



Modeling the release of organic contaminants during compost decomposition in soil



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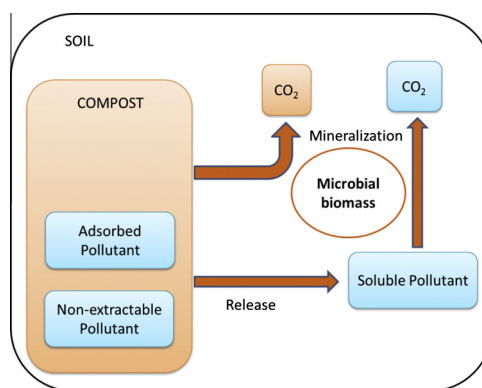
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HIGHLIGHTS

- COP–Soil simulated the interactions between organic contaminants and soil organic matter.
- Organic matter decomposition improved the simulation of organic pollutant dynamic.
- Model of K_d as a function of organic matter quality led to more accurate simulations.
- Inclusion of specific biomass predicted successfully the PAH mineralization.

GRAPHICAL ABSTRACT



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ABSTRACT

Composts, incorporated in soils as amendments, may release organic contaminants during their decomposition. COP–Soil is presented here as a new model to simulate the interaction between organic contaminants and compost, using one module for organic matter and one for organic pollutants, with these modules being linked by several assumptions. Published results of laboratory soil incubations using labeled carbon pollutants from compost were used to test the model for one polycyclic aromatic hydrocarbon (PAH), two surfactants and one herbicide. Several simulation scenarios were tested using (i) the organic pollutant module either alone or coupled to the organic matter module, (ii) various methods to estimate the adsorption coefficients (K_d) of contaminants on organic matter and (iii) different degrading biomasses. The simulations were improved if the organic pollutant module was coupled with the organic matter module. Multiple linear regression model for K_d as a function of organic matter quality yielded the most accurate simulation results. The inclusion of specific biomass in the model made it possible to successfully predict the PAH mineralization.

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Abbreviations: OP, organic pollutant; S_w , water-soluble fraction; SND, soluble in neutral detergent; HEM, hemicellulose-like fraction; CEL, cellulose-like fraction; LIG, lignin-like fraction.

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1. Introduction

Across Europe in recent years, as a result of the implementation of the EU Landfill Directive 99/31/EC, there has been a substantial increase in organic waste treatment by composting, and there is still a large potential for further increase (Barth et al., 2008). The addition of compost improves the physical properties of soil and enhances nutrient availability and microbial activity, therefore enhancing the ability of soil to sustain plant growth (Diacono and Montemurro, 2010). In addition, composting can help to stabilize and/or degrade organic pollutants (OPs) in contaminated soils, thus contributing to their bioremediation (Sayara et al., 2010).

However, composts may contain OPs, such as semi-volatile organic compounds and pesticide residues, which are often present in initial feedstock materials (Brändli et al., 2005; Cai et al., 2007). Although they are partially biodegraded into metabolites or mineralized into CO₂ by microorganisms during composting, most OPs can be adsorbed and/or sequestered in the organic matrix, forming non-extractable residue (NER) (Lashermes et al., 2012b). Thresholds for various OP concentrations have been proposed by the European Commission to prevent soil contamination after recycling of sewage sludge (CEC, 2000) or composts that include sludge as input material Barth et al. (2008). The use of ¹⁴C-labeled OPs made it possible to study the formation and behavior of NER during composting (Lashermes et al., 2012b) and investigate their bioavailability and biodegradability in soil after compost application (Richnow et al., 1994; Haudin et al., 2013). When compost is spread onto soil, organic matter is mineralized to some extent, and OPs can undergo physicochemical and biological processes that may change their chemical forms and their bioavailability. A fraction of OPs can even be accumulated in crops (Cai et al., 2008). Thus, due to their interaction, the dynamics of organic matter and OPs during compost decomposition in soil should be studied simultaneously. Haudin et al. (2013) studied carbon mineralization from composts in soil and the fate of four ¹⁴C-OPs introduced into soil by composts and found that there is a positive relation between the mineralization of organic carbon and that of glyphosate, LAS and nonylphenol.

