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2,4-Dichlorophenoxyacetic acid (2,4-D) sorption and degradation dynamics in three agricultural soils

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Pesticide availability varies with its residence time in soil.

Abstract

The fate and transport of 2,4-dichlorophenoxyacetic acid (2,4-D) in the subsurface is affected by a complex, time-dependent interplay between sorption and mineralization processes. 2,4-D is biodegradable in soils, while adsorption/desorption is influenced by both soil organic matter content and soil pH. In order to assess the dynamic interactions between sorption and mineralization, 2,4-D mineralization experiments were carried using three different soils (clay, loam and sand) assuming different contact times. Mineralization appeared to be the main process limiting 2,4-D availability, with each soil containing its own 2,4-D decomposers. For the clay and the loamy soils, 45 and 48% of the applied dose were mineralized after 10 days. By comparison, mineralization in the sandy soil proceeded initially much slower because of longer lag times. While 2,4-D residues immediately after application were readily available (>93% was extractable), the herbicide was present in a mostly unavailable state (<2% extractable) in all three soils after incubation for 60 days. We found that the total amount of bound residue decreased between 30 and 60 incubation days. Bioaccumulation may have led to reversible immobilization, with some residues later becoming more readily available again to extraction and/or mineralization.

Keywords: Sorption; Mineralization; 2,4-Dichlorophenoxyacetic acid (2,4-D); Bound residues; Water quality

1. Introduction

The extensive use of pesticides in agriculture is compromising soil and water quality. One major concern is protecting contamination of water resources (Younes and Galal-Gorchev, 2000). Sorption and degradation are key processes affecting the fate and transport of pesticides in the environment (Linn et al., 1993; Rudel et al., 1993). Degradation is a fundamental attenuation process for pesticides in soil (Guo et al., 2000). This process, catalyzed by soil microbes, is governed by both abiotic and biotic factors. Degradation is affected by a variety of interactions among microorganisms, various soil constituents, and the specific pesticide involved. Sorption is similarly key to controlling pesticide advective-dispersive transport, transformation and bioaccumulation processes (Calvet, 1989).

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Several interactions are known to exist between sorption and degradation (Guo et al., 2000). It is commonly accepted that sorption limits pesticide degradation by reducing their partitioning into the soil liquid phase (Smith et al., 1992; Guerin and Boyd, 1997). Sorbed chemicals are generally assumed to be less accessible to microorganisms, which preferentially or exclusively utilize chemicals in solution. Nevertheless, an inverse relationship between sorption and degradation does not necessarily imply that degradation of sorbed chemicals is negligible. Reductions in the degradation rate are often not proportional to increases in sorption (e.g., Moyer et al., 1972). Sorption is a slow, time-dependent process that may proceed over a relatively long period of time (e.g., more than 1 day) to reach equilibrium (Pignatello, 1998). With longer contact times between the soil and the chemical, the fraction of extractable residues is expected to decrease, while conversely the amount of bound residues should increase (Boivin et al., 2004; Mordaunt et al., 2005). These findings suggest that aging of pesticides has an effect on sorption-desorption behavior and hence on the biological availability of pesticides in soil. Aging is known to be one of the more critical factors governing the fate and transport of pesticides in soils (Sharer et al., 2003; Walker et al., 2005). Aging enhances the retention of sorbed organic chemicals by facilitating the formation of bound residues via chemical and/or physical non-equilibrium sorption processes, thus causing the chemical to become less susceptible to desorption and degradation. Still, relatively few laboratory studies have been carried out to assess the dynamic interplay between sorption-desorption and degradation as a function of different residence times in soil.

2,4-Dichlorophenoxyacetic acid (2,4-D) belongs to a group of chemicals known as phenoxy compounds, which are potentially toxic to humans. The herbicide is widely used to control broad leaf weeds and grasses in crops, and has been frequently detected in groundwater supplies in Europe and North America (e.g., Gold et al., 1988; IFEN, 2004). We selected 2,4-D as a model pesticide for our study because of its unique behavior in soil. This chemical is both very degradable and vulnerable to leaching. For example, 2,4-D can be completely dissipated within 20 days in various land-use types (Voos and Groffman, 1997). Microflora able to mineralize this chemical have been found naturally in cultivated soils (Vieublé Gonod et al., 2003). At the same time several factors combine to make the chemical vulnerable to rapid advective-dispersive transport and leaching, such as having a relatively low molecular mass, a limited volatilization rate (i.e., a relatively low Henry's constant), a negative charge at low soil pH, and relatively high solubility. Several studies indicate that 2,4-D sorption in soil is a function of soil pH, and to some extent also on soil organic matter content (e.g., Dubus et al., 2001; Spark and Swift, 2002).

