Compost Addition on Polluted Soils to Ensure Fruit and Vegetable Safety

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Abstract

Agricultural pollutions affect food safety, environmental quality and human health. In the case of persistent soil pollution such as chlordecone in French West Indies, crops, mainly horticultural ones, can be polluted over the Maximum Limit of Residues. Actually, there is no remediation solution for these polluted soils. Interactions between organic matter and pesticides are known to help reduce the bioavailability of pesticides in soils. So sequestering pesticides in soils by adding compost could be an alternative way of reducing their diffusion into food chains. We added 5% organic matter to the soil upper layer of horticultural fields and pots. The soil to crop transfer for radish, lettuce and cucumber decreased from 33 to 75% according to the crop and the soil type. Organic amendment significantly reduced transfer to the radish tuber; that was 1.4-fold less contaminated than the control and to the cucumber fruit, control being 60% more contaminated. The long-term efficiency of pesticide sequestration needs to be tested. We demonstrated that this sequestration depended on the soil type and their clay physical properties. In nitisol, chlordecone sequestration is mainly due to chemical interactions with the compost particles whereas in andosol, it is also partly due to the physical impact of the added compost (allophane collapse). Increasing soil organic matter content reduces pesticide mobility in the soil and hence its bioavailability for plants. Adding organic amendment to soils is a promising way to reduce the risk of pesticide contamination of food and thus decrease the human exposure.

INTRODUCTION

The consequences of pesticide pollution in soil and water may be extremely damaging for both the environment and human health. In agriculture, the use of persistent pesticides before the 90's, such as organochlorine, led to long term pollution of soils. These kinds of persistent pollutants are known for their particular affinity to organic matter, with a high K_{oc} ($\log K_{oc}>3.5$), and low solubility. Thus even if the pesticide use is forbidden for decades, soils still are the current pollution reservoir, and contaminate all

the resources: waters (river and groundwater), ecosystems (specifically aquatic ones), food chains and consequently human beings.

In the French West Indies, chlordecone (CLD), an organochlorine insecticide ($C_{10}Cl_{10}O$), had been used to control the banana black weevil (*Cosmopolites sordidus*) more than twenty years ago, from 1971 to 1993, and now contaminates the environment (Coat et al. 2011). It causes a diffuse and long term pollution as a large area of former banana plantations is still polluted (Cabidoche et al, 2009; Clostre et al, 2014, Levillain et al, 2012). These areas contaminate some agricultural products (Cabidoche and Lesueur Jannoyer, 2012; Clostre et al, 2015 ; Jondreville et al, 2013). Through food, the population is exposed to the pollutant, which causes public health problems such as increase of prostate cancer (Multigner et al, 2010) and impairment in the child development (Boucher et al. 2013; Dallaire et al, 2012). It is thus necessary to control the fate of chlordecone in the soils and in the whole environmental compartments in order to decrease the crops and food chains contamination and to reduce population exposure.

Remediation strategies rely on three main processes to reduce the environmental impact of contaminated soils: extracting the pollutant, enhancing its degradation or decreasing its availability. To remediate this diffuse pollution, phytoextraction (Topp et al. 1986) and microbial degradation (Orndorff and Colwell 1980; George and Claxton 1988) have not been very successful to date. Opposite to extraction and degradation, CLD sequestration in soils could be a way to control further release of CLD from contaminated soils towards other environmental compartments until efficient decontamination techniques become available. The aim of our study is to assess if pollutant sequestration could be an innovative way to remediate soil pollution in the case of CLD pollution. Thus we tested the effect of compost addition on the pollutant transfer from soil to plant for 3 crops (cucumber, lettuce, radish) known to be contaminated at different levels when grown on polluted soils (Clostre et al, submitted; Woignier et al, 2012).

MATERIALS AND METHODS

Characterization of soil samples

A contaminated non allophanic (nitisol) plot and a contaminated allophanic soil (andosol) were chosen for this study. Their main characteristics are given in table 1. Soil pH was determined with a glass electrode in a 1:2 soil: water suspension. Organic Carbon (OC) content was measured with a CHN analyzer (Thermo Finnigan Flash EA 1112, Thermo Finnigan Italia, Rodano, Italy).

