

The COP-SOIL model for mineralization and bioavailability of organic micropollutants during composts decomposition in soil

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Abstract

The COP-Soil model was developed to simulate behaviors of OPs with composts application into soil labeled by ¹⁴C-OPs. The COP-Soil model included two modules with some modification according to soil environment: just humified organic matter (derivative from dead biomass) was added into organic C module; while OP module kept the same compartments (the soluble, adsorbed, non-extractable and mineralized fractions). Run with Kd optimization in OP module alone improved significantly the simulation for a linear alkylbenzene sulfonate and one glyphosate composts, due to optimized Kd was much lower than that of batch experimental Kd. Coupling with organic C module and use of batch experimental Kd improved significantly the simulation for nonylphenol, 2 glyphosate composts due to small difference between Kd. Link dynamic Kd with organic C dynamic gave the best simulation among different runs. Specific biomass added into OP module predicted successfully fluoranthene mineralization.

Introduction

Across Europe in recent years, there has been a huge growth in organic waste treatment by composting (European Communities, 2005) that produces organic amendments useful to improve soil fertility. However, composts may contain organic pollutants (OPs) due to their presence in the initial feedstock materials (Brändli et al., 2005) and would be introduced into soil by composts application into soil. The characterization of OPs content and accessibility in composts is of paramount importance to estimate the environmental impacts after their application to agricultural soils (Bright and Healey, 2003; Semple et al., 2004) and Lashermes et al (2012a, b) have studied and modeled the dynamics of OPs fractionation successfully.

Until now, there is no model available which can simulate behaviors of organic C and OPs simultaneously with composts decomposition in soil. Our COP-COMPOST model can simulate behaviors of OPs during composting, which takes into consideration the transformation of organic matter quality, microbial biomass dynamics (Zhang et al., 2012), sorption-desorption and biodegradation of OPs (Lashermes et al., 2012b; Saffih-Hdadi et al., 2003). Zarfl et al. (2009) have proposed a model to describe the fate of sulfadiazine and its metabolites in manure-amended soil, but this model cannot simulate organic C dynamic from manure, which may have a substantial impact on the fate of OPs, such as co-metabolism, formation of non-extractable residues and OP adsorption on organic matter from manure.

The present work has three main objectives: (i) to extend the application of COP-COMPOST model into soil environment; (ii) to model kinetic distribution and degradation of OPs in soil calibrated by laboratory experiments; (iii) to model the fate of OPs coupling with organic matter transformation and the corresponding microbial biomass dynamics.

Material and Methods

Modeling the Coupling between Organic Pollutants and Organic Matter

The COP-SOIL model was adapted from the composting model COP-COMPOST (Lahermes et al. 2012b) in order to simulate the fate of OPs during compost decomposition in soil environment. The model was programmed in Matlab® language (The Mathwork, USA).

The COP-SOIL model is divided into organic C module and OP module, which can be used separately or coupled (as in COP-COMPOST model described in Lahermes et al. 2012b). In organic C module, organic C was divided into several compartments (water soluble (Sw), soluble in neutral detergent (SND), hemicelluloses-like (HEM), cellulose-like (CEL) and lignin-like (LIG)), characterized by their own specific degradability according to the van soest fraction method (Van Soest and Wine, 1967). The compartment SND was split into SND-slow and SND-fast, with higher degradability for SND-fast.

Hypothesis 1: The biochemical nature of organic matter influences its own degradability (Corbeels et al., 1999) as well as its capacity of OP sorption (Benoit et al., 1996, Xing et al., 1994). The assumption that the OP sorption coefficient (Kd) was the weighted mean of the sorption coefficients in the different organic C pool relative to the proportion of total organic C as described in Lahermes et al. (2012b) could not be supported because too many parameters were needed to be estimated. Therefore, we assumed a new equation which linked the dynamic Kd during soil-compost incubation with the different organic C pools:

Hypothesis 2: OPs can be degraded by specific biomass modeling with a Monod kinetic or through co-metabolism. OPs degradation by co-metabolism has been well simulated during anaerobic digestion (Delgadillo-Mirquez et al., 2011), composting (Lahermes et al., 2012b) and soil incubation (Saffih-Hdadi et al., 2003). In the new version of our model, we assumed that the two processes can co-exist, depending on the ability of the soil microorganisms to degrade the OP (Laine et al., 1997).

