Soil carbon management and filtering of organic pesticides

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Abstract

Soil organic carbon (SOC) content is known to be sensitive to changes in land-use and management in a particular land-use system. We hypothesized (1) that in aggregated soils the filtering capacity for organic pesticides depends on physical, chemical and biological properties at the aggregate scale, impacting water sorptivity, pesticide sorption and degradation, respectively, and that these are related to the SOC content; and (2) that the filtering capacity is not equivalent to the filtering efficiency during transport. The impact of decreased SOC on soil filtering capacity and efficiency for pesticides was investigated using radiolabelled 2,4-D in laboratory experiments. Substituting space for time, two pairs of sites with the same soil type, texture, land-use and climatic conditions, but with significantly different SOC content within each of the pairs were selected. For the pair of hydrophobic pastoral soils, the SOC loss had a significantly ($P \leq 0.05$) negative impact on the soils' chemical and biological filtering capacity, but a significantly positive impact on the physical filtering capacity for 2,4-D. The physical filtering capacity clearly dominated the filtering efficiency. For the pair of orchard soils, a SOC loss did not significantly ($P \leq 0.05$) impact on the filtering efficiency for 2,4-D, even though the physical and biological filtering capacity were significantly changed. The results show that hydrophobicity is a risk to soils' filtering efficiency in soils with high SOC contents.

Key Words

Leaching, degradation, sorption, sorptivity, hydrophobicity, 2,4-D.

Introduction

In areas with regular application of pesticides the intactness of the soil's filtering capacity for pesticides protects aquifers. Leaching through soils has been identified as a major source of pesticide contamination of aquifers. The ubiquity of pesticide detections in groundwater (Barbash *et al.* 2001; Gaw *et al.* 2008) indicates that this filter is overloaded and/or its efficiency decreases. Global pesticide production has increased linearly from 1960 until 2000. If this trend continues the amounts produced in 2020 are predicted to be 1.7 times higher than in 2000 (Tilman *et al.* 2001). Governments look for guidance what kind of soil properties should be monitored to predict early changes in the generic performance of the soil's ecosystem service of filtering. The SOC content of the topsoil seems to be an obvious candidate as it is very sensitive to any land-use change or modification of management practices within a particular land-use (Bellamy et al. 2005).

The SOC content of topsoils is linked to the filtering of pesticides. We defined the generic filtering capacity of aggregated soils as the capacity of aggregates to take up pesticides from the soil solution (physical filtering), to adsorb and degrade them (chemical and biological filtering). We identified 'filtering indicators', i.e. hydrophobicity, SOC, microbial biomass and respiration rates representing the physical, chemical and biological filtering, respectively. Based on two case studies, each consisting of a pair of soils with the same land-use, climate and texture but with significantly different SOC contents, we predicted that a SOC loss decreased the soil's generic capacity to filter pesticides only as long as no hydrophobicity occurs (Aslam *et al.* 2009). The first objective of this study was to verify these predictions with measurements of the soils' physical, chemical and biological filtering processes for 2,4-D, i.e., water sorptivity, 2,4-D sorption and degradation. We defined a soil's filtering efficiency for a pesticide as the actual filtering during transport. We hypothesize that the changed filtering capacity of a soil does not necessarily mean a changed filtering efficiency due to potential interactions of filtering processes and non equilibrium conditions during transport. The second objective of this study was to show the effect of SOC loss on the soil's filtering efficiency for 2,4-D in the two case studies, and to compare the soil's filtering capacity with its filtering efficiency.

