



Endosulfan leaching from Typic Argiudolls in soybean tillage areas and groundwater pollution implications



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HIGHLIGHTS

- Information provided by intact columns test approach to data from field conditions.
- When assessing leaching of endosulfan isomers metabolites should also be studied.
- The soil type and land use are critical to estimate leaching behavior of endosulfan.

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ABSTRACT

Endosulfan has been recently added to Persistent Organic Pollutants (POPs) list and due to its extensive and massive use and environmental persistence constitutes a potential hazard to groundwater resources. Undisturbed soil columns were used to evaluate endosulfan leaching in two series of Typic Argiudolls considering natural and agricultural land use. Columns were spiked with $10 \mu\text{g L}^{-1}$ of technical endosulfan and eluted under saturated flow with five pore volumes of distilled water. Alfa and beta isomer residues were detected in the upper soil level, with decreasing values through the profile, being influenced by soil texture and land use. The endosulfan sulfate metabolite was mainly found in the upper level linked to high dehydrogenase activity. Results from leachates (total endosulfan $27\text{--}87 \text{ ng L}^{-1}$) showed higher α -isomer mobility, and suggest alkaline hydrolysis of both endosulfan isomers. The agricultural use modified the physico-chemical properties and structure of soils leading to vertical migration of endosulfan isomers under saturated conditions. Intact column test provided information close to field data showing its utility for the assessment of groundwater pollution by endosulfan.

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1. Introduction

Increased use of pesticides in agricultural fields has become one of the major environmental threats to water resources. Pesticide transport and fate are influenced by many processes, including volatilization, leaching, adsorption and biochemical decomposition (Jarvis et al., 1991). Among them, leaching receives particular attention due to their potential impact on groundwater resources (Loague et al., 1998). Numerous factors influence leaching processes such as unsaturated zone characteristics, irrigation, rains and temperature. Macro-porosity structure and soil organic matter that are largely influenced by land use, also affect water infiltration and pesticide sorption (Lipiec and

Stêpniewski, 1995; Malone et al., 2003). Thus, large amounts of clay and organic matter decrease pesticide mobility in soil (Martinez Vidal et al., 1994). Moreover, recharge by rains or irrigation water and the adsorption–desorption interactions with soil particles would determine the extent of pesticide mobility through the soil profile. The persistence also determines whether these compounds will be transported and become a pollutant to groundwater or not. Although pesticide adsorption and mobility in soil might be studied through different approaches, the information provided using intact columns fits well with field conditions since they resemble the characteristics of the unsaturated zone (Beltrán et al., 1995).

During the last 30 years, soybean cropping area grew 600% in Argentina; it was associated with the adoption of direct seeding technique and endosulfan was the most widely used insecticide. Technical grade endosulfan is a typical mixture containing 95% of two diastereoisomers, known as α -endosulfan and β -endosulfan, in ratios varying from 2:1 to 7:3 (Kennedy et al., 2001; Herrmann, 2002). Endosulfan

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isomers can be transformed to the more hydrophilic endosulfan diol, lactona, ether and hydroxy ether; however, the main metabolite formed through biological transformation is endosulfan sulfate (Ghadiri and Rose, 2001; Goswami et al., 2009). This insecticide has been used worldwide for about five decades on a variety of vegetable crops, fruit, cereals and tobacco since it was recognized as an effective pesticide against a broad number of insect and mites (Antonious and Byers, 1997). Endosulfan residues (isomers and endosulfan metabolite) have been detected in soils, water, air and food products, due to its widespread use, persistence and potential for environmental transport (Weber et al., 2010).

The environmental persistence of endosulfan is shorter than other organochlorine pesticides, with field based half-lives between 3 and 8 months for technical endosulfan and the sulfate metabolite in soil (Pesticide Manual, 2003), and up to 30 months for the beta isomer (European Commission, 2005). However, on the concept of "joint persistence" (Fenner et al., 2003) the half-lives for the combined toxic residues (α - and β -isomers plus the sulfate metabolite) varied between 9 months and 6 years (EPA, 2002). Endosulfan isomers and endosulfan sulfate were included in the Stockholm Convention list of Persistent Organic Pollutants (POPs) on April 2011 (UNEP/AMAP, 2011). This would require involved countries to take steps for a ban on production and use and this process would take up to 10 years. In Argentina, endosulfan phase out is effective since July 2013.

The Quequén Grande River (QGR) represents a characteristic soybean area where groundwater supplies all uses. Endosulfan has been used during the last 15 years with evident environmental impact (Gonzalez et al., 2012, 2013). As pesticides are applied on soil surface, the transport mechanisms involved on groundwater pollution would

mainly occur in the soil profile, where most of the degradation processes take place. So, endosulfan residues in surface soil will constitute a hazard to groundwater resources, once they migrate through the soil profile. In order to assess groundwater environmental risk it is necessary to provide data and information about the contaminants mobility throughout the unsaturated zone. The main objective of this study was to evaluate the leaching of technical endosulfan in Typic Argiudolls under different land uses. For this purpose, the movement of technical endosulfan through soil profile was evaluated in undisturbed soil columns under controlled conditions.