Hypothesis 3: The model assumed that the NER was formed through physical and chemical stabilization of adsorbed OPs (Kästner et al., 1999). The formation of NER was assumed to depend not only on the chemical reactivity of the OPs but also on the microbial activity, whose influence was reported by Benoit and Barriuso (1997). The equation of NER formation was taken from Lahermes et al. (2012b):

Data Used for Model Calibration and Evaluation

The soil-compost mixtures (50 g: 3 g in dry mass) were incubated under controlled aerated conditions for 140 days (Haudin et al., accepted). The composts was taken from Lahermes et al. (2012a), where the fate of four ¹⁴C-OPs ([methyl-¹⁴C] N-(phosphonomethyl) glycine or GLY, [3C-ring-¹⁴C] fluoranthene or FLT, [U-ring-¹⁴C] 4-n-nonylphenol or NP, [U-ring-¹⁴C] sodium linear dodecylbenzene sulfonate or LAS) initially brought to a same initial mixture of wastes (aerobic digested sewage sludge (20%), branches (25%), grass clippings (15%), hedge trimmings (20%) and leaves (20%)) had been studied during the composting.

Each OP had 3 replicates for the composting treatment and each composts had 4 replicates for the soil-compost incubations. Therefore, average data of CO₂ mineralization from composts of 48 replicates and the biochemical fractions of composts at day 0 were used to test the organic C module. Due to low mineralization potential, CO₂ mineralization from soil was not considered.

The OPs were measured during the incubations by sequential extractions at day 0, 14 and 140, the fraction recovered through CaCl₂ extraction was defined as “soluble fraction”, while the one obtained through methanol extraction for FLT, LAS and NP or through NH₄OH extraction for GLY was defined as “adsorbed fraction”. After chemical extractions, soil-compost mixture was combusted and ¹⁴C-CO₂ released was trapped and counted by Liquid Scintillation Counting, which was defined as “non-extractable fraction”. These three fractions and ¹⁴C-CO₂ mineralization of ¹⁴C-OPs (trapped in the NaOH solution) were adjusted to 100% according to recovery rate at each sampling date and used to calibrate the OP module. Average data from 4 replicates was used to calibration OP module, that is, each OP had three sets of data.

The batch experimental adsorption coefficient (Kd) on soil-compost mixture was determined as the following. The composts and the soil were used to determine Kd before the incubation separately according to Lahermes et al (2010) and Zhang et al (2011). Kd was determined as the ratio between the proportion of adsorbed ¹⁴C-OP and the proportion of ¹⁴C-OP in solution after 24 h equilibration.

Kd in soil-compost mixture was calculated as the equation according to the mixture rule.

Model Calibration and Evaluation

To run the organic C module, 14 parameters were necessary, where twelve fixed parameters were obtained from Zhang et al (2012) and two (K₁ and W) were optimized by inverse modeling using CO₂ mineralization data from organic matter (Haudin et al., accepted). The optimization was performed using the *fmincon* function of the MATLAB Optimization Toolbox (Mathworks, USA), which applies a sequential quadratic programming algorithm. The objective function was taken from Zhang et al (2012).

S_w , SND, HEM, CEL and LIG at day 0 is 17.4%, 21.9%, 10.8%, 21.1% and 28.8%, respectively (Lashermes et al., 2012 a). Due to the adsorption of soluble organic matter on soil matrix, which was different from composting environment, the content of S_w at day 0 (originally assumed as biodegradable inside the COP-COMPOST model) was reduced to half and the remaining part was included into SND-slow. According to Zhang et al. (2012), SND-fast fraction was near 0 at the end of composting, so SND-fast was assumed to be equal to 0 at the beginning of the soil-compost incubation.

Because the incubation was done with the mixture of 3g composts and 50 g soil, and when initial biomass 0.05% of initial TOC in composts was taken from Zhang et al (2011), initial biomass from soil should also be considered into the mineralization effect of organic C in composts. Because TOC was 43.7% at day 0 in composts, there was an equivalent initial biomass 0.8833% of initial TOC brought into the soil by composts. In the other word, there was 0.22 mg C per g of soil/compost mixture, which was in the range from 1.4 to 8.6 mg microbial carbon per g of organic matter (approximately 0.056 to 0.430 g C 100 g⁻¹ dry mass, Eiland et al., 2001).

The parameters of the OP module were optimized for each chemical and each soil-compost mixture (four replicates from soil incubation). The objective function (RMSE-OP_{tot}) was defined as the sum of all the RMSE-OP (j) calculated between the experimental and simulated values of the j variables (j=1-4 for the soluble and adsorbed fractions, NER and ¹⁴C-CO₂, respectively). The best simulation produced the lowest RMSE-OP_{tot} value. Two statistical criteria (the efficiency coefficient Ef and the mean difference D) were used in complement to evaluate the simulations (Smith et al., 1997).