The crystalline structure of clay was studied by X-rays diffraction (Cu Kα) with a Philips PW 1830. The presence of halloysite clay, with a phyllosilicate structure, and of allophane clay, with a fractal structure (Chevalier et al. 2008), was confirmed by Infrared Spectroscopy with a IR-FT Nicolet 510P spectrometer (ThermoFischer Scientific Inc., Waltham, MA, USA); samples were diluted in KBr pellets with a $5\ 10^{-3}$ mass ratio.

Porous properties

These measurements aimed at characterizing the possible changes in the microstructure of the soils caused by compost addition. Porous properties were measured as detailed in Woignier et al, 2013. Super critical drying was necessary to account for specific surface area and the pore size distribution (Pauthe et al. 1991).

Pore size distributions were assessed by Barrett-Joyner-Halenda method of N_2 adsorption-desorption isotherms (Barrett et al. 1951). The N_2 absorption-desorption isotherms of the samples were measured using a volumetric absorption analyzer (ASAP

2020, Micromeritics France SA, Verneuil en Halatte, France). The N_2 isotherms were plotted as a function of relative pressure (P/P0 = 0.025-0.99).

Trials

Two contrasted modalities of organic matter amendments were studied: 0% (control), and 5% w/w of commercial compost (70 t/ha). The components of the compost used in this study (Vegethumus manufactured by Fayssinet) are sheep manure, pulp and cake from fruits (olive, cacao, coffee and sunflower), wool stuffing and magnesium. Its main characteristics are 24.8% water content, 46.6% organic matter content, C:N ratio=13, humifying capacity= 0.70; humic yield = 577 kg t^{-1} raw material. This compost has the characteristics of an organic amendment, with a slow mineralization dynamic and with an important contribution to soil organic matter content (Fernandes et al. 2010).

Plant experiments were conducted under controlled and in field conditions. Radish (*Raphanus sativus),* cucumber (*Cucumis sativus*) and lettuce (*Lactuca sativa*) were grown in pots on aged andosol collected from the field and after incorporation of the compost treatment 3 months before. Radish (Raphanus sativus) and cucumber (Cucumis sativus) were also grown in field conditions on aged nitisol and after incorporation of the compost treatment 3 months before. Three to six repetitions were performed for each crop. Crops were harvested at the commercial stage, CLD concentration was measured in the fine roots, the tuber and leaves for radish, and only the edible part for lettuce (leaves) and cucumber (fruits).

We calculated transfer from soil to plant, defined as the ratio of CLD content in the plant sample (expressed in µg of CLD content kg^{-1} fresh matter) to soil CLD content (expressed in µg of CLD kg^{-1} dry matter).

CLD analysis for plant and soil samples

CLD soil analyses were performed at the French analysis laboratory of Martinique County (LDA972). Extraction was carried out with dichloromethane and acetone (v:v 50:50). After concentration and purification, CLD content was measured using a Gas Chromatograph - Electron Capture Detector (GC-ECD) VARIAN (Palo Alto, CA, USA) GC 3800 and GC–MS–MS method (gas chromatography coupled with mass spectrometric detection) with VARIAN GC 450 and MS 240. The resulting average extraction coefficient was 0.85. For identification, three transitions from precursor ion m/z 272 were monitored. Validation of extraction efficiency and quantification rely on standard addition method and tracers.

CLD plant analyses were performed at the French analysis laboratory of the Drôme County (LDA26). A first extraction was carried out with acetone followed by a second one with dichloromethane and NaOH for alkalinization. The CLD recovery performances were 84%. After purification, CLD content was measured either by using VARIAN (Palo Alto, CA, USA) and Agilent (Santa Clara, CA, USA) Gas Chromatographs with Electron Capture Detector (GC-ECD) or Thermo (West Palm Beach, FL, USA) TSQ Quantum Ultra High Performance Liquid Chromatograph–Mass Spectrometer (HPLC–MS), depending on the matrix interferences with the GC–ECD. Two transitions from precursor ion m/z 272 were monitored. Validation of calibration and quantification rely on standard addition method and tracers.