2. Materials and methods

2.1. Study area

The QGR watershed, located in the southeast of Buenos Aires province of Argentina, has a total area of 9990 km² (Fig. 1). A thick sequence (up to 290 m) of Tertiary and Quaternary sediments overlies the Paleozoic rocks, forms the Pampean aquifer. This multilayered unconfined aquifer is the most important and the main exploited in the region (Llambias and Prozzi, 1975). The climate in the catchment is dry sub-humid mesothermal type "B2" (Thorntwaite, 1948). The average annual temperature is 14 °C, being July the month of lower temperatures with an average of 7.3 °C, and January the hottest month with an average temperature of 21 °C (Kruse et al., 1997). The mean rainfall for the period 1960–2009 was about 891 mm. The highest precipitation values are recorded between October and March (Gonzalez et al., 2012).

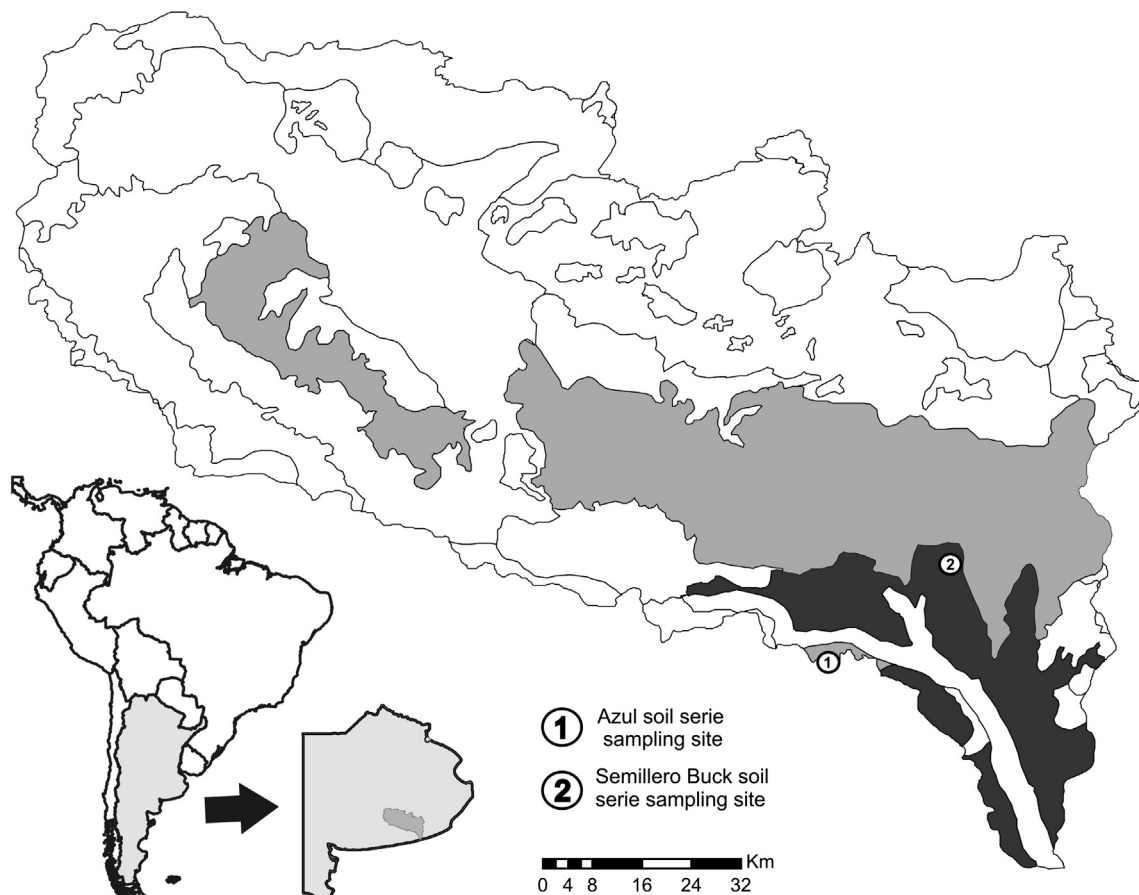


Fig. 1. Study area location and distribution of the main group of soils. Black areas correspond to the group characterized by Semillero Buck series soil and grey area to the group characterized by Azul series soil.

2.2. Soil series

Mollisols (Soil Survey Staff, 1999) are the main soils in the study area, which are common in subhumid to semiarid areas plains worldwide. Typic Argiudolls constitute the dominant subgroup as a result of humid climate on loessic materials. These soils are highly fertile, used mostly for extensive and intensive agriculture, with enrichment of organic matter and nutrients in surface horizon and high levels of clay in B horizons (Alvarez et al., 2008). Azul and Semillero Buck series were selected considering their areal distribution and predominance in the distal region of the watershed (Fig. 1).

2.2.1. Soil physicochemical characteristics

Soils from Semillero Buck series had a fine texture and are classified as sandy clay loam while, soils from Azul series had a coarser texture (sandy loam, Table 1). The clay content increases concomitantly with depth in Semillero Buck soil, while in Azul series this parameter kept constant through the soil profile. CEC values are in agreement with clay content. A differential response of soils series to the same agricultural practice (direct seeding) was reported (Grondona et al., 2013). Regarding OM, cultivated soils had lower values in the upper 0–5 cm than natural soil, due to agricultural practices over a considerably long period (Urricariet and Lavado, 1999). In the subsurface layers, Semillero Buck series kept this pattern throughout the soil profile, but in Azul series, cultivated soils had higher OM content than natural ones. Semillero Buck soils are slightly acid to neutral (pH 6.3–7.3) and Azul soils are slightly to moderately alkaline (pH 7.7–8.2), but in both cases tillage leads to soil acidification.

