet to determine how digestate addition to soil influences the dissipation and mineralization behavior of pesticides.

As mentioned earlier, biobed systems do not only rely on the full mineralization of the pesticides but combine pesticide mineralization, degradation, and sorption/sequestration leading to overall pesticide dissipation, and as a consequence of this, to water purification. Therefore, it is mandatory not only to look at the mineralization (which can be also fairly low for some specific recalcitrant pesticides) but to analyze the overall dissipation potential of the pesticides in the biomatrix, considering also sequestration of pesticide in the soil matrix, which also leads to reduced availability of pesticides for leaching. Additionally, Nowak et al. (2011 and 2013) reported the importance of biogenic non-extractable residues. They stated that microbes utilized carbon from pollutants to build up their own biomass. This microbial biomass containing ^{14}C from pesticide labeling and full degradation of the pesticides will contribute to the non-extractable fraction, even if it was already turned over completely. However, determining this specific pathways and fraction of microbially immobilized pesticide originated ^{14}C is out of scope of this paper. As different pesticides react diversely in the soil systems