The aim of this study was to assess the dynamic interactions between 2,4-D sorption and degradation, and to identify the main factors influencing both processes. Soil incubation experiments were carried out to monitor both 2,4-D mineralization and time-dependent soil/liquid phase partitioning of 2,4-D and its metabolites in three cultivated soils (clay, loam, sand) from initial treatment to 60 days of incubation. Measurements were made of time-dependent ^{14}C and carbon dioxide release rates, the overall kinetic release process, extractable residues, and bound residues.

2. Materials and methods

2.1. Soils and herbicide used

The laboratory experiments were carried on samples collected from the surface (0–15 cm) horizons of three agricultural soils in Lorraine, France: a relatively fine-textured vertic stagnic cambisol (further referred to as clay soil), a medium-textured stagnic luvisol (named loamy soil) and a coarse textured fluvic stagnic cambisol (named sandy soil); (WRB, 1998). Selected physical and chemical properties of the three soils are given in Table 1. The soils were treated with 2,4-D and [U-phenyl-^{14}C]2,4-D (radiochemical purity >99%; specific activity 7.7 Mbq mg^{-1}). 2,4-D is a weak acidic molecule (pK_a 2.6) with a relative molecular mass of 221 g mol^{-1} and a solubility of 23,200 mg L^{-1} in water at pH 7, 22 °C. Its octanol/water partition coefficient is 2.83 (log K_{ow}).

2.2. Laboratory experiments

The soils were air-dried and sieved to 2 mm. Samples (50 g) of the ≤2 mm soil aggregates were placed in glass dishes (6 cm diameter). Water was added to the soil samples until approximately 80% of field capacity. We subsequently applied to each sample a mixture of 2,4-D and [^{14}C]2,4-D (59.5 kBq) in aqueous solution. The solution was sprayed onto the soil aggregate surfaces by means of a micro-syringe that dispensed very small

Table 1
Selected characteristics of the three soils (surface layers, 0–15 cm) used in this study

Soil type	Clay (%)	Loam (%)	Sand (%)	OM (%)[a]	pH_{H_2O}	C/N[b]	C.E.C.[c] (cmol kg^{-1})
Clay soil	41	49	10	3.3	7	9.9	18.7
Loamy soil	31	50	19	2.5	5.9	9.1	14.8
Sandy soil	11	23	66	1.5	5.8	9.6	5.5

[a] Organic matter content (%).
[b] Organic carbon/nitrogen ratio.
[c] Cation exchange capacity.

droplets. The amount of added herbicide represented 0.75 mg per sample (15×10^{-6} g/g sol), equivalent to a conventional field treatment dose of 1800 g ha^{-1}. All treatments involved three replicates. We also used blank treatments (i.e., without 2,4-D), consisting of the same 50 g of soil and the same volume of water. Each soil sample was placed in a radio-respirometer (1.5 L) that contained flasks of an aqueous sodium hydroxide solution (0.5 M; 10 mL) and distilled water. The sodium hydroxide was used to trap carbon dioxide evolving from the soil, as well as ^{14}C-labelled carbon dioxide stemming from 2,4-D ^{14}C-ring degradation. The distilled water flask served to reduce water losses from the soil by maintaining a constant humidity in the system. The radio-respirometers were incubated in the dark at 20 ± 1 °C.

2.3. Release kinetics and extractable residues

Pesticide residues were extracted from the soil immediately after application, and after 5, 10, 30, and 60 days of incubation. Soil samples were rotary shaken at 20 ± 1 °C for 20 h with aqueous calcium chloride (0.01 M, 150 ml) in polytetrafluoroethylene (PTFE) centrifuge flasks. The release kinetics of 2,4-D into water at each of these extraction times was determined by measuring the radioactivity in the supernatant solution after shaking for 1, 2, 5, 10, 20, 30, 60, 180, 420 and 1200 min. Each measurement was done on a 1 mL sample, which was centrifuged at $5000\times g$ for 20 min using a Beckman Avanti™ J-25 (Beckman Instruments, Inc, Fullerton, CA). The radioactivity of the supernatant solution was measured by liquid scintillation using a Packard 1900 CA Tri-carb liquid scintillation analyzer (Packard Instrument Company, Medriden, CT) after adding 10 mL of a scintillation cocktail (UltimaGold™, Packard Bioscience). The counting time was 10 min, while a quench correction was made by the scintillator analyzer after calibration.