Methods

Study sites and soil sampling

The first pair of sites was under horticultural production (organic versus integrated apple orchard) in the

Hawke's Bay region, and the second pair was under long term permanent pasture in the Waikato, NZ. The apple trees in the organic orchard received compost once a year at a rate of 5 to 10 t/ha, and were not irrigated. The tree rows were grassed and regularly mowed as necessary. A 0.5-m wide strip under the trees of the adjacent integrated apple orchard had been kept vegetation free by regular herbicide applications. The apple trees had been drip-irrigated during the vegetative period, and 50 kg N/ha as calcium ammonium nitrate fertiliser had been applied annually. The second pair of sites consisted of 'camp' and 'non-camp' areas on the same paddock of a permanent pasture that was regularly grazed by sheep. Areas with a slope of about 40° constituted the main grazing area, which was too steep for sheep to rest ('non-camp' sites). The remainder had little (<10°) to no slope and was used by sheep to rest at night ('camp' sites). Such camp-site areas are known to accumulate sheep manure and have increased SOC (Haynes and Williams 1999). Six undisturbed soil cores (0.3 x 0.2 x 0.1 m) were collected from both systems in February 2007. Each field-moist soil slab was divided into four parts. Two parts of the cores were used for measuring water sorptivity, 2,4-D sorption and degradation. For the transport experiments, three undisturbed soil cores (5.15 cm diameter and 11 cm long) were taken from each site at the end of summer 2008 after a prolonged dry period.

The filtering capacity: physical, chemical and biological filtering of 2,4-D

Water sorptivity of the macro-aggregate fractions of the four soils was measured with a modified set-up of an existing method (Gerke and Kohne 2002). Sorption of 2,4-D to the four soils was measured in batch equilibrium experiments (OECD 2000) with intact macro-aggregates. The degradation of 2,4-D was determined in incubation experiments at the aggregate scale, using a modified method of Gonod *et al.* (2003). All experiments were conducted with [Ring-U-14] 2,4 dichlorophenoxyacetic acid.

The filtering efficiency of 2,4-D: soil column leaching experiments

Bromide, a conservative tracer in our soils, suitable to quantify the soil's physical filtering efficiency, and 2,4-D quantifying the combined effects of the physical, chemical and biological filtering efficiency, were applied in a combined pulse of about 80 mL to the initially dry soil columns with a tension disc infiltrometer. The pulse was leached with 0.01 M $CaCl_2$ using a disc infiltrometer set to –1.5 hPa at the upper boundary of the soil columns. The lower boundary of the soil columns ended in a vacuum box set to the same tension. We took leachate samples in regular intervals and analysed them for both solutes. The residual 2,4-D in the soil columns was determined at the end of the experiments. All experiments were conducted in triplicate. We determined the soils' filtering efficiency for bromide and 2,4-D at specified pore volumes (PV). The filtering efficiency gives the fraction of the total applied solute mass that remained in the soil at a specific PV.

Statistical analysis

The physical, chemical and biological filtering capacity and the filtering efficiency were analyzed with an analysis of variance (GenStat 9.1.0.150). The differences between averages were interpreted to be significant if they were larger than their respective least significant differences (LSD) at the 95% confidence level. The impact of SOC on the soils' physical, chemical and biological filtering capacity for 2,4-D was analyzed with multiple regressions between the aggregate sizes and their SOC contents and the respective filtering process.

Results

Physical, chemical and biological filtering capacity

SOC loss led to a decrease in water sorptivities in the orchards surveyed but to an increase in water sorptivities in the pastures surveyed (Table 1). Under pasture the sorptivity increased with decreasing water repellency. In multiple regressions with the macro-aggregate size and their SOC contents as the independent and the water sorptivities as the dependent variable, both, the aggregate size and the SOC contents were significant factors with regression coefficients of 0.92 and 0.8 for the orchard and pasture soils, respectively. SOC was positively related to the sorptivity in the orchard soils, but the opposite was found for the pasture. SOC loss led to a decrease of 2,4-D sorption in both systems. Sorption of 2,4-D was a function of the SOC content ($R^2 = 0.95$). All aggregates showed an exponential mineralisation of 2,4-D with an initial lag phase. The occurrence of a lag phase suggests that the degradation was driven by specialised degrading populations. Co-metabolism can account for up to 30% of 2,4-D mineralisation (Robertson and Alexander 1994). 2,4-D degradation was significantly higher in the 'low-carbon' integrated orchard than the 'high-carbon' organic orchard (Table 1). The reason for this is hypothesized that 2,4-D specific degrader populations already existed in the integrated orchard while the organic orchard had not received any herbicides for the last 12 years. The camp and non-camp pasture sites had the same herbicide application history. The 'high-carbon' camp site pasture degraded 2,4-D significantly faster than the 'low-carbon' non-camp site (Table 1).