2.2.2. Soil sampling and leaching columns test

Two land uses were selected within each soil series: soils under extensive agricultural use (transgenic soybean, wheat and sunflower crops) and surrounding soil with natural vegetation. Four conditions were established according to soil series and land use: Azul Natural, Azul Cultivated, Semillero Buck Natural and Semillero Buck Cultivated. Soil columns were taken by introducing an aluminum core (13 × 60 cm) into the soil. Columns were sealed from both ends with aluminum foil to avoid contamination and stored at 4 °C until required for analysis.

Columns were immersed in distilled water and irrigated on the surface and once completely saturated pore volume was estimated as the total amount of absorbed water. Columns were placed on a support equipped with irrigation equipment and an aluminum funnel to collect the discharge (Fig. 2). The experiment was carried out under greenhouse conditions (14 °C min., 20 °C max.). Each column was spiked with 50 mL of a 10 µg L⁻¹ solution of technical grade endosulfan (Master® 35%). Spiking dose represents overloads of pesticides onto soil as a consequence of applications over the recommended doses or consecutive applications with gaps shorter than those suggested by

good agricultural practices. Thus, ten times the recommended dose for common practices were spiked. Once spiking solution was totally absorbed, up to 6.2 L of distilled water under saturated flow were added. This amount represented local rainfall, transpiration and evaporation requirements and it was the equivalent to five pore volumes. Leachates were sampled from the discharge funnel every 100 mL (approximately 0.1 pore volume) in amber glass bottles and stored (4 °C) until analysis within the next 2 days.

2.3. Column subsampling and physico-chemical parameters analysis

Columns were stood for 24 h after the last leachate collection. The cores were longitudinally opened by means of a grinder, and air-dried for other 24 h. Each column was characterized and subdivided in different soil layers according to the observed changes in color or structure. Subsamples of each layer were used for determination of particle size distribution by the pipette method (Galehouse, 1971). Moreover, each column was subdivided from top to bottom in 5 cm sections for pesticide analysis, dehydrogenase activity, desorption studies and organic matter content (OM, Walkley and Black, 1965). Soil pH and electrical conductivity (EC) were carried out in dry soil/deionized water suspension 1/2.5 (w/v). Water content was determined by constant-weight drying in an oven at 110 °C. Cation exchange capacity (CEC) was measured by the ammonium acetate method (Sumner and Miller, 1996).

2.4. Desorption studies

The 0–5 and 5–10 cm layers were used for evaluating the endosulfan transference from soil matrix to the aqueous phase simulating new saturation event under real conditions (rain, flooding). The availability of endosulfan isomers and sulfate metabolite in the liquid phase was assessed by desorption studies. Soil was air dried, crushed and sieved through a 2 mm sieve. Desorption was run in duplicated batch experiments. Soil (1 g) and MilliQ water as desorption solution (20 mL) were shaken in centrifuge tubes end-over-end for 24 h at 20 °C, then centrifuged at 1720 ×g for 15 min. The supernatant was analyzed for pesticide residues and data were expressed as ng of pesticide in solution per gram of soil.

2.5. Pesticide extraction and purification

All samples were handled on glass or aluminum material pre-washed with hexane and spiked with PCB #103 as internal standard. Solutions from leachates and desorption studies were liquid–liquid extracted (Gonzalez et al., 2012). Briefly, solutions were horizontally shaken for 2 h with a mixture of dichloromethane:hexane (2:1), obtaining the organic layer for further clean up.

Table 1

Physicochemical properties of soil columns. OM: Organic matter; CEC: cation exchange capacity, * Grondona et al., 2013.

Series	Land use	Elution time (min 100 ml ⁻¹)	*Porosity	*Dispersivity (m)	Depth (cm)	*OM (%)	*CEC (meq _c 100 g ⁻¹)	*Sand (%)	*Silt (%)	*Clay (%)	pH
Semillero Buck	Natural	50	0.415	0.0415	0–5	5.6	17.7	66.5	17.9	15.6	7.3
					5–15	6.0	25.0	51.5	25.0	23.6	7.2
					15–30	5.5	29.0	36.6	32.0	31.4	7.2
	Cultivated	90	0.47	0.0206	0–5	3.6	20.4	53.4	20.1	26.4	6.3
					5–25	3.6	19.7	51.1	24.5	24.4	6.9
					25–30	2.1	22.3	45.1	23.5	31.4	6.6
Azul	Natural	45	0.377	0.0065	0–5	6.8	16.2	74.3	13.0	12.8	7.7
					5–25	1.6	10.8	78.1	8.6	13.4	8.0
					25–30	1.3	11.3	79.7	8.5	11.9	8.2
	Cultivated	30	0.234	0.0319	30–35	1.9	11.3	75.3	11.7	13.0	7.9
					0–5	2.7	12.5	78.6	9.9	11.4	7.9
					5–20	2.1	12.0	79.7	9.3	11.0	7.9
					20–25	2.2	16.9	47.4	40.7	11.9	8.0
					25–40	2.7	19.2	59.6	21.5	18.9	7.9

