Transport of organic contaminants in subsoil horizons and effects of dissolved organic matter related to organic waste recycling practices

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Abstract

Compost amendment on agricultural soil is a current practice to compensate the loss of organic matter. As a consequence, DOC concentration in leachates can be increased and potentially modify the transport of contaminants. In this study we focused on processes controlling the mobility of DOC and of organic contaminants (pesticides and drugs) potentially present in cultivated soils receiving organic waste composts. We sampled undisturbed soil cores in the illuviated horizon of an Albeluvisol in Paris Basin. Three series of percolation experiments were made in presence and absence of DOM extracted from soil surface horizon with two different pesticides and pharmaceutical compounds. Results show that organic pollutants behaviour greatly depends on their intrinsic properties. Meanwhile, DOM behaves as a highly reactive solute, which can also affect the fate of the organic contaminants.

Introduction

Organic waste recycling through compost amendment on agricultural soil is a current practice to compensate the loss of organic matter. It contributes to N and P fertilization, increases soil aggregate stability and limits soil compaction. Long-term applications can result in a net increase of soil organic matter content in the surface soil layer. As a consequence, DOC concentration in leachates can be increased and potentially modify the transport of contaminants. In this study a focus is made on organic contaminants, which are potentially present in cultivated soils receiving organic waste composts: pesticides used in conventionally managed crops (epoxiconazole, isoproturon) and organic waste contaminants such as antibiotics and pharmaceutical compounds (sulfamethoxazole, ibuprofen). Our objective is to characterize transport mechanisms in deep soil layers which may indirectly be affected by leaching from topsoil layers where tillage practices and organic waste addition are known to modify water retention properties [1], hydraulic conductivities [2], sorption and biodegradation of organic contaminants such as pesticides [3, 4]. As repeated organic waste addition modifies both the genesis of DOM and its downwards fluxes [5], we address the question of the effects of DOM on the transport of the above-mentioned molecules through the illuviated Bt horizon, characteristic from Luvisol, containing low content in organic C and enriched in eluviated clays and iron oxides.

Material and Methods

Soil cores sampling
Eleven undisturbed soil cores (5300 cm3) were sampled in the illuviated horizon (Bt horizon at 60-90 cm depth) of an Albeluvisol located in Paris Basin (QualiAgro experimental Site, SOERE_PRO long term observatory, Feucherolles, Yvelines, France). Further, the surface horizon (Ap horizon at 0-28 cm depth) was in two different plots: a control plot without compost application (Control) and a plot receiving a combined compost of sewage sludges and green wastes (SWG). The soil characteristics of the different horizons are presented in Table 1.

Leaching experiments
Percolation experiments under unsaturated steady-state flow conditions were performed using rainfall simulation. A first experiment was setting up to monitor and model DOC leaching in the Bt Horizon in absence and presence of DOM extract from the soil surface. Two soil cores received 3 consecutive

rainfalls separated by a one-week flow interruption. The rainfall solution was made of an aqueous solution of deionised water and added concentrations of major ions to mimic the ionic composition of the soil solution collected in the field at 45 cm depth. For the last rainfall simulation, we used an aqueous DOM solution extracted from the surface soil of the Control plot. A second experiment was designed to study the mobility of isoproturon, epoxiconazole, sulfamethoxazole and ibuprofen in absence (experiment IIa) or in presence of different DOM solution (experiment IIb and IIc). Three series of two consecutive rainfalls separated by a one-week flow interruption were performed on triplicated cores. In experiments IIb and IIc, DOM solutions were extracted from surface soils sampled in the Control plot and the SGW plot respectively. To mimic soil solutions reaching the Bt layer after leaching out of soil surface layers [5], we tried to fix a concentration of 14 mg.l^{-1} DOC in the inflow solutions in experiments I, IIb and IIc. Especially, flow interruptions were carried out to quantify source/sink processes and to characterize the release of DOM when flow proceeds again.

