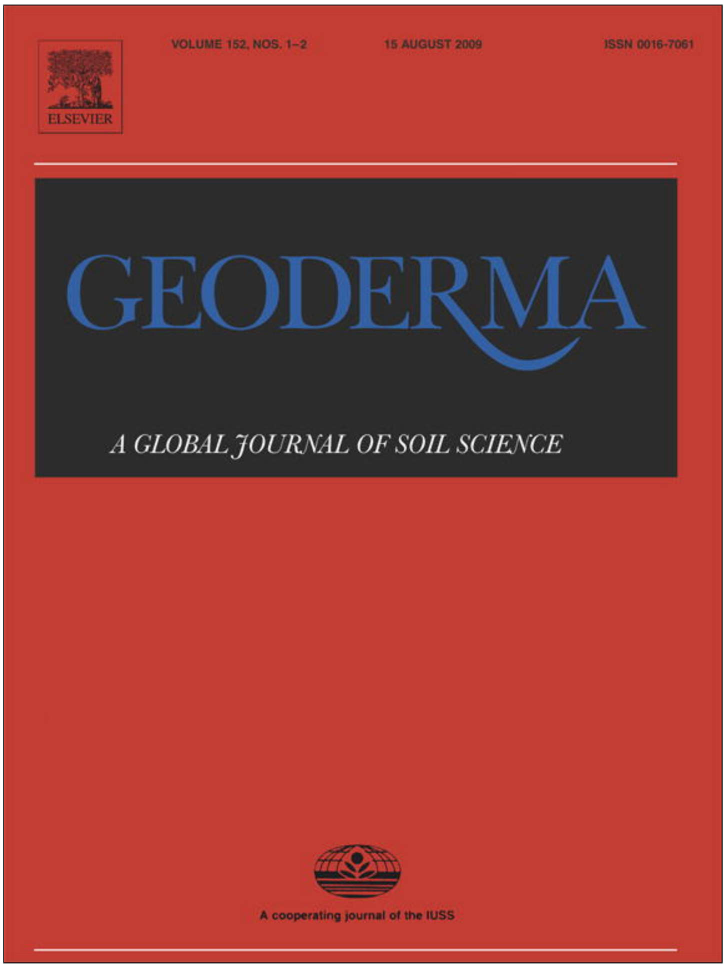
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Does an increase in soil organic carbon improve the filtering capacity of aggregated soils for organic pesticides? — A case study

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ABSTRACT

Organic carbon is the backbone of the soils ecosystem service to protect ground and surface water bodies against the contamination with pesticides. Our objective was to study the long-term effects of organic carbon (OC) inputs on the soil's generic filtering capacity for organic pesticides. We defined the generic filtering capacity of an aggregated soil for organic pesticides as the capacity of the soil aggregates to take up pesticides from the soil solution, to adsorb them to the soil matrix, and to degrade them. For this purpose, we identified three pesticide filtering indicators. (1) The lack of soil hydrophobicity indicated the intactness of soils to absorb soil solution; (2) the SOC contents indicated the soils capacity to adsorb and (3) the microbial activity the capacity to degrade pesticides. We analyzed how these pesticide filtering indicators changed as a result of long-term OC additions for soils under different land use in a case study. The first land use pair consisted of soils under apple orchards. In one orchard (= 'organic') the topsoils in the tree row regularly received compost and were permanently grassed. The tree row of the other neighboring orchard (= 'integrated') was vegetation-free. After 12 years the topsoils of the 'organic' orchard had 32% more SOC than those of the 'integrated' orchard. The second land use was a permanent pasture grazed by sheep. After 20 years the camp sites ('manured sites') had 28% more SOC than the non-camp sites of the same paddock. The OC addition, for both land uses, significantly increased the values of the pesticide filtering indicators for sorption and degradation. In the orchards, the OC addition did not affect the intactness of the soil's capacity to take up soil solution into aggregates. However, in the pastoral system the OC addition increased the degree of soil hydrophobicity further impairing the soil's capacity to absorb soil solution. We conclude that an increase in soil organic carbon improves the soil's generic capacity to filter organic pesticides only as long as no soil hydrophobicity occurs.

1. Introduction

In areas with intensive food production and the regular application of pesticides the intactness of the soil's filtering capacity for pesticides protects surface- and groundwater resources from the accumulation of pesticide residues. Leaching through soils has been identified as a major source of pesticide contamination of aquifers (Barbash et al., 2001; Gaw et al., 2008). 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). In this context governments and regional councils look for guidance what kind of soil properties they should monitor to predict early any changes in the generic performance of the soil's ecosystem service of filtering pesticides. The SOC content of the topsoil seems to be an obvious candidate for monitoring. The SOC content of the topsoil is known to underpin the soil's capacity to filter organic pesticides (see below), and to be very sensitive to any land-use change or modification of management practices within a particular land-use (Bellamy et al., 2005; Schipper et al., 2007). Additionally, the SOC contents are already routinely measured by environmental agencies in many countries for example as part of the Kyoto obligations (SRLUCF, 2000).