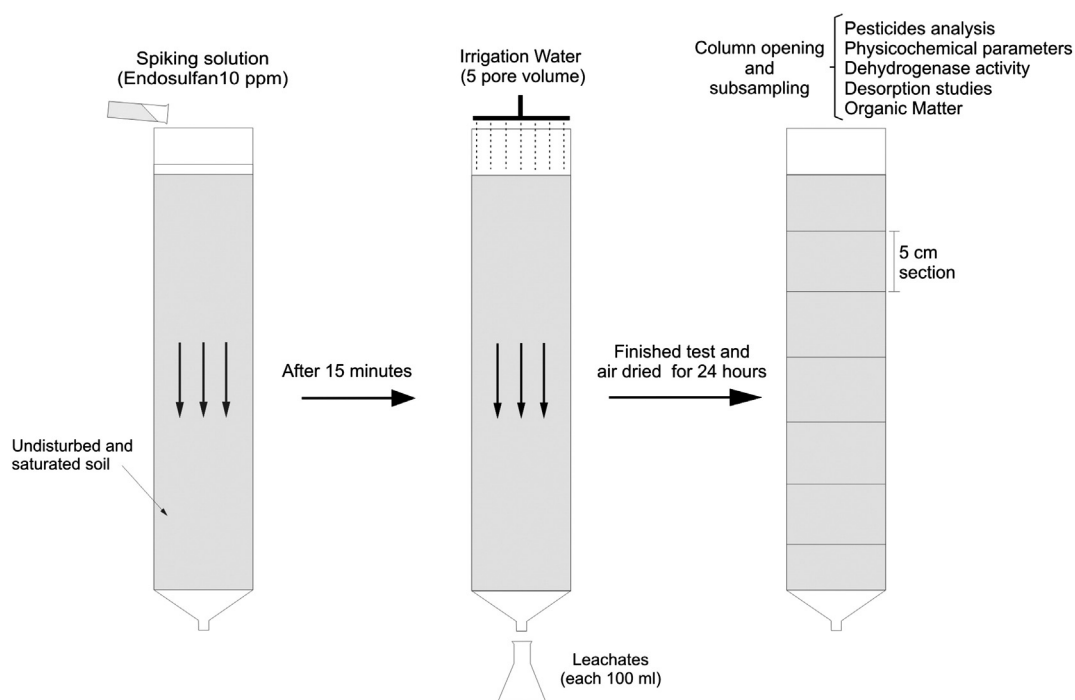


Fig. 2. Setup of soil column test system.

Soil subsamples were air dried to constant weight and 5 g were ground in a mortar with anhydrous sodium sulfate and extracted for 8 h with a mixture of hexane:dichloromethane (1:1) in a Soxhlet apparatus and concentrated under vacuum and nitrogen flow to 1 mL (Metcalf and Metcalf, 1997).

Clean up of all samples was performed by adsorption chromatography using 3 mL SPE empty cartridge filled with 1.5 g of activated (200 °C, 24 h) silica gel, conditioned with 5 mL hexane, and eluted with 15 mL of hexane and 30 mL of hexane:dichloromethane (1:1) mixtures; extracts were concentrated to 1 mL and kept at -20 °C in sealed vials until analysis.

2.6. Pesticide quali-quantitative analysis

Endosulfans (α -isomer, β -isomer and endosulfan sulfate) were analyzed according to Miglioranza et al. (2003), using a Shimadzu GC-ECD 17A equipped with a fused-silica capillary column of 30 m, SPB-5 (0.25 mm i.d., 0.25 μ m film thickness; Supelco, USA). The oven temperature started at 100 °C, held 1 min, followed by increases of 5 °C min^{-1} up to 150 °C, held 1 min, then 1.5 °C min^{-1} up to 240 °C, and then 10° min^{-1} up to 300 °C for 3 min. Inject port was set at 275 °C, and detector at 300 °C. The carrier gas was ultrahigh-purity helium (1.5 mL min^{-1}). Quantification was done using standard purchased from Ultra Scientific (North Kingstown, RI, USA).

2.7. Quality control and assurance

Laboratory and instrumental blanks indicate that there were not contaminations during laboratory handling and blank corrections were not necessary. Recoveries, calculated by spiked matrixes, were greater than 90%. Instrumental detection limits (DL) for endosulfan, were calculated following the methodology of Keith et al. (1983) and ranged between 0.08 and 0.33 ng mL^{-1} . Method DL ranged between 0.008 and 0.033 ng g^{-1} for soil and between 0.015 and 0.165 ng L^{-1} for water samples.

2.8. Dehydrogenase activity (DHA) determination

Soil enzyme activities show a quick response to changes induced by natural and anthropogenic disturbances, and can be therefore used as effective indicators of soil quality. Particularly, dehydrogenases do not accumulate extracellular in the soil and might be used as an indicator of overall soil microbial activity (Quilchano and Marañon, 2002). DHA was studied along the soil profile by triplicate, 1 g of wet soil was incubated during 24 h at 25 °C and darkness with 0.2 mL of 0.4% 2-p-iodophenyl-3 p-nitrophenyl- 5 tetrazolium chloride (INT) as a substrate. The iononitrotetrazolium formazan (INTF) formed was measured spectrophotometrically at 490 nm (Trevors, 1984; García et al., 1997).