Analytical techniques are further described in Woignier et al. (2012). The resulting CLD data for both laboratories are given with 30% relative error. Results are given on a dry weight basis for soil and fresh weight basis for plant as these units are those used in

regulations. Quantification limits of chlordecone were 10 µg.kg−1 (dry soil) for soil samples and 1 µg.kg-1 (fresh matter) for plant samples. Both LDA972 and LDA26 comply with ISO 17025 standards and have been accredited by COFRAC, the French Accreditation Committee, for CLD analysis.

The CLD content we refer to in this paper is the sum of CLD and its main metabolite, 5b-hydroCLD, soil content. 5b-hydroCLD acute toxicity is known to be close to that of CLD (Carver and Griffith, 1979). This study took place in an environmental and public health framework, with the aim of reducing ecosystem and consumer exposure to CLD, which is why the two molecules were summed.

Statistical analysis

For pots experiments in andosol, three to six replicates were grown under each treatment (no compost or added compost) for each crop: five for radish, three for cucumber and six for lettuce. Differences between treatment (compost and control) were tested by ANOVA followed by Tukey's test ($p < 0.05$).

For field experiments on nitisol, four (control) and six (compost) replicate samples of radish, and nine (control) and 12 (compost) replicate samples of cucumber were analysed. Data were analysed by non-parametric ANOVA (Kruskal-Wallis and Mann-Whitney tests, $p < 0.05$).

RESULTS AND DISCUSSION

MO addition decreases the soil to crop transfer of pollutant

In the controlled conditions, and whatever the considered crop part, the radish grown in andosol showed a strong decrease of CLD amount with organic matter addition. Fine roots, tuber and leaves are respectively 4, 15 and 5 fold less contaminated than in the control conditions (figure 1). In the field conditions, and for the control (without compost addition), the fine roots of the control radish were 3-fold more contaminated than those grown with 5% compost amendment; edible tubers were 1.4-fold more contaminated for the control and no significant reduction was observed in leaves probably due to their very low CLD content (close to the detection level) (table 2).

According to the soil type, after addition of compost, contamination is 1.4 fold less in the tuber for nitisol, and 15 fold less in andosol, thus organic amendment is more efficient when applied on polluted allophanic soil. Along time, organic amendment is still efficient for lettuce, 6 months after application, but the duration of this positive effect has to be assessed for larger periods.

If we compared the transfer coefficient, we showed that, for radish, whatever the treatment, CLD transfer was 70–90 times higher to fine roots than to tubers and around 800 times higher to fine roots than to leaves. For cucumber and lettuce, the transfer coefficient for the fruit or leaves is 1.6 to 2 fold less in the case of organic amendment, for the two soil types (table 3).

Our results are in accordance with previous works done on high hydrophobic compounds characterized by high $\log K_{ow}$ value. Hydrophobic pesticides tend to sorb to the root epidermis; after which, they are progressively adsorbed onto the lower part of the plants with poor partition into the xylem sap (Campanella et al. 2002; Trapp and Karlson 2001). As a result, highly hydrophobic chlorinated pesticides are poorly translocated to upper plant parts. This could be due to the fact that the main pollutant transfer route from soil to plant is a passive transfer from the contaminated water soil solution that passes

through the root cellular barriers and moves upstream through the xylem sap flow to the aboveground compartments (Cabidoche and Lesueur-Jannoyer 2012).

MO addition affects soil structure

Organic amendment is more efficient in the case of allophanic soil, why?

In the case of non allophanic soils, contrarily to andosols, we did not observed any modification of the specific surface area, pore volume and pore size distribution after the addition of organic matter (figure 2). This difference is to be attributed to the peculiar microstructure of andosols formed by highly porous allophane aggregates. They exhibit a fractal and tortuous structure in the size range of 1–100 nm (Chevallier et al. 2008) with poor mechanical properties. The fractal micro-structure of andosols is fragile and was altered by the incorporation of composts and subsequent decomposition. We demonstrated that the addition of compost in the allophanic soils led to the closure of pores and to a reduction in the fractal range (Woignier et al, 2013). During incubation, chemical reactions and some fluid displacements induced capillary stresses inside the fractal aggregates leading to closure of the mesopores (figure 2a). In the case of non allophanic soil the layer like microstructure of halloysite clay is not fractal and is less sensible to the capillary forces than the spongy allophane structure (figure 2b).