The filtering of organic pesticides involves chemical, biological and physical processes (Parkin, 1993; Small and Mular, 1987). In this study we define the generic filtering capacity of an aggregated soil for organic pesticides as the capacity of the soil aggregates to take up organic pesticides from the soil solution, to adsorb them to the soil matrix, and to degrade them.

SOC is directly linked to the chemical filtering of organic pesticides as it is a key sorbent for many pesticides. The sorption can, for example, be approximated by a soil matrix to soil solution partitioning coefficient.

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For many pesticides this coefficient is proportional to the SOC content of the soil (Khan, 1978), and, therefore, SOC is often used to rank the sorption capacity of soils for different pesticides (Wauchope et al., 2002).

The degradation of pesticides as the biological filtering process is indirectly linked to SOC. Pesticides are mainly degraded by microbial decomposition processes. For example, pesticide half-lives or pesticide degradation rates were found to be correlated with microbial biomass (Kördel et al., 1995) or the number of soil microorganisms (Flury et al., 1998). The microbial biomass and activity in turn is known to be positively correlated with the SOC contents (Sparling, 1992; Tessier et al., 1998).

The sorption and degradation of pesticides is only possible if the solutes are in contact with the soil matrix, i.e., the physical filtering process is that they are taken up by capillary forces into the soil aggregates. Soil hydrophobicity abolishes these capillary forces (Bachmann et al., 2005) and impairs the soil's physical filtering process. Soil hydrophobicity in turn is also known to be correlated with the SOC contents (Chenu et al., 2000; Kawamoto et al., 2007; Urbanek et al., 2007).

The hypothesis of our study was that a change of the SOC content is equivalent to a change of the soil's generic filtering capacity for organic pesticides. An increase of SOC would be equivalent to an improvement and a loss of SOC to a decline of this filtering capacity. To our best knowledge this hypothesis has not yet been investigated.

Based on two case studies we used two steps to prove or disprove our hypothesis:

1. We newly defined a set of aggregate-scale soil properties that represent the chemical, biological and physical processes that govern the soil's generic filtering capacity for organic pesticides. We termed them ‘pesticide filtering indicators’.
2. We analyzed if and how the pesticide filtering indicators change when the SOC content increases in two case studies. Each case study consisted of a pair of soils with the same land-use, climate, soil type and texture. The two soils within each pair differed only with respect to SOC.

2. Methods and materials

2.1. Pesticide filtering indicators

Physical, chemical and biological processes contribute to the capacity of a soil to filter a pesticide (Fig. 1). For each of these three processes we identified at least one soil property that is directly linked to it (Fig. 1). These soil properties we termed ‘pesticide filtering indicators’. A significant change in any of the pesticide filtering indicators is equivalent to a change in the soil's generic capacity to filter pesticides.

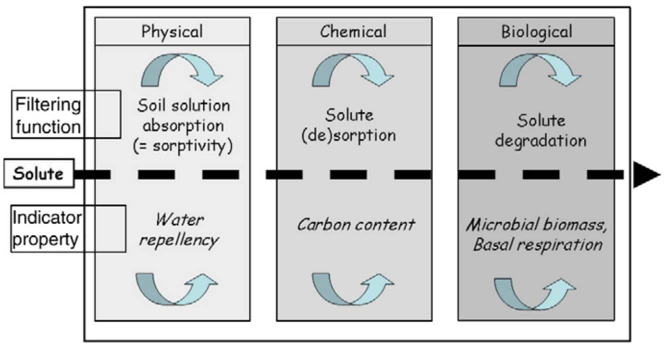

Fig. 1. The soil's generic capacity to filter organic pesticides. Each of the physical, chemical, and biological components of the filtering of an organic pesticide by an aggregate is represented by a pesticide filtering indicator.

2.1.1. Indicator for the intactness of the generic capacity of soil aggregates to absorb soil solution

In a structured soil, aggregates represent a physical barrier for the downward transport of pesticides (Fig. 1). Once the pesticides have been taken up from the soil solution into the aggregates, they are either immobile (Phillip, 1968; Van Genuchten and Wierenga, 1976) or travel much slower than in the inter-aggregate macro-pores (Gerke and van Genuchten, 1993). Also, pesticides can only be adsorbed or be degraded by microorganisms once the soil solution containing the pesticide is in contact with the soil matrix of the aggregates. Therefore, the transfer of solutes into the aggregates is the first step of filtering an organic pesticide. Generally, the uptake of soil solution into aggregates is driven by the capillary forces of the meso- and micro-pores within aggregates. Those capillary forces increase the finer the texture, the higher the SOC contents and the drier the soil. However, the occurrence of soil hydrophobicity leads to a total lack of capillary forces (Bachmann et al., 2005), impairing the soil's physical filtering capacity. Other soil properties such as texture lead only to gradual differences in the rates and capacities of water uptake but never to a complete lack of capillary forces. We, therefore, selected the lack of soil hydrophobicity as an indicator for the intactness of the soils capacity to take up soil solution. We used the contact angle between the solid–water–air phases boundary at the aggregate surface as a measure of the degree of soil hydrophobicity. Soils are hydrophobic if they have contact angles larger than 90°. Aggregates with contact angles of and larger 90° lack capillary forces (Doerr et al., 2000) and, therefore, they cannot take up soil solution. The larger the contact angle the higher is the degree of soil hydrophobicity.