2.9. Statistical analysis

Nonparametric ANOVA Friedman tests followed by a *t*-paired test for dependent samples were applied to assess differences among soil sections (within soil profile). Differences between land use and soil series were tested by ANOVA followed of Tukey test and the non-parametric Kruskal Wallis test was used when parametric assumptions were not fulfilled. The Spearman correlation test was used to determine correlation of pesticide residues and DHA with soil OM or between pesticide desorption and soil levels. The significance level was set at ≤ 0.05 and Infostat Software Package (Di Rienzo et al., 2010).

3. Results and discussion

3.1. Distribution of pesticide residues in soil profiles

Independently of soils series and land uses the highest endosulfan concentrations were found in the upper soil layer (0–5 cm, Fig. 3), showing pesticide retention and low migration through soil profile. A similar behavior was reported by Fenoll et al. (2011) for clay loam soils. The total endosulfan concentrations in the upper layer ranged from 120 to 140 ng g^{-1} dry weight in cultivated soils and between 30 and 60 ng g^{-1} dry weight in natural soils. The compound distribution

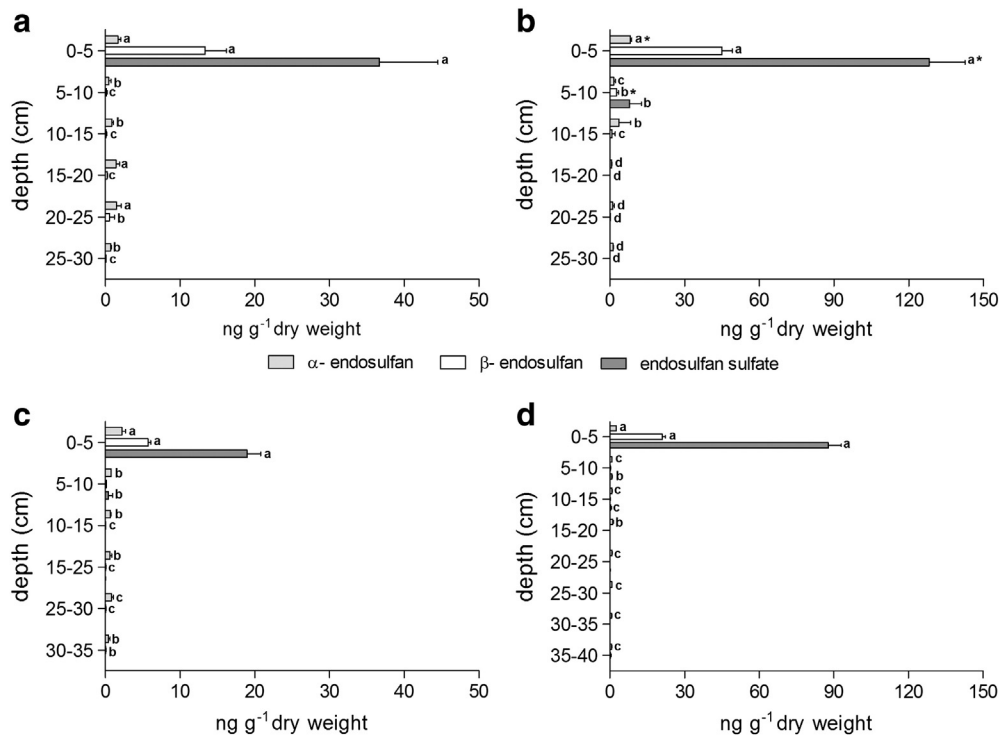


Fig. 3. Endosulfan isomers (α - and β -) and endosulfan sulfate levels in soil profiles of columns from Semillero Buck (a: natural, b: cultivated) and Azul (c: natural, d: cultivated) series. Different lowercase letters indicate significant differences through the soil profile within each column for each compound ($p < 0.05$), * indicates significant differences between soils series and land uses for the same level of profile ($p < 0.05$).

pattern was E. sulfate $>$ β - $>$ α -. This predominance of the sulfate metabolite that represented more than 40% of total endosulfan, showed the high microbial metabolism in the upper layer, associated with the greater OM content and soil aeration. Moreover, the (α - + E. sulfate)/ β -isomer ratio resemble that of the applied technical mixture (70:30). This result suggests the metabolism of α -isomer to E. sulfate, known as the main metabolite formed in soil (Ismail et al., 2005; Goswami et al., 2009).

OM and clay content are the main soil properties involved on soil pesticide retention but differences in pesticide levels between the upper layers of natural soils were not explained by those parameters. Semillero Buck series, with lower OM and higher clay content than Azul series, showed higher pesticide concentrations (Table 1, Fig. 3a, c). Other soil properties and processes might be considered; endosulfan metabolism is affected by soil pH being higher under alkaline conditions (Awasthi et al., 2000). The pH values of natural Azul series soils (Table 1) could explain the lower pesticide levels due to endosulfan metabolism to non determined compounds such as endosulfan diol (Awasthi et al., 2000). Conversely, for cultivated soil (Fig. 3 b, d), the higher retention of endosulfan isomers by Semillero Buck series was related to the OM and clay contents, and pH values (Table 1).