Along time, CLD sequestration enhancement is concomitant with CLD migration/relocalization in the granulometric fraction corresponding to prehumified or partially mineralized organic debris with the tendency of an increased CLD rate in the intermediate fractions (50-200 µm) and a reduced one in the finest fraction (0-50µm) compared to the same fraction in the control (Woignier et al, in press).These results support the hypothesis that, for non allophanic soil, chemical processes contribute to enhance CLD sequestration in soil. For allophanic soil, both chemical and physical processes contribute to increase CLD sequestration in soil.

Indeed the amount, but also the chemical nature of soil organic matter, are key factors driving organic pollutants interactions within soil and their dissipation processes (Ehlers et al. 2010).

Practices reduce the pollutant availability in soil

Enhancing the CLD sequestration in soil thus reduces the CLD transfer in the water soil solution and, as a consequence, the transfer to plants as well. Compost amendment could lead to reduce or secure the recommended soil CLD concentration thresholds to grow vegetables and comply with regulations. Indeed Cabidoche and Lesueur-Jannoyer (2012) found a simple linear relationship between soil chlordecone content and yam tuber chlordecone content, thus, decreasing the transfer ratio, leads to increase the threshold below which a vegetable can be grown without risk of exceeding the Maximum Residue Levels (MRL).

The compost addition is a common practice that can easily be integrated (or reintegrated) to cropping systems. Nevertheless, to be relevant, this practice has to be refined by further research before the application in farm context. We must assess the quantity of organic amendment to add as well as the time duration of the treatment, according to soil type and soil pollution level. Then, a balance would have to be found between the frequency and the quantity of compost addition.

CONCLUSIONS

Increasing soil organic matter content reduces pesticide mobility in the soil and hence its bioavailability for plants. Adding organic amendment to soils is a promising way to reduce the risk of pesticide contamination of food and thus decrease the human exposure. Further study is needed to assess the efficiency with time of the pollutant sequestration in soil and to assess the sustainability of this practice. Then, recommendations could be made to adapt agricultural practices and design cropping systems that cope with regulation and thus ensure food safety.

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Literature Cited

Boucher, O., Simard, M.N., Muckle, G., Rouget, F., Kadhel, P., Bataille, H., Chajès, V., Dallaire, R., Monfort, C., Thomé, J.P., Multigner, L. and Cordier, S. 2013. Exposure to an organochlorine pesticide (chlordecone) and development of 18-month-old infants. Neurotoxicol. 35 (0):162-168.

Cabidoche, Y.M., Achard, R., Cattan, P., Clermont-Dauphin, C., Massat, F. and Sansoulet, J. 2009. Long-term pollution by chlordecone of tropical volcanic soils in the French West Indies: A simple leaching model accounts for current residue. Environ. Pollut. 157 (5):1697-1705.

Cabidoche. Y.M. and Lesueur-Jannoyer, M. 2012. Contamination of Harvested Organs in Root Crops Grown on Chlordecone-Polluted Soils. Pedosphere 22 (4):562-571.

Campanella, B.F., Bock, C. and Schroder, P. 2002. Phytoremediation to increase the degradation of PCBs and PCDD/Fs. Potential and limitations. Environ Sci Pollut Res Int 9 (1):73-85

Chevallier, T., Woignier, T., Toucet, J., Blanchart, E. and Dieudonné, P. 2008. Fractal structure in natural gels: effect on carbon sequestration in volcanic soils. Journal of Sol-Gel Science and Technology. 48(1):231-8.