2.1.2. Indicator of the generic capacity of soil aggregates to adsorb organic pesticides

The sorption of pesticides mainly takes place inside the soil aggregates, where the residence time of the contaminants is long as a result of slow flow rates. We used the SOC content of aggregates to indicate the soil's generic capacity to adsorb organic pesticides based on the principle that the SOC content can be used to rank the sorption of pesticides in different soils (Wauchope et al., 2002).

2.1.3. Indicator of the generic capacity of soil aggregates to degrade organic pesticides

Like the sorption, the degradation of organic pesticides occurs within soil aggregates. We selected the microbial biomass and the basal respiration rate of aggregates as a combined indicator for the soils' generic microbial activity that was shown to be directly related to pesticide degradation (Flury et al., 1998; Kördel et al., 1995).

2.1.4. Calculation of effective bulk-soil values of the pesticide filtering indicators

Several studies have observed that different aggregate sizes also have different physical, chemical and biological soil properties such as contact angles, SOC contents and microbial activities (Franzluebbers and Arshad, 1997; Goebel et al., 2004; Gupta and Germida, 1988; Six et al., 2000). We measured the filtering indicators separately for a range of aggregate sizes and then used the aggregate size distribution to derive an effective value of each pesticide filtering indicator for the bulk-soil.

2.2. Study sites

We selected the top 0.1 m of a pair of Fluvisols (FAO-classification, Driessen et al., 2001) under orchard and a pair of Cambisols (FAO-classification, Driessen et al., 2001) under pasture land-use.

The pair of Fluvisols under apple orchards were located in the Hawke's Bay region (North Island of New Zealand) near Havelock North and were already studied in the context of soil quality (Deurer et al., 2008; Vogeler et al., 2006). The average annual temperature at the site is 13 °C and the mean annual rainfall 770 mm. The highly aggregated soils

Table 1
Soil texture, soil organic carbon (SOC), mean weighted diameter (MWD) of aggregates and aggregate size distribution (% weight) of topsoils (0–0.1 m depth) under orchard and pastoral land use.

Soil properties	Apple orchard		Permanent pasture	
	Organic	Integrated	Camp	Non-camp
Texture	Silt loam	Silt loam	Silt loam	Silt loam
Sand (wt.%)	2.7	0.4	28.9	20.4
Silt (wt.%)	65.2	71.1	49.2	52.2
Clay (wt.%)	32.1	28.5	21.9	27.4
pH (H_2O)	6.7	6.4	4.5	4.7
[1]SOC (kg C m^{-2})	3.8 (0.3) a	2.6 (0.2) b	8.7 (1.4) a	6.3 (0.8) b
[2]MWD (mm)	1.92 (0.19) a	1.28 (0.13) b	2.48 (0.22) a	2.71 (0.17) b
[2]Macroaggregates (wt.%)	81 (1.9) a	83 (2.2) a	90.8 (1.6) a	90.1 (1.9) a
[2]Microaggregates (wt.%)	9.0 (1.4) a	7.0 (1.1) b	2.4 (0.6) a	2.7 (0.6) a
[2]Not aggregated (wt.%)	10.0a	10.0a	6.8a	6.6a

Mean values in the same row of each system are significantly different ($P<0.01$) if labeled with different letters. The values in brackets denote the standard deviations.
[1]$n=3$, relates to bulk soil, [2]$n=6$.

with more than 80% macro-aggregates had a silt loam texture and were taken from two neighbouring apple orchards (Table 1). The SOC contents and aggregate size distributions were different in each of the two soils (Table 1) due to different management practices in the two orchards (see below).

The pair of Cambisols was taken from a pasture site in the Waikato region (North Island of New Zealand) near Hamilton. The site is part of a long-term phosphate fertilizer trial in hill country pastures (Dodd and Ledgard, 1999). The average annual temperature is 12 °C and the mean annual rainfall 1180 mm. The highly aggregated soils with more than 90% macro-aggregates had like the soils under orchard a silt loam texture. The soils were taken from the same pasture paddock (Table 1). The SOC contents and aggregate size distributions were different in each of the two soils (Table 1) as they received different amounts of manure (see below).