Table 1. Main soil characteristics - surface soil sampled in the control and SGW amended plots used to obtained DOM extracts and the Bt soil layer used in the transport experiment

Soil		pH (water)	Organic C (%)	Clay (%)	Loam (%)	Sand (%)	DOC water extract (mg l^{-1})
Ap horizon (0-28 cm)	Control	7.03	10.18	146	790	64	11.16
	Amended	6.91	15.80	147	784	69	9.63
Bt horizon (60-90 cm)	**Control**	**7.70**	**2.04**	**325**	**648**	**27**	

Organic contaminant and tracer quantification
Together with the first rainfall of experiments II, a pulse containing isoproturon, epoxiconazole, sulfamethoxazole and ibuprofen as well as calcium bromide (water tracer) was injected. Actual concentrations in the pulse solutions were in a same range of values for each column experiment: 68–78 mg.l^{-1} Bromide, 39-52 mg.l^{-1} Sulfamethoxazole, 93-100 µg.l^{-1} Ibuprofen, 51-59 µg.l^{-1} Isoproturon, 90-117 µg.l^{-1} Epoxiconazole (Table 2). The displacement experiments were performed at a rainfall intensity of about 2 mm.h^{-1} and the pulse duration was fixed at 24 hours, which corresponded to about 2.28 ± 0.02 pore volumes. In the percolating solutions, concentrations of DOC, organic pollutants (UPLC-MS-MS) and bromide (HPLC-UV) have been monitored.

DOM Characterization
To follow the DOM quality evolution and characterize the differences between incoming DOM and leaching DOM, we monitored the DOM quality with SUVA and 3D-fluorescence spectra.

Hydrodynamic and solute transport modelling
During the percolation experiments the volumetric water content was monitored with TDR probes of 8 cm length, coupled to a TRASE system at two depths. The water matric potential was measured with SKT sensors coupled to a CR-23 data-logger. These data combined with the breakthrough elution curve of bromide were used to model the water and solute transport in the soil cores, with a 1D water flow and solute transport model, HYDRUS-1D [6].

Results

DOM dynamics
During experiments I and IIa, DOM concentrations rapidly decreased to reach a threshold level of 1 mg DOC l^{-1}, but transiently increased after flow interruption (Figure 1). This experiment allowed characterizing the dynamics of DOM produced and transported in the Bt soil layer. When DOMs solutions were used, we observed a progressive increase of DOC outlet concentrations to reach the concentration of the injected DOM. Aromaticity of DOM was modified during the different rainfalls

and in particular it increased during the endogenous DOM elution. HYDRUS-1D was successfully used to describe the water transport in the experiment I (Figure 2). The transport of bromide was described by a dual-porosity model as non-equilibrium transport occurred in the soil cores. About 65.5% of water content was found as immobile (Table 3). Assuming that DOM behaves as a reactive solute undergoing adsorption/desorption reactions onto the solid phase, we simulated DOM transport by fixing the hydrodynamic properties and the transport parameters (dispersion, immobile water content) previously obtained and by estimating the sorption and degradation parameters (Figure 1). A constant production of DOM of 3.6 $10^{-4}d^{-1}$ was introduced in the model following [5].