Endosulfan isomers levels below the first layer (0–5 cm) were between 4 and 5 ng g^{-1} dry weight for all soils. These values are higher than background levels reported for these soils by Gonzalez et al. (2013), indicating the vertical migration of both isomers. Except for natural soil from Semillero Buck (Fig. 3 a) and cultivated Azul series soils (Fig. 3 d) where E. sulfate was found up to 10 cm, this metabolite was below detection limit in the remaining deeper layers.

3.2. DHA activity

DHA is a good indicator of soil quality reflecting the metabolic activity of the soil and is proportional to the microorganism biomass. Several environmental factors such as soil moisture, oxygen availability, pH and OM content influence DHA but depth of the soil profile is one of the

most known factors reducing its levels (Wolińska and Stepniewska, 2012). In line with this statement and with the high microorganism abundance in the oxic-surface layers, DHA activity was high in the 0–5 cm layer with decreasing activity with depth in all soil profiles (Fig. 4).

In Semillero Buck series DHA activity was higher in cultivated soils but in both land uses it correlated well ($r = 0.9$, $p < 0.01$) with the soil OM content (Fig. 4 a). Soil enzymatic activity is strongly connected with soil OM which acts as substrate for microbial development. This positive correlation between DHA and OM content was previously reported for other soils (Koper et al., 2008; Wolińska and Stepniewska, 2011). DHA was also in agreement with its inhibition at low pH levels (Fernandez-Calviño et al., 2010). Thus, tillage with the concomitantly use of insecticides, herbicides and fertilizers leads to variations on soil quality. A direct relationship was found between DHA and the occurrence of E. sulfate metabolite up to 10 cm in cultivated soils. However, there is not enough evidence to discriminate if E. sulfate occurrence is linked to a high intrinsic microbial activity in the 5–10 cm or to a DHA enhancement due to the endosulfan migration through the profile.

Minor differences in DHA activity between land use in Azul Series soil (Fig. 4 b) were found and even cultivated soil showed slightly high values. Conversely to Semillero Buck series (Fig. 4 a) there was no correlation with OM content. The optimum pH for DHA activity was reported between 7.1 and 7.8 (Ros et al., 2003; Brzezińska et al., 2001) which is coincident with the pH values of cultivated soil. So, soil acidification by tillage favored the microbial activity.

3.3. Concentration of pesticide residues in leachates

The main pathway for contaminant transport to groundwater is leaching from surface soil after pesticide application. Column elution time (ET), defined as the time (min) necessary to obtain 100 mL of leachate, was dependent on soil characteristics (Table 1). Azul series showed shorter ET (30–45 min) according to its higher sand percentage. In Semillero Buck series the higher clay content (mainly in upper layers)

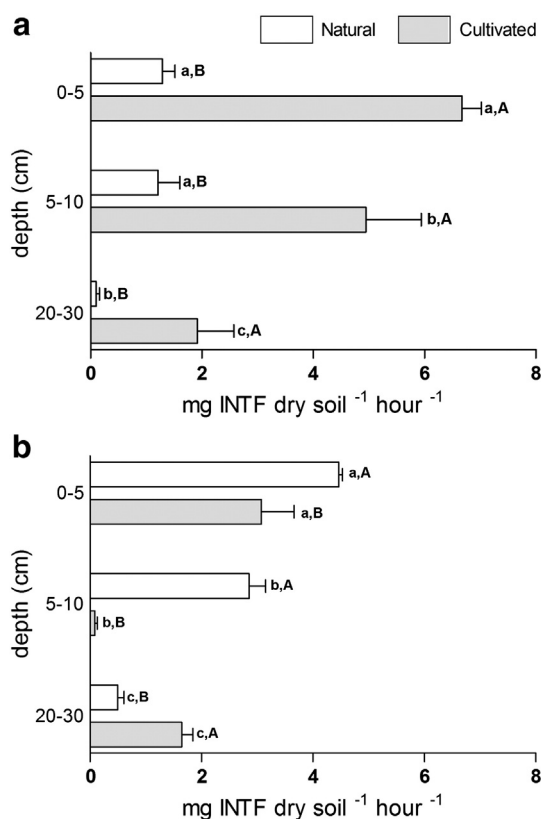


Fig. 4. Distribution of dehydrogenase activity in soil profiles from Semillero Buck (a) and Azul (b) series. Different lowercase letters indicate significant differences through soil profile within each column ($p < 0.05$); Different uppercase letters indicate significant differences within land use for the same soil level and type ($p < 0.05$).

leads to a lower flow velocity and therefore a higher ET (up to 90 min). Both isomers (α - and β -) moved through the soil profile being detected in all leachates, while the E. sulfate metabolite was below the detection limit (Fig. 5). Despite the higher pesticide retention in soils from Semillero Buck series (Fig. 3), both isomers leached more than in Azul series. Considering the sand content in the latest, it might be hypothesized that the greater interaction with the alkaline aqueous phase might favor endosulfan hydrolysis leading to a lower content of both isomers and the sulfate metabolite in leachates.

The endosulfan content in leachates from Semillero Buck series was independent of soil physicochemical properties (Fig. 5 a). Conversely, in Azul series soils, the quantity of endosulfan isomers in leachates (Fig. 5 b), would be explained by soil parameters. The lower OM content and loss of soil structure of cultivated soil, related to natural ones, might lead to lower interaction areas between solute and matrix and thus greater pesticide leaching.