2.2.1. Apple orchards

The soils were taken from two adjacent apple orchards. The 'organic' orchard (Latitude 39° 39' 38.7″ S, Longitude 176° 52′ 41.3″ E) was managed according to the BIO-GRO standards (http://www.biogro.co.nz) and the neighboring 'integrated' orchard (Latitude 39° 39′ 38.3″ S, Longitude 176° 52′ 43.9″ E) was managed according to the standards of integrated fruit production (Wiltshire, 2003) since 1997. Apples of the variety 'Braeburn' are produced in the organic and of the variety 'Pink Lady™' in the integrated orchard. The organic apple production system resulted in an accumulation of SOC in the topsoil compared to the integrated apple production system (Table 1). In the organic orchard greenwaste compost has been applied to the topsoil of the tree rows once a year at a rate of 5 to 10 t ha^{-1}, while in the integrated orchard prunings and leaf fall are the only regular organic carbon additions to the soil. Moreover, the tree rows in the organic orchard were grassed and regularly mowed as necessary, while in the adjacent integrated orchard a 0.5-m wide strip under the trees has been kept vegetation-free by regular herbicide applications. Both orchards received lime at a rate of 300 kg ha^{-1} every 4 years. In the organic orchard lime-sulfur and copper have been used as fungicides if needed. Irrigation, nutrient, and pest management in the integrated orchard followed the guidelines of integrated fruit production (Wiltshire, 2003).

2.2.2. Pasture site

The second pair of soils was taken from the same paddock with permanent pasture. The paddock has a size of about four ha and had not received any P fertilizer during the last 20 years. The cover grass, a perennial ryegrass-clover mixture (*Lolium perenne* L. and *Trifolium repens* L.) was regularly grazed by a flock of sheep. The paddock could be separated into two types of areas. Most of the area had a slope of about 40° and constituted the main grazing area and that was too steep for sheep to rest (= 'non-camp' sites). The main grazing area was interspersed with small areas (~10–20 m^2) with little (<10°) to no slope and they were used by sheep to rest in the night (= 'camp' sites). Such camp-site areas are known to accumulate sheep manure and increase SOC (Haynes and Williams, 1999). In the context of organic carbon additions of our study we denoted the non-camp and camp sites also as 'manured' and 'non-manured' sites, respectively.

2.3. Soil sampling

We collected soil samples from both orchards and the pasture systems at the end of summer in February 2007 for the analysis of the aggregate size distribution and the determination of SOC content. Six replicates were randomly selected within three adjacent tree rows of the organic and the integrated orchards, and within six different camp and non-camp site areas. Each set of camp and non-camp site areas had the same slope and aspect and only small elevation differences (~20 m). Rectangular metal sheet cores ($0.3\times0.2\times0.1$ m) were used to take undisturbed soil samples from the topsoil (0–0.1 m) from randomly selected areas. Each field-moist soil sample was divided into four parts and stored at 2 °C. Two of these parts were used to determine the aggregate size distribution (ASD) as well as physical, chemical and biological properties of macro-aggregates. The remainder of the soil was stored as backup. The bulk soil organic carbon content and bulk densities were measured on undisturbed 100 cm^3 cores (Grossman and Reinsch, 2002) taken in triplicate from the topsoil at each site.

2.4. Measurement of the aggregate size distribution

We used the wet sieving technique (Elliot, 1986) to determine the aggregate size distribution. Details of the method are given elsewhere (Elliot, 1986; Six et al., 2000; Hernandez-Hernandez and Lopez-Hernandez, 2002). Aggregates were separated into eight selected aggregate size classes (>4.75, 4.75–2.8, <2.8–2.0, <2.0–1.0, <1.0–0.5, <0.5–0.25, <0.25–0.09 and <0.09–0.053 mm). Following others (Elliot, 1986) all aggregates larger than 0.25 mm were classified as macro-aggregates, all aggregates smaller than 0.25 mm and larger than 0.053 mm were micro-aggregates. Soil that passed through the 0.053 mm sieve was classified as non-aggregated soil. The aggregate size distribution was derived as the mean weighted diameter (MWD) (Van Bavel, 1949). Percentages of macro-aggregates, micro-aggregates and non-aggregated soil were calculated by summing the mass fractions of each size.

2.5. Measuring the pesticide filtering indicators of soil aggregates

The analysis of the pesticide filtering indicators focused on the soil fraction size >0.25 mm since this represents the most important fraction in the studied soils as macro-aggregates contributed more than 80% of total soil weight (Table 1). The aggregate size distribution allows integrating the values of the respective filtering indicators across the aggregate sizes to yield an effective indicator value for the bulk-soil of each system.

2.5.1. Soil carbon content

Air-dried sieved soil and soil of the four aggregate size fractions (>4.75, 2.80–4.75, 1.00–2.80 and 0.25–1.00 mm) were finely ground to <1.00 mm size and thoroughly mixed. The samples were then analyzed by the Dumas Method for %C using a LECO CNS-2000 Analyzer (Laboratory Equipment Corporation Ltd, Castle Hill, NSW, Australia). The SOC value in %C was converted into the total carbon content, C_t (kg m^{-2}) using the bulk density values. The total carbon mass stored in the soil is the environmentally relevant entity if systems with different bulk densities are compared. We assumed that the total carbon content was equivalent to SOC content as all soils had pH values below 7 (Table 1).

