Effects of clay microstructure and compost quality on chlordecone retention in volcanic tropical soils: consequences on pesticide lability and plant contamination

Fernandes P.[A], Jannoyer-Lesueur M[A], Soler A[C], Achard R.[C], Woignier T.[B, D]

[A] CIRAD/PRAM, UPR Fonctionnement agroécologique et performances des systèmes de culture horticoles, B.P. 214 Petit Morne, 97232, Le Lamentin, Martinique, paula.fernandes@cirad.fr ; magalie.jannoyer@cirad.fr
[B] IRD/PRAM, UMR Ecologie Fonctionnelle et Biogéochimie des Sols, B.P. 214 Petit Morne, 97232, Le Lamentin, Martinique, thierry.woignier@univ-montp2.fr
[C] CIRAD/PRAM, UPR Fonctionnement Systèmes de cultures bananes plantains et ananas, B.P. 214 Petit Morne, 97232, Le Lamentin, Martinique, alain.soler@cirad.fr ; raphael.achard@cirad.fr
[D]CNRS-Université de Montpellier, France.

Key Words
Fractal structure, chlordecone, organic matter, allophane, contamination, French West Indies.

Abstract
The scientific and economic context of our study is related to the pollution of the soils, fresh and marine water by a persistent organochlorine pesticide (chlordecone) in a tropical context (French West Indies). The former application of chlordecone results today in a diffuse pollution in agricultural soils, which are sources of contamination for cultivated roots, tubers, vegetables and terrestrial and marine ecosystems. Chlordecone is a very though and stable molecule (considered as a POP), it is mainly present in solid phase and has a strong affinity with organic matters. To prevent consumers and ecosystems exposure, it is thus necessary for us to evaluate the factors that influence chlordecone migration in the environment. In our research, we studied the impacts of clay microstructure on the chlordecone retention, comparing allophanes (amorphous clays present in andosols) and halloysite clays (type 1/1). We showed that allophane aggregates had a greater ability to trap chlordecone mainly due to their fractal structure. We also measured the effects of added composts on soil microstructure and on chlordecone lability and transfer rate from soil to plant 3 and 6 months after incorporation. The intensity and persistence of these effects were related to the initial quality and richness of the added composts.

Introduction
Chlordecone is a very though pesticide which was used for 2 decades in both Guadeloupe and Martinique (from 1971 to 1993) mainly for the control of the banana black weevil. Chlordecone has a great soil and organic matter affinity (in the literature Koc varies from 17500 L/kg according to Kenaga (1980) to 2000-2500 L/kg according to ATSDR (1995) but a low water solubility (Dawson *et al.* 1979). Thus, chlordecone mainly diffuses in environment through water elution (Cabidoche *et al*. 2009), soil erosion and transport of clay particles. In Martinique, andosols and nitisols are the most frequent polluted fields and are considered as the pollution reservoirs (Cabidoche *et al*. 2006).

Volcanic soils like andosols contain amorphous clays (allophanes), issued from the transformation of volcanic materials (Colmet Daage and Lagache 1965). These amorphous clays present very different structures and physical properties compared to usual clays (Woignier *et al*. 2007). Allophanes aggregates develop a fractal structure in andosol which leads to peculiar physical features: large pore volume and pore size distribution, a high specific surface area and very large water content (Chevalier *et al*. 2008). These soils have been strongly polluted and the clay microstructure should be an important physico-chemical characteristic governing the fate of the pesticide in the environment.

Methods
In our research we studied the lability of chlordecone by laboratory lixiviation experiments on two contaminated soils: an andosol and a nitisol (respectively containing two different type of clays: allophane and halloysite) and we characterized the changes of clays microstructure induced by two contrasted composts (Table 1) (Li *et al.* 2003). The incubation was realized at 28-30°C, 90% of maximal retention capacity (to preserve the physical structure of allophane) and 5% (w/w) of compost was added. We also studied their effects on plant contamination (i) a radish after 3 months of incubation and (ii) a lettuce after 6 months.

Table 1. Characteristics of the two commercial composts used

	Biogwa	Vegethumus
Water content	47 %	24.8 %
Organic matter content	20.6 %	46.6 %
Humic yield (CBM)	49 kg C/t of fresh product	577 kg C/t of fresh product
Humic potential (K_1)	0.11	0.70

Results

Effect of the clay microstructure on the lability of chlordecone

Figure 1 shows the evolution, during the incubation time, of water extractible chlordecone after compost addition. The results demonstrate that chlordecone amounts extracted by water decrease according to incubation time for both soil types and composts.