Validation of the filtering indicators

The effective filtering indicator property values, contact angle, SOC content, microbial biomass and respiration rates are summarised in Table 1 (Aslam *et al.* 2009). The lack of water repellency successfully indicated that sorptivities in the orchard soils were not limited. The occurrence of water repellency successfully indicated the extremely small sorptivities of the pastoral soils. The SOC content was in principal a useful indicator for 2,4-D sorption to orchard and pasture soils. Basal respiration rate and microbial biomass carbon successfully indicated 2,4-D degradation provided the sites had a similar history of 2,4-D applications. Overall the data on 2,4-D collected here supported the hypothesis that the topsoil's filtering capacity for pesticides depends on physical, chemical and biological properties of the aggregate structure.

Table 1. Effective physical, chemical and biological indicator property values (Aslam *et al.* 2009) and the measured physical, chemical and biological filtering of 2,4-D in the orchard and pasture systems.

	Physical		Chemical		Biological		
	Contact angle (°)	Water sorptivity ($mm/s^{0.5}$)	SOC (%)	Sorption coefficient (l/kg)	Microbial biomass (mg C/kg soil)	Respiration rate (µg CO_2/g soil day)	2,4-D half-life (d)
Orchards							
Integrated	<90	0.025	1.8	3.1	402	30	59
Organic	<90	0.060	3.9	2.7	1298	63	90
LSD	n.s.	0.025	0.3	n.s.	95	9	21
Pastures							
Non-camp	101	0.010	4.8	8.8	571	57	88
Camp	95	0.003	8,5	18.4	853	80	66
LSD	2	0.005	0.5	3.5	91	8	14

Filtering efficiency during solute transport

We quantified the filtering efficiency of our soils for bromide and 2,4-D in column experiments. The 'high SOC' organic orchard soil had a significantly higher filtering efficiency for bromide than the 'low SOC' integrated orchard soil (Figure 1a). We observed an unexpected early breakthrough of 2,4-D in the soils possibly due to preferential flow through macro-pores. The physical filtering process, the uptake of water by aggregates obviously did not happen in the early stages of the experiment. After 480 mm of drainage, the organic orchard tended to be the more efficient filter for 2,4-D, but the difference was not significant (Figure 1b). In the pastoral soils, the observed preferential flow of 2,4-D was attributed to macro-pores and water repellency. After 420 mm of drainage the filtering efficiency of the 'high SOC' camp site pasture soil was significantly lower 2,4-D than the filtering efficiency of the 'low SOC' non-camp site pasture soil (Figure 1c, d). The lack of physical filtering in the camp site soil clearly dominated all other filtering processes.