2.5.2. Microbial biomass and basal respiration

The microbial biomass carbon of the four aggregate size fractions was determined by the substrate-induced respiration method (Höper, 2006). We modified the method to be able to use intact aggregates. We carefully rewetted the field-moist aggregates (18 g on an oven-dry matter basis) with a syringe to 60% of the water-holding capacity prior to the measurement. We dissolved 6 mg Glucose per g of dry soil in the water that was used for rewetting the aggregates. The basal respiration was measured as described elsewhere (Pell et al., 2006). This method involved the measurement of soil respiration on field-moist aggregates (18 g on an oven-dry matter basis) after 17 h of incubation at 22 °C.

2.5.3. Degree of soil hydrophobicity

The degree of soil hydrophobicity of the four aggregate size fractions was measured by the molarity of ethanol droplet (MED) test method and the results were quantified in the form of the contact angles between the water drop and the soil aggregate surface (Roy and McGill, 2002). Following others (Kawamoto et al., 2007), we pre-treated all samples to avoid any bias due to different soil water contents. The aggregates were oven dried at 65 °C for 48 h and then placed in plastic bags for 24 h at room temperature to reach steady state conditions before we conducted the MED test. With the MED test we could only derive contact angles equal or larger 90° (Roy and McGill, 2002) which is equivalent to the occurrence of soil hydrophobicity.

2.6. Statistical analysis

The results of each production system (apple orchards, pastoral sites) were analyzed with a two-way ANOVA with the Genstat 9.1.0.150 software. We assumed that our data was normally distributed. A rigorous test to identify if this is true was not possible due to the small sample size. The first factor was the soil carbon status ('high SOC' versus 'relatively low SOC') and aggregate size (1–4) was the second factor. We interpreted the differences between means of properties to be significant if they were larger than their respective least significant differences (LSD) at the 95% confidence level.

In both land use systems we observed, and interpreted, the spatial difference in SOC to be equivalent to a long-term SOC increase as a result of regular OC additions in the sense of a space-for-time substitution.

3. Results and discussion

In the case of the orchards, the OC additions in the organic orchard in the form of regular compost applications and the use of a grass cover in the tree row led to 3.8 kg SOC m^{-2} in the topsoil (0–0.1 m). This is about 30% ($P<0.05$) higher SOC than in the integrated orchard which received no regular inputs of organic matter (2.6 kg SOC m^{-2}, Table 1) (Deurer et al., 2008). Other studies have also observed significantly higher SOC contents as a result of regular compost applications (Celik et al., 2004; Foley and Cooperband, 2002). Further, maintaining the soil surface covered by vegetation is a known strategy for soil carbon sequestration (Lal, 2004).

In the case of the pasture systems, the non-camp sites receive less organic matter than the camp sites where sheep manure accumulates (Haynes and Williams, 1999). As a consequence, the topsoil (0–0.1 m) of the camp sites sequestered 8.7 kg SOC m^{-2}; 30% ($P<0.05$) higher SOC than the non-camp site with 6.3 kg C m^{-2} (Table 1).

3.1. Impact of OC addition and SOC increase on the aggregate size distribution

The increase in SOC did not influence the total amount of macro-aggregates (Table 1) in both land use systems, however, the macro-aggregate size distribution changed. Under orchard land use, SOC increase led to a significant increase of the largest aggregate size (Fig. 2, A) and subsequently to an increase of the MWD (Table 1), while under pastoral land use, the SOC increase led to a significant decrease of the largest aggregate size fraction (Fig. 2, B) and of the MWD (Table 1). The aggregate size distribution of the orchard soils changed in the same way as was expected (Carter, 1992; Chung et al., 2008; Franzluebbers, 2002; Gupta and Germida, 1988; Hernandez-Hernandez and Lopez-Herndandez, 2002) when a system with (= soil under organic orchard) is compared to a system without SOC conservation (= soil under integrated orchard). For example those other studies found, that the amount of macro-aggregates in the largest macro-aggregate size class and the MWD was higher in the no-tillage systems with higher SOC than the equivalent continuous-tillage systems which usually have less SOC. A higher MWD was also observed as a result of compost addition and subsequent increase in SOC (Celik et al., 2004).