Clostre, F., Lesueur-Jannoyer, M., Achard, R., Cabidoche, Y.M., Cattan, P. and Letourmy, P. 2014. Decision tool to design soil sampling at field scale for heterogeneous pesticide pollution: Chlordecone as a case study. Env. Sci. and Poll. Res. 21 (3): 1980-1992. DOI 10.1007/s11356-013-2095-x

Clostre, F., Letourmy, P. and Lesueur-Jannoyer, M. 2015. Organochlorine (chlordecone) uptake by root vegetables. Chemosphere, 118 (0), 96-102 doi:http://dx.doi.org/10.1016/j.chemosphere.2014.06.076

Clostre, F., Letourmy, P. and Lesueur Jannoyer M. 2014. Organochlorine (chlordecone) uptake by root vegetables. Chemopshere (in press)

Clostre, F., Letourmy P., Turpin B., Carles, C. and Lesueur Jannoyer, M. Soil type and growing conditions influence uptake and translocation of organochlorine (chlordecone) by Cucurbitaceae species. Water, Air and Soil Pollution (submitted)

Coat, S, Monti, D., Legendre, P., Bouchon, C., Massat, F. and Lepoint, G. 2011. Organochlorine pollution in tropical rivers (Guadeloupe): Role of ecological factors in food web bioaccumulation. Environ. Pollut. 159 (6):1692-1701.

Dallaire, R., Muckle, G., Rouget, F., Kadhel, P., Bataille, H., Guldner, L., Seurin, S., Chajès, V., Monfort, C., Boucher, O., Thomé, J.P., Jacobson, S.W., Multigner, L. and Cordier, S. 2012. Cognitive, visual, and motor development of 7-month-old Guadeloupean infants exposed to chlordecone. Environ. Res. 118 (0):79-85.

Ehlers, G.A.C., Forrester, S.T., Scherr, K.E., Loibner, A.P. and Janik, L.J. 2010. Influence of the nature of soil organic matter on the sorption behavior of pentadecane as determined by PLS analysis of mid-infrared DRIFT and solid-state 13C NMR spectra. Environ Pollut 158 (1):285 - 291.

Fernandes, P., Jannoyer-Lesueur, M., Soler, A., Achard, R. and Woignier, T. 2010. Effects of clay microstructure and compost quality on chlordecone retention in volcanic tropical soils: consequences on pesticide lability and plant contamination. 19th World Congress of Soil Science, Soil Solutions for a Changing World

George, S.E. and Claxton, L.D. 1988. Biotransformation of chlordecone by Pseudomonas species. Xenobiotica 18 (4):407-416.

Jondreville, C., Lavigne, A., Clostre, F., Jurjanz, S., Dalibard, C., Liabeuf, J.-M., et al. Contamination of grazing ducks by chlordecone in Martinique. In EAAP - 64th Annual Meeting, Nantes, France, 2013 (Vol. 19, pp. 166-166, Book of abstract): Wageningen Academic Publishers

Levillain, J., Cattan, P., Colin, F., Voltz, M., and Cabidoche, Y.-M. 2012. Analysis of environmental and farming factors of soil contamination by a persistent organic pollutant, chlordecone, in a banana production area of French West Indies. Agriculture, Ecosystems & Environment, 159(0), 123-132

Multigner, L., Ndong, J. R., Giusti, A., Romana, M., Delacroix-Maillard, H., and Cordier, S. 2010. Chlordecone Exposure and Risk of Prostate Cancer. Journal of Clinical Oncology, 28(21), 3457-3462

Orndorff, S.A. and Colwell, R.R. 1980. Microbial transformation of kepone. Appl. Environ. Microbiol. 39 (2):398-406.

Pauthe, M., Quinson, J.F., Hdach, H., Woignier, T., Phalippou, J. and Scherer, G.W. 1991. Autoclave treatment effect on silica alcogel texture. J Non-Cryst Solids. 130(1):1-7.

Topp, E., Attar, A. and Korte, F. 1986. Factors affecting the uptake of 14C-labeled organic chemicals by plants from soil. Ecotoxicol Environ Saf 11 (2):219 - 228.

Trapp, S. and Karlson, U. 2001. Aspects of Phytoremediation of Organic Pollutants. J. Soils Sed. 1:1-7.

Woignier, T., Clostre, F., Macarie, H. and Jannoyer, M. 2012. Chlordecone retention in the fractal structure of volcanic clay. J. Haz. Mat. 241–242 (0): 224-230.

Woignier, T., Fernandes, P., Soler, A., Clostre, F., Carles, C., Rangon, L. and Lesueur Jannoyer, M. 2013. Soil microstructure and organic matter: Keys for chlordecone sequestration. J. Hazard. Mater. 262 (0): 357-64.