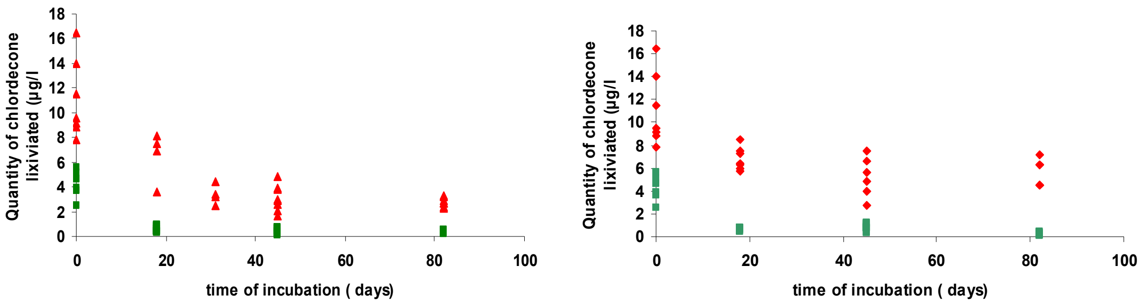

Figure 1. Quantity of lixiviated chlordecone (µg/l) for different incubation times from andosol (red dots) and nitisol (green dots) after compost addition (left: Vegethumus, right: Biogwa).

Vegethumus appears to be more efficient in the reduction of chlordecone lability than Biogwa, probably due to its higher organic matter content and K_1. This is confirmed by measuring the effect of composts on soil N mineralization (Figure 2), which shows that Vegethumus provides significantly greater amounts of mineral N in both soils.

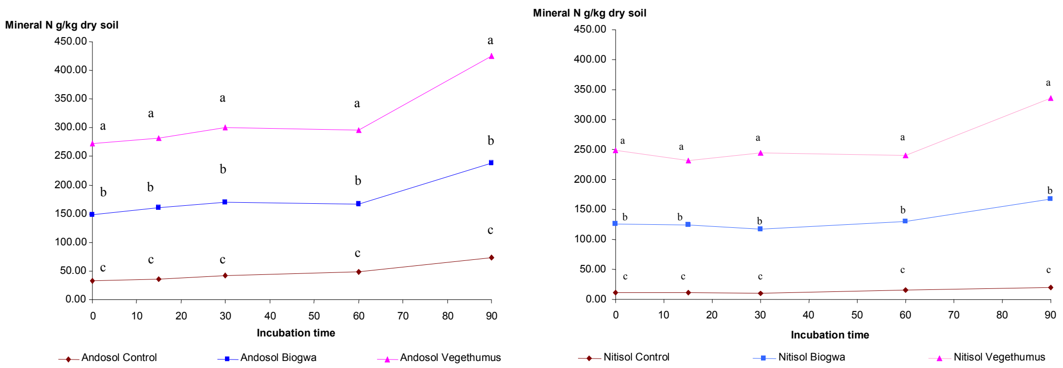

Figure 2. Effect of compost addition on production of total mineral N on andosol (left) and nitisol (right). For each date, means with different letters are significantly different ($p < 0.001$).

Considering the effect of composts on the poral volume (Figure 3), the pore size distribution shows that the porosity of the andosol is greatly reduced with the incubation time by the addition of organic matter and that this effect is more important in the case of Vegethumus. This effect is also associated with the reduction of specific area. In the case of nitisol, the effect of compost addition is not noticeable. But compost addition induces a dramatic reduction of microporosity in the case of andosol where allophanes develop a fractal structure. This phenomenon could explain the lower lability of chlordecone by retaining the molecule in this very tortuous and closed porosity. Thus, in the case of nitisol, the impact of compost addition could be more related to the high affinity of chlordecone for organic matter, as the modification of the porosity is poorly influenced.

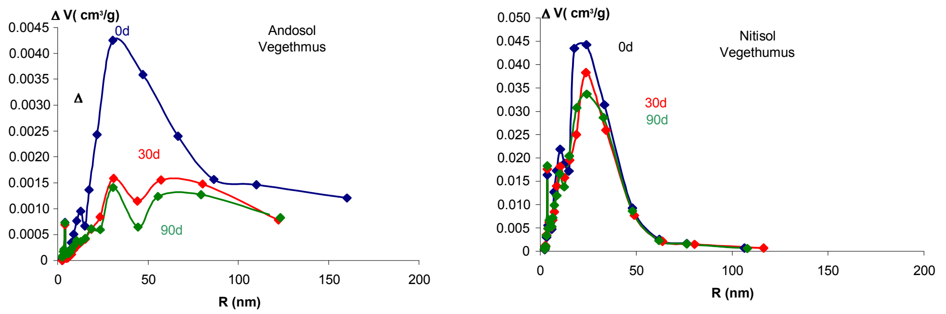

Figure 3. Evolution of the distribution of size pores according to the incubation time (0 day : blue ; red : 30 days ; green : 90 days) after addition of Vegethumus (left : andosol, right : nitisol)

Effect of the added composts on plant contamination after 3 months of incubation

Three months after the incorporation of compost, radishes were seeded in the incubated soil. Chlordecone contamination was measured in small roots, main root (edible part) and leaves at harvest time.