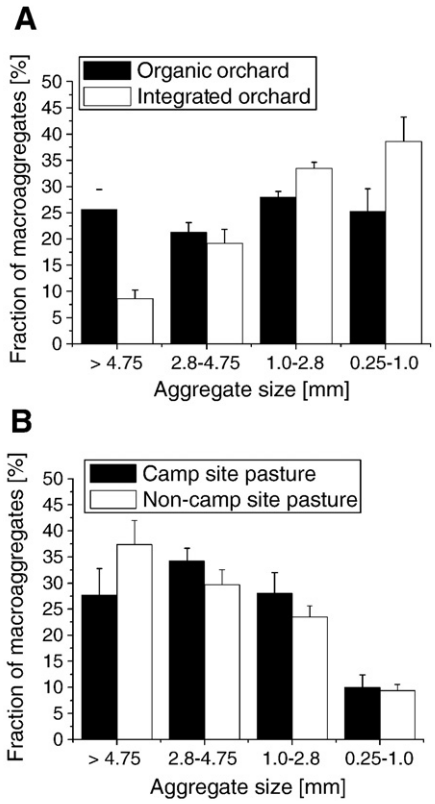

Fig. 2. Macro-aggregate size distribution in a silt loam soil under orchard and pastoral land use ($n=6$). A) Organic and integrated orchard. The columns are the mean fractions of macro-aggregates that are significantly ($P<0.05$) different in all aggregate sizes apart from 2.8–4.75 mm. B) Camp (= manured) site and non-camp (= non-manured) site pasture. The fractions of macro-aggregates are significantly ($P<0.05$) different in all aggregate sizes apart from 0.25–1.0 mm. The error bars denote one standard deviation.

The pasture systems had about two times higher SOC in the top 0.1 m as the orchard systems, and the MWD was higher (Table 1). A significantly positive correlation of MWD with SOC was found for arable silt loam soils by others (Le Bissonais and Arrouays, 1997). The decrease in the largest aggregate size (>4.75 mm) in the pastoral system when the SOC increased (Fig. 2) has been also reported by others for pasture systems (Harris et al., 1966).

3.2. Impact of OC addition and SOC increase on the soils capacity to filter organic pesticides

The soil's generic capacity to filter organic pesticides is an ecosystem service that safeguards water resources against contamination with organic pesticides. Governmental agencies that are responsible for the state of the environment need to know, if sustaining or increasing SOC levels in topsoils under primary production is equivalent to sustaining or increasing the soil's generic capacity to filter organic pesticides.

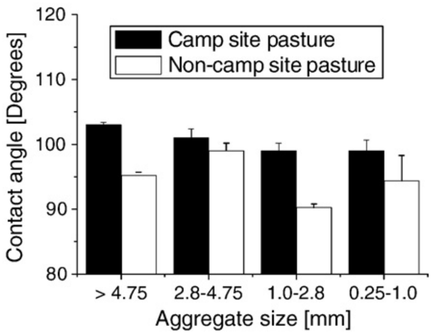

Fig. 3. The columns are the mean contact angles of four soil aggregate size fractions under pastoral land use ($n=3$). The error bars denote one standard deviation. The contact angles of the individual aggregate sizes of the camp and non-camp site pastures were significantly different ($P<0.05$) with the exception of the aggregate size 2.8–4.75 mm.

We focused only on the soil's generic capacity to filter and not on its specific capacity to transport pesticides rapidly, for example, by preferential flow processes through macro-pores. The occurrence of preferential flow critically depends on the climatic conditions (Loll and Moldrup, 2000) that are independent of SOC. Also, to estimate the soil's actual capacity to filter a particular organic pesticide the specific physico-chemical properties of the pesticide need additionally to be known.

3.2.1. Indicator for the intactness of the generic capacity of soil aggregates to absorb soil solution

The macro-aggregates of both orchard soils had contact angles smaller than 90°. The macro-aggregates of the orchard soils will, therefore, especially when dry, exert strong capillary forces, and will absorb water. Both orchard soils were not hydrophobic and we concluded that the capacity of soil aggregates to absorb soil solution was intact.

The soil aggregate size fractions from the camp and non-camp sites were hydrophobic with contact angles equal or larger 90° (Fig. 3). They have lost their capacity to absorb soil solution. There are two possible consequences for organic pesticides dissolved in the water at the soil surface of camp and non-camp sites. Firstly, the water and organic pesticides will run-off especially from areas on a slope such as the non-camp sites. Secondly, the water with organic pesticides might pond in surface depressions especially in flatter areas like the camp sites, and, once a specific ponding height is reached (Bachmann et al., 2007; Deurer and Bachmann, 2007), rapidly and preferentially leach downwards through macro-pores and cracks (Dekker and Ritsema, 1996).

The macro-aggregate size fractions of the camp site had significantly higher contact angles than those of the non-camp site (Fig. 3). The effective contact angle for the macro-aggregates was with 101° significantly ($P<0.05$) higher for the camp than with 95° for the non-camp site pasture. It seems highly likely that the greater SOC content was primarily responsible for the increase in the contact angles of the pastoral soils. We base this conclusion on several studies that have reported that the SOC contents were positively correlated with the degree of soil water repellency under various climatic conditions (Chenu et al., 2000; Kawamoto et al., 2007; Urbanek et al., 2007).