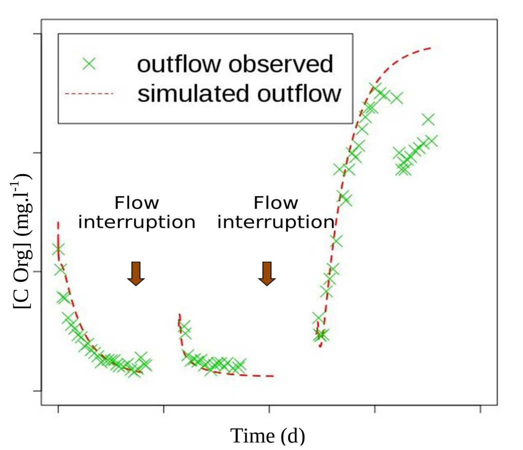

Fig 1. Simulation of Carbon transport during the three rainfalls of experiment I

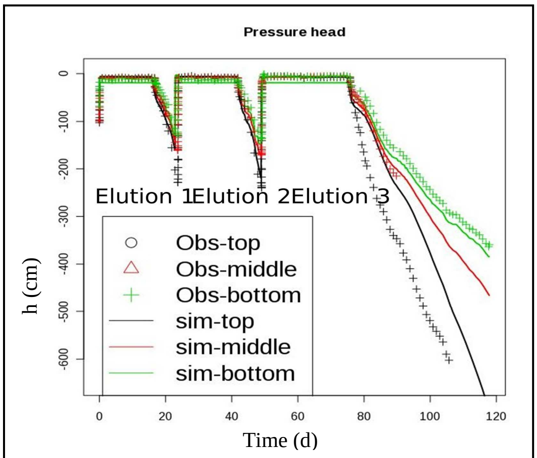

Fig 2. Simulation of water matric potential during the three rainfall of experiment I

Table 2. Concentration range and mass balances estimated from the solute recovery in the different experiments : Br bromide; SMX sulfamethoxazole, IBP ibuprofen ; IPU isoproturon ; EPX epoxiconazole

Solute	Br	SMX	IBP	IPU	EPX
Concentration range	68-78 mg l^{-1}	39-52 µg l^{-1}	93-100 µg l^{-1}	51-59 µg l^{-1}	90-117 µg l^{-1}
Mass recovery (%)					
Exp IIa	56-67	28-39	1-2	20-28	0-2
Exp IIb	62-77	43-44	1-2	17-33	12
Exp IIc	53-67	46-55	3-5	25-38	12-26

Contaminants transport (Experiment II)

Organic contaminant transport was highly depending on the molecular properties (Table 2). Sulfamethoxazole was rapidly displaced through the columns as well as isoproturon, whereas epoxiconazole and ibuprofen were more retarded by sorption processes. The mobility of the more hydrophobic compounds epoxiconazole and ibuprofen was increased in presence of DOM (experiments IIb and IIc, Table 2).

Tableau 3 : Water and solute parameter values estimated with HYDRUS-1D. Standard deviations are in parenthesis. θ_R, θ_S, α and n are the parameters describing the van Genuchten water retention curve, residual water content, saturated water content and two shape parameters, respectively. Ks is the saturated hydraulic conductivity, θ_{im} is the immobile water content, α_s is the solute mass exchange between mobile and immobile water and λ is the dispersivity.

		θ_R	θ_S	α	n	Ks	R^2	D_L	θ_{im}	α_s
		$cm^3.cm^{-3}$	$cm^3.cm^{-3}$	cm^{-1}	-	$cm.j^{-1}$	-	cm	$cm^3.cm^{-3}$	d^{-1}
Column Bt01	mat 1	0,001 (0,000)	0,40 (0,00)	0,022 (0,001)	1,14 (0,01)	62,97 (6,51)		12	0.21	7,77E-02
	mat 2	0,001 (0,000)	0,42 (0,00)	0,008 (0,001)	1,12 (0,02)	10,27 (1,30)	0,84	12	0.32	1,84E-04
	mat 3	0,001 (0,000)	0,37 (0,10)	0,003 (0,000)	1,10 (0,03)	57,33 (17,08)		12	0.24	1,49E-01
Column Bt02	mat 1	0,002 (0,000)	0,39 (0,00)	0,027 (0,001)	1,12 (0,00)	69,47 (2,37)		12	0.22	2,97E-03
	mat 2	0,001 (0,000)	0,43 (0,00)	0,006 (0,000)	1,15 (0,00)	10,66 (0,42)	0,88	12	0.35	8,31E-01
	mat 3	0,001 (0,000)	0,37 (0,00)	0,003 (0,000)	1,08 (0,01)	86,64 (3,12)		12	0.21	4,58E-01

Conclusion and perspectives

Results show that the pollutants behave differently according to their intrinsic properties. Meanwhile, DOM behaved as a highly reactive solute, which can also affect the fate of the organic contaminants. DOC was continuously generated within the Bt horizons columns during flow (baseline) and interruption (peak at the beginning of elutions) and this dynamics could be attributed to adsorption/desorption kinetics as well as microbial processes. DOM increased the mobility of more hydrophobic compounds epoxiconazole and ibuprofen. No clear effects of the origin of DOM on the mobility of the different contaminants were observed. Modelling will be used to test different hypotheses concerning the interactions between DOM and organic pollutants transport.

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