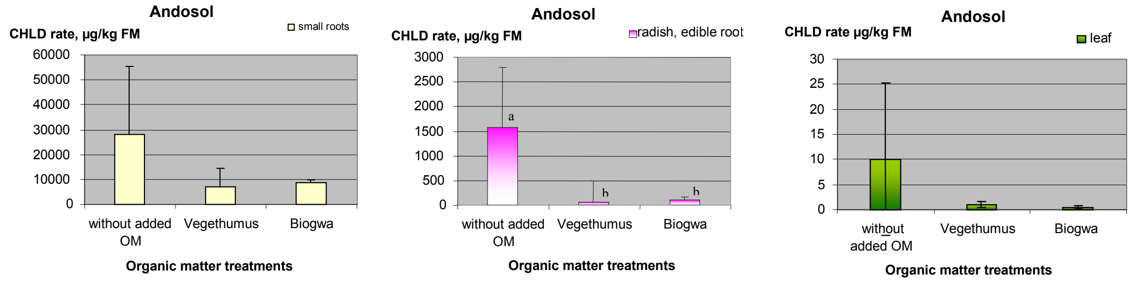

Figure 4. Chlordecone content (µg/kg of fresh material) of radish (in yellow : small roots ; in pink : main root ; in green : leaves) cultivated on contaminated andosol according to the different added composts. Means with different letters are significantly different ($p < 0.05$).

Figure 4 shows that plant contamination transfer decreases drastically between small roots, main root and leaves, even in the control. Nevertheless, the addition of compost reduces noticeably, in both cases, the contamination of plant tissues. The direct contact between roots and soil chlordecone seems to be the main factor of plant contamination as the diffusion in the plant is similar for all the treatments.

Effect of the added composts on plant contamination after 6 months of incubation

After six months of incubation, effects of added composts start to differ noticeably. Contamination of lettuce is significantly increased (4-fold) with Biogwa, compared to Vegethumus where the contamination remains very low (figure 5). This could be explained by the important differences of quality and biochemical composition of the two composts. Biogwa has the characteristics of an organic fertilizer, mineralized after a short period and contributing poorly to soil organic matter. At the opposite, Vegethumus has the characteristics of an organic amendment, with a slow mineralization dynamic (20% after 6 months) and with an important contribution to soil organic matter content (70% of added C integrates the soil organic matter).

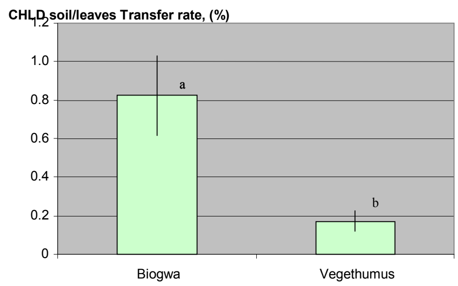

Figure 5. Effect of compost after 6 months of incubation on chlordecone transfert (%) from the andosol to the plant (lettuce). Means with different letters are significantly different ($p < 0.05$).

Conclusion

Andosol (allophane clay) and nitisol (halloysite clay) behaviour differed in the processes involved in chlordecone retention. The structural properties and the spatial arrangement of allophane aggregates constitute a trap for chlordecone molecule, thus mechanically retained. Compost addition modified the andosol porosity (poral volume and specific area) according to the compost quality and highly reduced chlordecone lability. In the case of nitisol, the retention of the molecule seems more directly affected by added organic matters such as composts, leading to a chemical retention of chlordecone. The intensity of the compost effects is driven by its initial richness (C and dry matter) while the persistence could depend of the complexity of its biochemical composition, conditioning its decomposition kinetic. Andosol is able to retain pesticides stronger than nitisol, combining physical trapping and chemical retention. As a consequence, andosol could be highly polluted but less contaminant for crops and environment because of these effects. Further investigations should be realized to confirm these results at a larger scale before making recommendations for the management of polluted fields.

Acknowledgments

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