There is no research yet that has investigated if the small-scale spatial variability of the degree of soil hydrophobicity within a system with a specific range of SOC contents such as the camp or non-camp site is again correlated to the variability of SOC or rather with other factors. For example, in both of our pastoral systems, the aggregate size with the highest contact angle (camp site = >4.75 mm; non-camp site = <4.75–2.8 mm; Fig. 3) did not correspond with the highest SOC content (camp site and non-camp site = <1.0–0.25 mm; Table 2). We hypothesize for our site that at the small spatial scale of aggregates the variability of soil hydrophobicity is driven by the small-scale variability in the quality of SOC. Some studies have already identified a general link between the quality of the soil organic matter and soil water repellency (Doerr et al., 2000; Ellerbrock et al., 2005; Woche et al., 2005). More research is needed on the spatial scale dependency of the soil organic matter quantity and quality and soil hydrophobicity.

It is not clear if the accumulation of sheep manure at the camp site has enhanced the occurrence of soil hyrdophobicity. We know of no study that has systematically investigated if there is a connection of the type and amount of animal manure and the occurrence of soil hydrophobicity.

3.2.2. Indicator of the generic capacity of soil aggregates to adsorb organic pesticides

The long-term OC additions led to significantly higher SOC contents of macro-aggregates (Table 2). The effective SOC contents for the macro-aggregates was with 3.4% significantly ($P<0.05$) higher for the organic than with 1.9% for the integrated orchard. Simultaneously, it was with 8.5% significantly ($P<0.05$) higher for the camp than with 4.8% for the non-camp site pasture. The orchard and pasture soils had at least 80% macro-aggregates (Table 1). Based on SOC as our generic indicator we conclude that the long-term OC additions, as they occurred in the organic orchard and the camp site pasture, increased the soils capacity for pesticide sorption.

In both the organic orchard and the camp-site pasture system, the SOC contents were significantly higher in the smallest macro-aggregates compared with the larger sizes (Table 2). Meanwhile, in both the integrated orchard and the non-camp site pasture system, the SOC contents were not significantly different across the different macro-aggregate sizes (Table 2). These observations corroborate the model of a hierarchical aggregate organization (Tisdall and Oades, 1982). It suggests that different aggregate sizes are bound by distinct binding agents which influence the stability and turnover rates of the respective aggregates. Different studies also support this theoretical model suggesting that macro-aggregates are only temporarily bound by roots and fungal hyphae and consequently, they have the fastest turnover rates (Puget et al., 2000; Six et al., 2000). Therefore, in both systems, the smallest macro-aggregates seem to be simultaneously a 'hot-spot' to sequester or loose SOC. Others have observed the same; for example, Gupta and Germida (1988) compared a native prairie with a cultivated soil, and found that the smallest macro-aggregate size fraction (0.25–0.5 mm) exhibited the largest SOC loss. Others (Chung et al., 2008) found in their experiments with increasing C input rates the highest C stabilization in the smallest macro-aggregate fraction (2000–250 µm).

3.2.3. Indicator of the generic capacity of soil aggregates to degrade organic pesticides

The SOC increase led in both land use systems, orchards and pasture, to significantly ($P<0.05$) higher microbiological activity of the macro-

Table 2
SOC contents (= indicator of the generic capacity of soil aggregates to adsorb organic pesticides) of macro-aggregates in the topsoils (0–0.1 m) under apple orchard and pasture sites ($n=3$).

Aggregate sizes (mm)	Apple orchard		Permanent pasture	
	SOC (%)		SOC (%)	
	Organic	Integrated	Camp	Non-camp
>4.75	3.17 (0.27) a	1.84 (0.08) c	8.41 (0.01) a	4.55 (0.86) c
2.80–4.75	3.18 (0.22) a	1.89 (0.09) c	7.90 (0.27) a	4.77 (0.74) c
1.00–2.80	3.34 (0.02) a	1.96 (0.15) c	9.13 (0.25)b	4.98 (0.65) c
0.25–1.00	3.87 (0.63) b	1.91 (0.35) c	9.24 (0.56) b	5.45 (0.62) c
Mean	3.4a	1.9d	8.7a	4.9d
Effective[1]	3.4a	1.9d	8.5a	4.8d
LSD[2] (Land use)	0.25		0.48	
LSD[2] (AS[3])	0.50		0.97	

Mean values in the same row or column of each system are significantly different ($P<0.05$) if labeled with different letters. The values in brackets denote the standard deviations.
[1]Effective value for macro-aggregates: weighted with the fractions of macro-aggregates.
[2]LSD = least significant difference ($P<0.05$).
[3]AS = Macro-aggregate size.

Table 3
Microbial activities (= indicator of the generic capacity of soil aggregates to degrade organic pesticides) of macro-aggregates in the topsoils (0–0.1 m) under orchard and pastoral land use ($n=3$).