Woignier, T., Clostre, F. Fernandes, P., Rangon, L., Soler, A. and Lesueur Jannoyer, M. Sequestering pesticide with organic fertilizer or organic amendment, in Fertilizer Technology Vol. 2. In press

Tables

Table 1. Soil characteristics for the two soils (allophanic –andosol- and non allophanic –nitisol) used in our experiment

Soil type	C content (%)	pH	CLD content (mg kg^{-1})	Clay type
Allophanic soil	2.93	4.53	4.70	Allophane
Non allophanic soil	2.03	6.43	0.91	Halloysite

Table 2: CLD transfer rate from soil to crop for radish in the pot allophanic experiment and in the field non allophanic experiment (* significant difference with control, ns non-significant difference).

Soil type	Fine roots		Tuber		Leaves	
	control	compost	control	compost	control	compost
Allophanic soil	6.0	1.83(*)	0.334	0.022(*)	0.002	0.001(ns)
Non allophanic soil	2.47	0.79(*)	0.028	0.019(*)	0.003	0.001(ns)

Table 3: Reduction factor of soil to crop transfer for the eddible part of radish, lettuce and cucumber

	Radish (tuber)	Lettuce (leaf)	Cucumber (fruit)
Allophanic soil, pot experiment	-33%	-75%	-49%
Non allophanic soil, field experiment	-32%		-38%

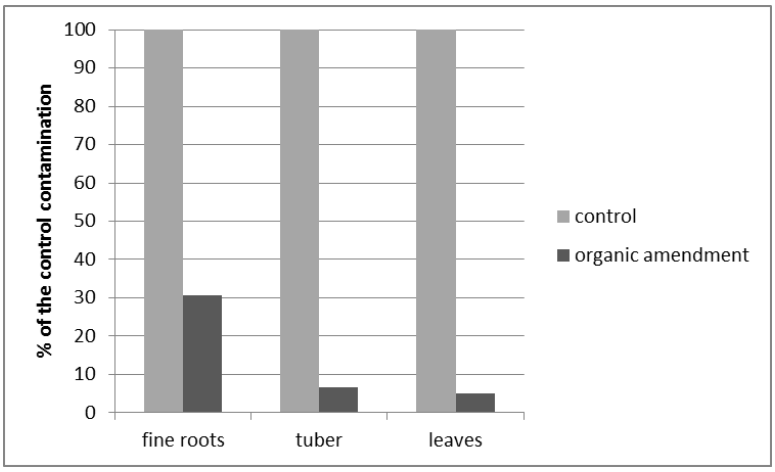

Fig. 1. Normalized CLD transfer (%) in radish organs for control (grey) and organic amendment (dark grey) in allophanic soil.

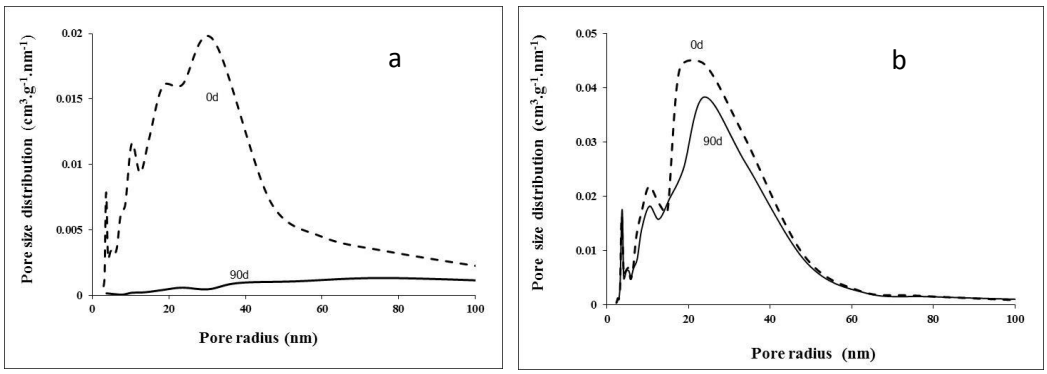

Fig. 2. Pore size distribution according to organic matter maturation time (0d: at incorporation date; 90d: 90 days after organic matter incorporation) in the two type of soils (a: allophanic soil, b: non allophanic soil)