Quantification and modelling the mobility of trace metals in cultivated plots amended by composts of organic urban residues

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INTRODUCTION

Organic amendments from urban and livestock residues may increase the contents of certain trace metals in amended horizons after years. However, the evolution of the mobile metal fraction appears less predictable, depending on the variations of total contents but also on variations of retention factors such as pH and organic matter [1, 2]. Our study aims to put in hierarchy these influences through experimental data and modelling, based on a long-term field experiment equipped with fibreglass wick lysimeters

Field experimental site QualiAgro

QualiAgro is devoted to assessment of long-term effects of spreading urban composts on agrosystems typical of Paris Basin. Crossing 2 levels of inorganic N fertilization and 4 repetition blocks, the 5 modalities concern applications of :

- BIO, co-compost of the fermentable municipal residues collected separately and green waste ("biowaste compost"),
- GWS, co-compost of sewage sludge and green waste,
- MSW, compost of municipal solid waste, using a fermentable fraction sorted after MSW collection,
- FYM, farmyard manure as a reference amendment,
- CTRL, control without amendments.

Maize and winter wheat are cultivated on a deep loess luvisol, according to common practices in the region, except for more intense organic amendments, applied every 2 years on wheat stubble and equivalent to 4 t organic C per ha.

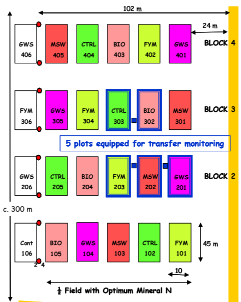


Fig. 1. QualiAgro experiment: half part with optimal N fertilisation and the 5 equipped plots

Table 1. Selected properties of plough amended horizons in 2009 (10 years of organic amendment except CTRL)

Table 1	Organic C	Total N	pH H2O	CEC	Total Cd	Cd EDTA	Total Cu	Cu EDTA	Total Zn	Zn EDTA
Plot	% w/w			mmol+/kg	mg/kg					
BIO	1.42	0.130	7.68	10.4	0.228	0.135	12.6	4.02	55.4	8.10
GWS	1.44	0.136	6.92	9.37	0.230	0.136	15.1	4.78	57.7	9.94
MSW	1.27	0.118	7.46	9.88	0.235	0.141	15.0	5.28	57.9	7.87
FYM	1.42	0.128	7.28	9.96	0.240	0.143	15.2	5.12	57.4	8.62
CTRL	1.02	0.093	6.72	7.81	0.213	0.118	10.7	2.84	48.4	4.02

Analyses of soil solutions collected *in situ* and modelling of transfers

Five plots, one for each modality, equipped for monitoring heat, water and solute transfers. The present study concerns waters collected with fibreglass wick samplers fixed on stainless steel plates of 25x25 cm kept against soil layers at 45 cm depth, during the period 2007-2010.

Chemical analyses of these clear unfiltered waters include :

- pH, dissolved organic carbon (**DOC**), carbonate (performed at INRA-AgroParisTech, Grignon, FR)
- major cations and anions, trace elements (Cd, Cu, Zn here reported (Laboratoire d'Analyses des Sols INRA of Arras, FR).

MODELING. Hydrodynamic was simulated from physical data and models as in [3], without taking into account the samplers.

For predicting metal concentrations, we tested several published "generalized Freundlich" equations [4]. We retained equations more in agreement with soil and average solution characteristics, and include them in Hydrus-1D. E.g., we simulated the fluxes of copper with Hydrus-1D completed by an equation of Tipping et al [2] predicting the Cu concentration from "reactive" soil Cu (EDTA extracted), soil OM content, pH and DOC.

MAIN RESULTS

Effect of amendments on leachates

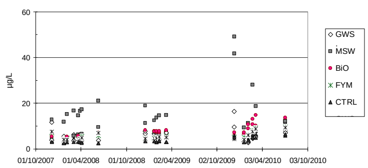


Figure 2. Example of [Cu] during 3 drainage periods (Dec. 2007-June 2010)

Table 2 resumes significant impacts of amendments on some characteristics related to dissolved trace metals.