Aggregate size [mm]	Apple orchard				Permanent pasture			
	Microbial biomass carbon [mg C (kg soil)$^{-1}$]		Basal respiration [μg CO_2 (g soil day)$^{-1}$]		Microbial biomass carbon [mg C (kg soil)$^{-1}$]		Basal respiration [μg CO_2 (g soil day)$^{-1}$]	
	Organic	Integrated	Organic	Integrated	Camp	Non-camp	Camp	Non-camp
>4.75	937(35) a	321(100) d	49(1.6) a	29(8.2) c	777(31) a	451(69) c	75(9.9) a	42(8.2) c
2.80–4.75	1017(71) a	321(61) d	59(16.3) a	28(11.4) c	762(83) a	511(84) c	82(10.2) a	50(14.2) c
1.00–2.80	1198(128) b	386(159) d	61(12.3) a	29(10.7) c	912(157) a	727(151) a	70(4.3) a	75(11.8) a
0.25–1.00	1648(174) c	496(69) d	79(10.7) b	34(9.1) c	1233(80) b	877(122) a	121(4.3) b	93(8.5) d
Mean	1200b	381d	62a	30c	921a	641d	87a	65c
Effective[1]	1298b	401.5d	63a	30.4c	853.3a	570.5d	80.1a	56.5c
LSD[2] (land use)	95.20		9.34		90.80		8.21	
LSD[2] (AS[3])	190.4		18.7		181.6		16.4	

Values in the same column or row of each system are significantly different ($P<0.05$) if labeled with different letters. The values in brackets denote the standard deviations.
[1]Effective value for macro-aggregates: weighted with the fractions of macro-aggregates.
[2]LSD = least significant difference ($P<0.05$).
[3]AS = macro-aggregate size.

aggregates (Table 3). The higher microbial activity in turn indicates an increase in the soils generic capacity to degrade organic pesticides.

We quantified the microbial activity in the form of the microbial biomass and the basal respiration rate. The effective microbial biomass was with 1298 mg C kg^{-1} soil and 853 mg C kg^{-1} soil significantly ($P<0.05$) higher for the organic orchard and the camp site pasture than with 402 mg C kg^{-1} soil and 571 mg C kg^{-1} soil for the integrated orchard and the non-camp site pasture, respectively. The effective basal respiration rates were with 63 μg CO_2 (g soil day)$^{-1}$ and 80.1 μg CO_2 (g soil day)$^{-1}$ significantly ($P<0.05$) higher for the organic orchard and the camp site pasture than with 30.4 μg (g soil day)$^{-1}$ and 56.5 μg CO_2 (g soil day)$^{-1}$ for the integrated orchard and the non-camp site pasture, respectively.

With the exception of the integrated apple orchard, biological activity measured via microbial biomass and basal respiration was significantly higher ($P<0.05$) with decreasing aggregate size and was highest in the aggregate size 0.25–1.0 mm. In aggregates ranging from smaller than 0.1 mm to 5 mm, the microbial biomass, basal respiration and nitrogen mineralization rates were highest in aggregates with a diameter of 0.5–1 mm (Schutter and Dick, 2002). Therefore, the smallest macro-aggregate size seems to be a 'hot-spot' for the microbial activity of our soils. A review of other studies shows that micro-aggregates (aggregates <0.25 mm) mostly had smaller microbial activities than macro-aggregates (aggregates>0.25 mm) (Franzluebbers and Arshad, 1997; Gupta and Germida, 1988; Hernandez-Hernandez and Lopez-Herndandez, 2002; Miller and Dick, 1995; Schutter and Dick, 2002; Singh and Singh, 1995).

4. Conclusions

We studied how the long-term OC addition (compost plus grass cover, manure) to soils affected the soil's generic capacity to filter organic pesticides. For this purpose we identified three pesticide filtering indicators. The lack of soil hydrophobicity indicated the intactness of soils to absorb soil solution; the SOC contents indicated the soils capacity to adsorb and the microbial activity the capacity to degrade pesticides. We found that a change of SOC was equivalent to a change of two (orchard soils) or all three (pasture soils) pesticide filtering indicators. Therefore, for the soils of our case study, we approved our hypothesis that SOC is a key soil property for the soils generic capacity to filter organic pesticides. An increase in SOC was in orchard and pasture soils associated with a better generic capacity to adsorb and degrade pesticides as was hypothesized. However, an increase in SOC for the pasture soils caused a higher degree of hydrophobicity and impaired further the soils capacity to absorb soil solution. We conclude that an increase in SOC is only equivalent to an increase in the soil's generic capacity to filter pesticides if no soil hydrophobicity occurs. If soils are potentially hydrophobic then soil hydrophobicity will occur whenever the soils dry out (Doerr et al., 2000) which regularly coincides with the typical time for pesticide applications, for example, the application of herbicides at the end of summer. We recommend monitoring simultaneously the change of SOC and the degree of water repellency to detect any changes in the soil's generic capacity to filter pesticides. For the same reasons, we suggest incorporating the degree of water repellency in the suite of soil quality indicators.

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