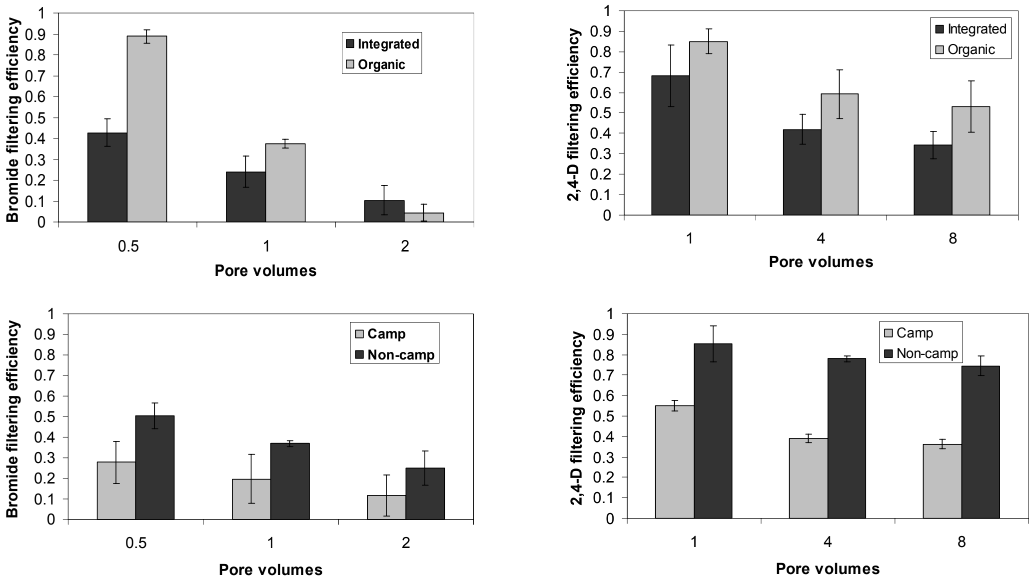

Figure 1. Bromide (a, c) and 2,4-D (b, d) filtering efficiency at specific pore volumes leached (a, b) in the integrated and organic orchard, and (c, d) in the camp and non-camp pasture. The bars denote one standard deviation. The amounts of drainage corresponding to 1 PV are 60 and 52 mm for the orchard and pastoral soils, respectively.

We analysed the impact of SOC loss on the soils' filtering function by comparing the filtering capacity and the filtering efficiency for bromide and 2,4-D. We concluded that for a conservative solute like bromide a SOC loss decreased the filtering efficiency in the orchard soils and increased the filtering efficiency in the pasture soils, as it is driven solely by the physical filtering capacity of the soil. For a reactive organic solute like 2,4-D, a SOC loss had the tendency to decrease the filtering efficiency in the orchard soils and significantly increased the filtering efficiency in the pasture soils. All soils were dry at the start of the experiment and the pasture soils were hydrophobic. Under these conditions the physical filtering process dominated and the significantly decreased physical filtering capacity was traced to the filtering efficiency.

Conclusions

The soils' filtering capacity for a specific solute describes the soils' potential to filter this solute. We validated our indicator framework for the soils' physical, chemical and biological filtering capacity for 2,4-D. The degree of water repellency as an indicator for the physical filtering capacity performed well. The SOC content was useful as an indicator for the chemical filtering capacity when SOC was the major sorbent. The SOC content was a useful indicator of the biological filtering capacity as long as the application history of the pesticide differed not too much and then dominated. At this stage it is suggested that the filtering indicators should be further tested with other agrochemicals. In the future the indicator framework might be used to assess the quality of a soil's filtering function for agrochemicals from the local to the landscape scale. We measured the filtering efficiency of our soils for bromide and 2,4-D. The filtering efficiency is the actual filtering during transport. The prediction of solute transport for the orchard soils was generally good. A problem was the early breakthrough of solutes by preferential flow, most probably through macro-pores. The other problem was that the soils were due to their high SOC contents prone to soil hydrophobicity, which also led to preferential flow in the pasture soils. We addressed the question how a SOC loss influenced soils filtering function. We analysed aggregated soils with silt loam texture under orchard and pastoral land-use with varying SOC contents. The occurrence of soil hydrophobicity was the key to distinguish how the SOC loss influenced the soils filtering capacity. A SOC loss decreased the soils' filtering capacity if the soils were not prone to hydrophobicity like the orchard soils. A SOC loss increased the soils' filtering capacity if the soils were prone to hydrophobicity. Usually hydrophobicity occurs in soils with high SOC contents. Research is needed to identify critical thresholds for SOC amounts above which severe hydrophobicity occurs limiting the soils' filtering function.

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