Table 2. Treatments ranked for pH or solute concentration (non parametric paired tests over 2007-2010)	
DOC: BIO^{a} > (SGW, FYM, MSW)^{b} > CTRL^{c}	**pH**: (BIO, FYM, MSW)^{a} > (CTRL, SGW)^{b}
Cu: MSW^{a} > BIO^{b} $\geq$ FYM^{bc} $\geq$ SGW^{cd} $\geq$ CTRL^{d}	**Cd**: SGW^{a} > BIO^{b} $\geq$ (MSW, CTRL)^{bc} $\geq$ FYM^{c}

Other solutes (not shown): amendments increase concentrations of Ca, K, Mg, Na, NO_3^-, $SO_4^{=}$, Cl^-

Comparisons between measured concentrations and predictions from generic adsorption equations

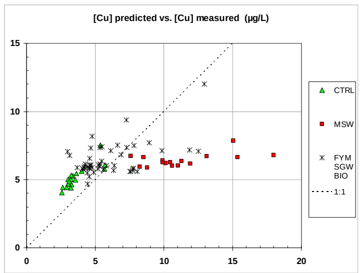


Figure 3 (example). Cu concentrations in leachates of the 5 plots during 3 years (Dec.2007-June 2010) compared with predictions from regression equation of Tipping et al (2003), using their unmodified coefficients of soil variables **OM**, **pH**, "**reactive Cu**" (estimated by EDTA), and **DOC**.

➔ Modelling rather satisfactory for 4 plots among 5;

➔ but not for the highest values, mainly found in plot MSW

Table 3. Summary of soil-solution equilibrium modelling

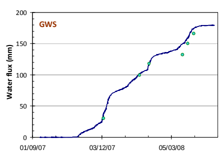
Cu	Tipping et al's equation satisfactory for magnitude and trends, but experimental highest variations not predicted
Cd	A simpler equation [5] predicts the order of magnitude, but not all differences between treatments
Zn	No satisfactory equation found in literature

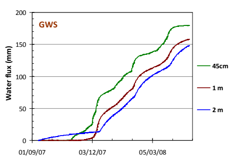
Water fluxes estimated from collected volumes by wick lysimeters at 45 cm depth and simulated by Hydrus-1D

Figure 4. Comparison between these experimental data (symbols) and simulated drainage under 45 cm (continuous lines) – case of GWS plot.

Figure 5: Simulated drainages at different depths in the same plot.

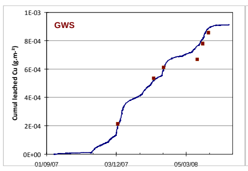
Other plots showed similar simulations, close to experimental data at 45 cm, with slightly higher recorded volumes in the CTRL plot (not shown)

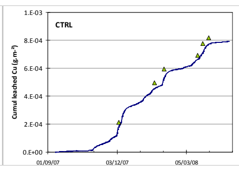




Simulated fluxes of trace metals and comparison with experimental data (drainage period 2007-2008)

Comparison of fluxes calculated from volumes and concentrations of solutions collected by lysimeters (symbols in Figures) with simulated metal fluxes at 45 cm, using Hydrus-1D implemented with equilibrium sorption equations parameterised for the distinct soil layers (continuous lines).





Figures 6-7: Flux of Cu at 45 cm depth in plots GWS and CTRL; simulations very close to experimental (similar results with FYM and BIO)

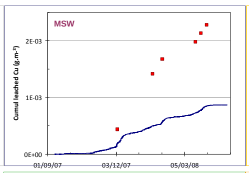


Figure 8: Flux of Cu in MSW plot. Like adsorption equation, transfer modelling underestimate the mobility of Cu

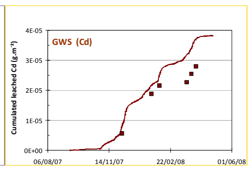


Figure 9: Flux of Cd (example of GWS) Transfer modelling overestimates or slightly overestimates the mobility of Cd

DISCUSSION and CONCLUSIONS

Simple adsorption equilibrium models help to unravel and quantify the impact of organic amendments on trace metal mobility, through the negative or positive influences of increasing soil OM, increased DOC, affected pH, and "reactive" soil metal fractions. But they fail to simulate part of the data, e.g., the highest concentrations of Cu, probably due to insufficient evaluations of the nature and role of DOC, as well as of the "reactive" metal fraction. Kinetic phenomena could also generate variations of leachate composition, which should be addressed by particular functions of Hydrus-1D or of other reactive transfer models. Yet, the presented simulations of fluxes with Hydrus-1D were partly consolidated by data obtained from interception plates at 45 cm, and help to quantify metal leaching toward deeper horizons and groundwater. They support that the risk of transfer would remain below 1 or 2 mg Cu/m^2/year, and between 0.01 and 0.04 mg Cd/m^2/year, to be compared to stocks of reactive metals in the plough horizons around 1800 mg Cu/m^2 and 50 mg Cd/m^2.

ACKNOWLEDGEMENTS and REFERENCES

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