Four sets of simulation (A, B, C, D) were conducted for OP parameter estimation. Run A and B were performed with the OP module only, so that the evolution of organic C would have no influence on the parameters; the OP and organic C modules were coupled in runs C and D. During all runs, the rates of NER formation Fr for the OP module alone and Fr_A and Fr_B for the coupled model) and the rate of OP degradation Dr were optimized, while the sorption coefficient (Kd) was treated separately in the different runs: in run A (without coupling) and run C (with coupling), batch experimental Kd values (calculated by the equation 7) were used as fixed values and Kd parameters were not calibrated; in run B, Kd was optimized for each OP; in run D, the dynamic Kd during soil-compost incubation was linked with organic C pool values for each OP. In order to evaluate the overall performance of the simulations, RMSE-OP_{tot} obtained in a run was multiplied by the number of parameters required estimation (as described in Lashermes et al, 2012b). The best run was the one that produced the lowest weighted sum of RMSE-OP_{tot}. The objective was to limit the number of parameters required estimation.

Results and discussion

Calibration of the Organic C Module

The mineralization of total organic C from composts was well simulated when initial microbial biomass was 0.8833 % of initial TOC brought into the soil by composts, with RMSE value of 8.50, D of 0.41 and Ef of 0.98. Lower initial microbial biomass (for example 0.05% of initial TOC) underestimated the CO₂ release at the beginning of the incubation and over-estimated it in the middle of the incubation period.

3.2. Simulation of the Evolution of OP Fractionation

The simulations generally improved from run A to run D, as shown by the decrease in the sum of RMSE-OP_{tot}. Coupling with the organic C module improved the simulation with marked decrease in the sum of RMSE-OP_{tot} between run A (without coupling) and C (with coupling); both runs used batch experimental Kd as fixed values for the Kd parameter, while Fr and Dr were optimized. For run A and C, the evolution of OP fractionation was best simulated for NP (average RMSE-OP_{tot} of 78.8 and

49.4, respectively) and LAS gave the poorest fits (average RMSE-OP_{tot} of 142.1 and 101.5, respectively), which was due to the reason that the batch experimental K_d was too high for LAS. The link of K_d parameters with organic C pools (run D) further markedly improved the simulation when compared with run C. The LAS was the best simulated OPs (average RMSE-OP_{tot} of 8.4) and GLY gave the poorest fits (average RMSE-OP_{tot} of 21.3).

Run D appeared to produce the most efficient simulations. Indeed, when optimizing only three parameters (Dr, Frc and Frb), it produced the lowest and weighted value of RMSE-OP_{tot} of 123.5 and 370.4, respectively. The simulated amounts of soluble and adsorbed fractions, NER and mineralized OPs with run D accounted for more than 98.5% of the variability of the corresponding experimental values, and the evolution of OPs fractionation during soil-compost incubation was predicted well, thus testifying that the COP-SOIL model was able to predict satisfactorily the experimental behavior of each OP studied. The best simulated pools were the soluble and adsorbed fractions, with average Ef values of 1.00 ± 0.00 and 0.99 ± 0.01 , respectively. Furthermore, average D values of 0.00 ± 0.00 and 0.02 ± 0.01 in the soluble and adsorbed fractions showed no bias in the simulations of these two pools. The simulations also agreed with the experimental evolution of mineralized ¹⁴C-CO₂, with an average Ef of 0.96 ± 0.01 and D of 0.29 ± 0.09 . In addition, the simulations agreed with the experimental evolution of NER, with an average Ef of 0.81 ± 0.04 and D of -0.10 ± 0.12 .

Though run D produce lowest sum and weighted sum of RMSE-OP_{tot}, this benefit is not for each compartment of OP. In fact, run D improved significantly the simulation for the soluble and adsorbed fractions for each OP, but the best simulation for NER and ¹⁴C-CO₂ was found in run C. For NP, the best run is run C because the sum of the soluble and adsorbed (<13%) was much lower than the sum of the NER and ¹⁴C-CO₂ (>87%). For GLY-1, the best run is run D because the sum of the soluble and adsorbed was near 70%.

Conclusion and perspectives (Times New Roman, bold, size 11)

Our COP-soil Model has been calibrated by data of composts decomposition in soil associated to Ops dynamic. Different categories of OPs (PAH, surfactant and herbicide) were used which suggested that it could be used widely in predicting fate of OPs brought by composts into soil. In another scenario of soil remediation, OPs exist in soil and composts are often added into soil to increase the mineralization of OPs (Semple et al., 2011). In this scenario, OPs need to repartition from organic matter of soil into that of composts because more of the latter is put into the soil, while organic matter in composts can be divided into several compartment (Sw, SND, HEM, CEL and LIG) and thus our COP-Soil model can be used before calibration.

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