The leaching test is useful to evaluate soil adsorption potential of a particular compound, being expectable that the pesticide leaching decreases with the increase in soil retention capacity. In this work, Semillero Buck soils were in line with this concept, but in soils from Azul series an inverse pattern was found (Figs. 3 and 5). Thus, beside the proposed enhancement of endosulfan transformation to not measured compounds (ie. endosulfan diol, lactona, ether) related to specific physicochemical characteristic of this soil, other factors might be involved. Thus, the high sand content of surface layer might allow endosulfan volatilization during the experiment (Table 1). On the other hand, the α -: β - isomers ratio in all leachates (Fig. 5) was higher than the technical commercial mixture ratio (70:30), showing a lower mobility of β -isomer, according with its high K_{oc} (Table 2).

Dispersivity and porosity are key parameters when describing contaminant lixiviation through the unsaturated zone (Ghodrati and Jury,

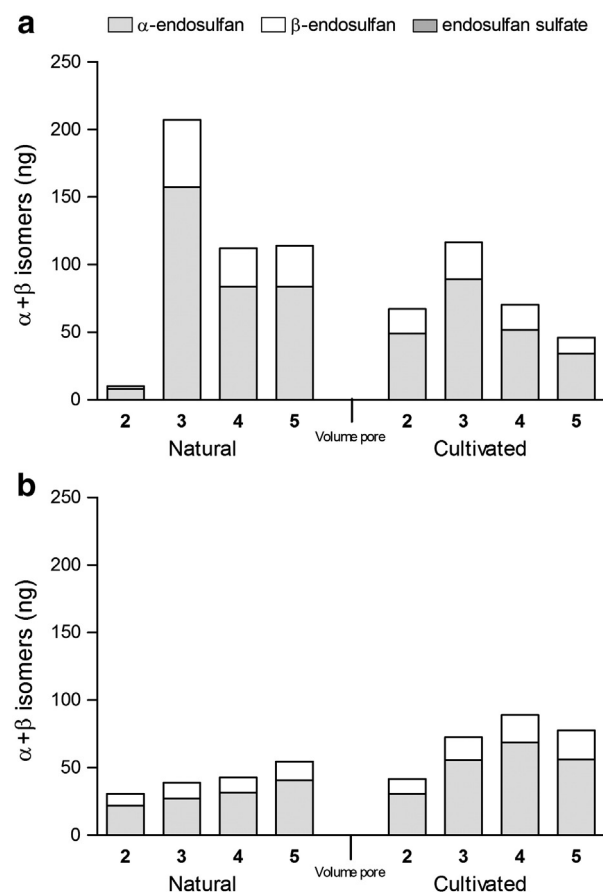


Fig. 5. Total mass of α - and β -endosulfan isomers in leachates of columns from Semillero Buck (a) and Azul (b) series.

1992). Cultivated and natural soils from Semillero Buck series had similar values of both parameters (Table 1) while cultivated soils from Azul series had lower dispersivity in agreement with its sand content (Grondona et al., 2013). Moreover, dispersivity and porosity of Semillero Buck series are higher than in Azul series. If dispersivity is greater, the input concentration of the compounds in the leachates will be achieved late. Considering land use, cultivated soils from Azul series with lower dispersivity showed higher endosulfan mass than natural ones for the same pore volume elution. In Semillero Buck series no relationship between the amount of pesticide in the leachate and this soil parameter was found. So, care should be taken in estimating pesticide leaching potential by means of these soil parameters.

3.3. Desorption studies

The aqueous availability of endosulfan isomers and metabolite assessed under controlled condition showed that the higher the soil concentration, the higher the desorption (Fig. 6) with statistically significant correlation ($p < 0.01$). Endosulfan sulfate showed the better

Table 2

Key physicochemical properties for endosulfan isomers and endosulfan sulfate. S_L : water solubility; $\log K_{ow}$: octanol–water partition coefficient logarithm; $\log K_{oc}$: organic carbon partition coefficient logarithm.

	α -Endosulfan	β -Endosulfan	Endosulfan sulfate
S_L (mol/m ³)	0.0063 ^a	0.089 ^a	≈0.089 (as β -isomer) ^b
$\log K_{ow}$	3.8 ^a	3.6 ^a	3.7 ^c
$\log K_{oc}$	3.6 ^b	4.3 ^b	3.2 ^b

^aShen and Wania (2005).

^bWeber et al. (2010)

^cAgency for Toxic Substances and Disease Registry.