Mathematical models are helpful in conceptualizing our understanding of complex processes and formalizing hypotheses on the interactions between OPs, organic matter and microbial biomass in the complex environment of soil (Mulder et al., 2001; Zarfl et al., 2009). In modeling the fate of OPs in a soil system, sorption, biodegradation, mineralization (Saffih-Hdadi et al., 2003) and the formation of non-extractable residues (Kästner et al., 1999) should be considered. Some models exist that describe the fate of OPs in soil, such as pesticides (Saffih-Hdadi et al., 2003; Bošnjak et al., 2010) and antibiotics (Zarfl et al., 2009), but the dynamics of organic C are not considered. To the best of our knowledge, there is no model that is able to simulate simultaneously the dynamics of organic C and OPs in the application of biosolids to soils.

The main objective of the present work was to develop a new model to simulate the behavior of organic C from compost and OP residues in compost (COP–Soil) after compost is spread on soil. This model describes the fate of OPs during the decomposition of compost in soil (i.e., mineralization, adsorption/desorption, and formation/remobilization of non-extractable residues), which is coupled to organic C dynamics. A second objective was to parameterize the COP–Soil model for four OPs, a PAH (fluoranthene, FLT), two surfactants (linear alkyl benzene sulfonate, LAS, and nonylphenol, NP) and a widely used herbicide (glyphosate, GLY), using experimental data collected by Haudin et al. (2013).

2. Experimental and modeling section

Our approach used a recent model named COP–Compost that simulates the microbial development and organic matter

transformations that occur during composting (Zhang et al., 2012) and their influence on the fate of OPs present in the initial waste mixture (Lashermes et al., 2013). We adapted this model to represent the fate of composted organic matter and OP residues present in final compost after compost is spread on agricultural soils (COP–Soil model).

2.1. Modeling the Coupling between organic pollutants and organic matter

The COP–Soil model includes an organic C module and an OP module, which can be used separately or coupled (Fig. S1). The organic C module was based on the module proposed by Zhang et al. (2012) which describes organic matter transformations during composting and is adapted to the soil environment. The organic C in compost was divided into several pools: available organic carbon (S_w), soluble in neutral detergent (SND), hemicellulose-like (HEM), cellulose-like (CEL) and lignin-like (LIG), as measured using the Van Soest fractionation method (Van Soest and Wine, 1967) and characterized in the model by their specific degradabilities. The SND pool was split into SND-slow and SND-fast, with a higher degradability assumed for SDN-fast.

Soil organic matter (SOM) consists mainly of plant and microbial residues and their degradation products rather than novel categories of cross-linked macromolecules (Miltner et al., 2009). Recent studies applying ¹³C-labeled bacterial biomass have shown that microbial biomass-derived C contributes significantly to the formation of refractory SOM (Kindler et al., 2006; 2009). Nuclear magnetic resonance (NMR) characterization indicates that degraded microbial biomass is very similar to SOM and confirms that microbial biomass carbon contributes to SOM formation (Miltner et al., 2009; Miltner et al., 2012). Therefore, humified organic C (HOC) was assumed to be derived from dead microbial biomass in the COP–Soil model:

$$\frac{dHOC}{dt} = X \cdot m_B \cdot w \quad (1)$$

where m_B (d^{-1}) is the death constant for microbial biomass (X , % of initial total organic matter, TOC) and w is the proportion of dead biomass in the pool (% of initial TOC) (Kästner et al., 2013). For the other processes, the same equations were taken from Zhang et al. (2012). A total of 14 parameters and 8 variables were necessary to run the organic C module (Table S1). Only one parameter, w , has not been defined already for composts.

The OP module was inspired by the COP–Compost model (Lashermes et al., 2013) and is based on the same four pools and the same equations. OPs were distributed among the mineralized (¹⁴C–CO₂), water-soluble (OP_w), adsorbed (OP_a) and non-extractable-residue (NER) fractions.

Three hypotheses were proposed for the coupling of organic C and OP modules in the soil environment:

Hypothesis 1. The biochemical nature of organic matter influences its degradability (Corbeels et al., 1999) as well as its capacity for OP sorption (Xing et al., 1994; Benoit et al., 1996; Aslam et al., 2013). Instantaneous equilibrium between soluble (OP_w) and adsorbed (OP_s) fraction was described with the equation:

$$OP_s = k_d \times OP_w \quad (2)$$

We assumed that Eq. (9) (shown later) describes the dynamic of K_d during soil–compost incubation as a function of the biochemical fractions of compost organic C and humified organic C.

Hypothesis 2. OPs can be degraded through co-metabolism by microorganisms that use the compost organic matter as their primary energy source or by a specific biomass that grows using

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