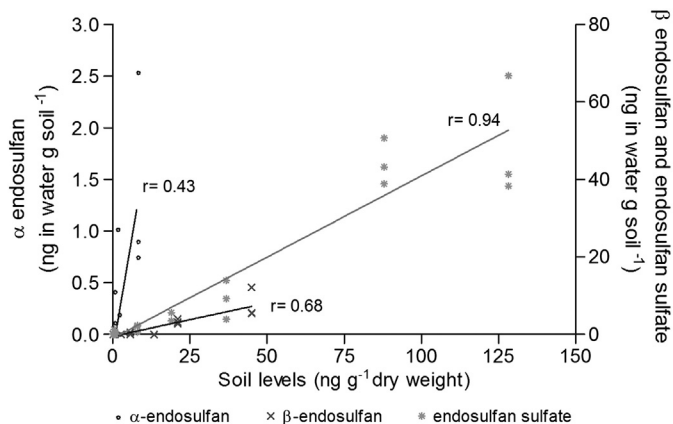


Fig. 6. Desorption of endosulfan isomers (α - and β -) and endosulfan sulfate from upper levels soils versus initial soil concentration. r : spearman correlation coefficient ($p < 0.01$).

correlation coefficient followed by β -isomer and a poor relation was found for α -isomer. This result was in agreement with the low α -isomer levels, mainly due to its metabolism to E. sulfate and the relatively higher water solubility of β -isomer (Fig. 6, Table 2).

When considering the percentage of pesticide desorbed relative to the initial soil concentration, the E. sulfate metabolite values varied from 25 to 100% but α and β -isomers do not overpass 23%. Since E. sulfate was not detected in the leachates this result deserves a special attention. According to the experimental design (spiking only with α - and β -isomers) endosulfan sulfate was formed “in situ” during the leaching test (3–5 days), without lixiviate but considering its physico-chemical characteristics (Table 2) E. sulfate would have the same or higher potential to lixiviate than endosulfan isomers (demonstrated also by desorption study results). The lack of E. sulfate detection in the leachates would be linked to the late metabolite formation. Column drainage to field capacity and the subsequent subsampling might bring a better scenario for metabolic transformation of α -endosulfan than saturation conditions during the leaching test. Moreover, Fenoll et al. (2011) found E. sulfate leaching after 6 pore volumes, so the amount of water used in the experiment would be not enough to allow the lixiviation of E. sulfate. However, on the basis of these results E. sulfate will behave as leaching pesticide under successive rain or irrigation events.

3.4. Endosulfan–soil interaction and implications for groundwater pollution

The effects of agriculture may take decades to produce impact in groundwater since the unsaturated zone provides a buffer area where degradation, adsorption and leaching process take place. Results from this work showed that endosulfan isomers and E. sulfate would be available to lixiviate when soils are subject to strong rain or flooding events as well as intensive irrigation after pesticide application. When management decisions for protection of groundwater quality are carried out is important to consider the time lag between pesticide application and the arrival to groundwater. Endosulfan isomer concentration in the whole leachates of each column ranged between 27 and 87 ng L⁻¹. Keeping in mind that a multiplier of 10 was used to calculate the spiking dose in column test and attempting to approach to field conditions, the same factor might be used to dilute the concentration of leachates leading to values about 2–8 ng L⁻¹. These results fit well with values reported for α - and β - endosulfan isomers in groundwater from the QGR watershed (0.1–1 ng L⁻¹) (Gonzalez et al., 2012).

Pollutant input into groundwater from the unsaturated zone is often closely related to fluctuations in groundwater levels by increasing percolation and pollutant transference to groundwater. Moreover, raised water table may capture pollutants present in soil for further transport (Van der Perk, 2006). Thus, additionally to the buffer effect of the

unsaturated zone due to degradation and adsorption processes, thickness and its variations with precipitation, evaporation and irrigation constitutes a crucial factor (Nielsen et al., 1986). With shallow depths to groundwater, the effect of thickness on the buffer action provided by the soil is lower. The groundwater depth in the study area is quite variable (2–14 m) and there is a prompt response of groundwater levels to heavy precipitations (Gonzalez et al., 2012). Thus, the joint action of lixiviation and water table level rising would lead to high potential of groundwater pollution by E. sulfate once it is formed “in situ” on soil surface.

4. Conclusions

Soil type and land use play a decisive role in estimating the potential pesticide leaching to groundwater. In this work, pH and clay content were the main soil characteristics related with endosulfan leaching, comparing both series and land uses. High pH might favor alkaline hydrolysis of endosulfan in the soil profile, while high percentages of clay showed greater retention of the compounds and therefore low leaching.

DHA values were directly related to the soil quality, there was no relationship between this parameter and endosulfan retention, but it was observed a direct relationship with the presence of the metabolite E. sulfate. As notable activity differences were observed between series and land uses, DHA provided soil-specific information. Further studies are needed to determine the relationship between DHA values and the other analyzed parameters (OM and texture) in the context of groundwater pollution assessment.

Results showed that agricultural practices modified the soil physico-chemical properties and structure allowing the vertical migration of compounds in Azul series. In addition, below 50 cm depth microbial activity is lower than in surface soil. Therefore, once isomers pass that depth, particle adsorption or physico-chemical processes would be the dominant processes determining pesticide fate. Future research on the assessment of endosulfan leaching to groundwater should consider the determination of all endosulfan metabolites, to provide a holistic view of the involved processes. This work showed that once on soil, endosulfan isomers and the sulfate metabolite would be available to reach groundwater after a rainfall or irrigation event. This situation will be of particular concern in those places where the aquifer is shallow.

Understanding pesticide behavior on agricultural and natural soils is essential to define strategies for a sustainable development of groundwater resources. The relevance of using undisturbed column test is demonstrated by its good approach to field conditions denoting its utility as a predictive tool for assessing groundwater pollution by endosulfan as well as by other pesticides with similar characteristics.

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