After completing the above kinetic release studies, the same samples were used to carry out a series of time-dependent residues experiments using both water (0.01 M calcium chloride) to obtain readily extractable 2,4-D residues and methanol for a more comprehensive extraction of 2,4-D residues. For these studies, the soil/water mixtures were centrifuged at $5000\times g$ for 20 min, the supernatant replaced with fresh aqueous calcium chloride (0.01 M, 150 mL), and the sample shaken as before for 20 h. This operation was repeated until the supernatant radioactivity became less than three times the background noise of the scintillator analyzer (1.7 Bq). To completely extract any remaining residues, the soil was subsequently extracted repeatedly with methanol (100 mL) until the supernatant radioactivity again became less than three times the background noise of the scintillator analyzer.

2.4. Extractable residue analysis

Using only methanol, a series of soil extractions was performed on specifically prepared additional samples to determine the nature of extracted residues. For these extractions, 100 mL was added to the soil samples and rotary shaken at 20 ± 1 °C for 20 h in PTFE centrifuge flasks. Samples were next centrifuged at $5000\times g$ for 20 min and the radioactivity of 1 mL of supernatant solutions determined using liquid scintillation as before. This process was repeated until the supernatant radioactivity became less than three times the background noise of the scintillator analyzer (1.7 Bq). After the methanol extractions, the supernatants were combined and concentrated for analysis of degradation products by high performance liquid chromatography (HPLC) using a radio-chromatography detector (Radiomatic/FLO ONE Beta − Series A-500, Packard Instrument Company, Meriden, CT). The HPLC was equipped with a 250-4 (250 mm long, 4 mm ID) C18 Merck LichroCART column coupled to a diode-array detector (Varian 9065, Varian BV, Middelburg, The Netherlands). Analyses were carried out for the following conditions: a wavelength of 282 nm, injection volumes of 80 μL, 30 min run times, 0.8 mL min^{-1} flow rates, and elution with an acetonitrile + aqueous phosphoric acid (1.0 M, pH 3) solution (first using a 60 + 40 solution by volume for 10 min, and a 65 + 35 solution for 20 min). Peaks were identified using a Ultima Flo™ Packard radio-chromatography detector (Packard Instrument Company, Meriden, CT) at a flow rate of 1.2 mL min^{-1} and using counting cell volumes of 500 μL. The limit of 2,4-D detection for these conditions was 1 Bq.

2.5. Non-extractable residues in soil

After exhaustive extraction of the residues with aqueous calcium chloride solution (0.01 M) and methanol, the soil aggregates were air-dried and pulverized. Non-extractable ^{14}C-residues were determined next by combustion of soil samples (300 mg) using an Oxidizer 307 (Packard Instrument Company, Meriden, CT). [^{14}C]Carbon dioxide released by the samples was trapped using Carbo-sorb E® (10 mL) and a scintillating solution (10 mL), while Permafluor E+® (Packard Bioscience) was subsequently added and the radioactivity of the trapped solution determined using liquid scintillation.

2.6. Data analysis

Descriptive statistical analyses (analysis of variance, principal component analysis) of the data were performed with the Statistica® software package, version 6 (StatSoft France, Maison-Alfort, France).

3. Results and discussion

3.1. 2,4-D mineralization

Fig. 1 shows the amounts of 2,4-D that were mineralized during the incubation experiments. Several transformation pathways such as hydrolysis, methylation and ring cleavage have been suggested for 2,4-D (Roberts, 1998). Mineralization appeared to be the main 2,4-D dissipation process during the incubation experiments with our three soils. The lag phases were significantly different between the three soils, although all were followed by rapid mineralization. For the clay soil, 25% of the applied dose was mineralized after 5 days of incubation, whereas only small amounts (2–3%) were mineralized for the other two soils. The longest lag phase was observed for the sandy soil. However, after 30–60 days of incubation, the extent of mineralization leveled out at about 54–66%, with no significant differences between the three soils ($p>0.05$). Other studies have reported similar mineralization rates in cultivated soils. For example, Vieublé Gonod et al., (2003) reported relatively short lag phases followed by mineralization rates of 35–50% of the applied dose after application of labeled 2,4-D to aggregates of different sizes. The occurrence of a lag phase followed by rapid mineralization indicates that while some 2,4-D decomposers were initially present in the soil, their numbers could have been the limited factor in the mineralization process. Since to our knowledge no 2,4-D previously was applied to the cultivated soils used in our study, we assumed that all three soils contained natural microflora able to mineralize the chemical. Soils never treated with 2,4-D have been known to host significant but low populations of microbial decomposers.

2,4-D biodegradation typically occurs either by means of specific degraders that use the herbicide as carbon and nitrogen sources, or by means of co-metabolism populations whose relative proportions vary with soil type (e.g., Soulas, 1993). The mineralization rate of 2,4-D has been found to be positively correlated with the size of the microbial biomass or the number of total bacteria in soil, and with soil organic matter content (Entry et al., 1995; Voos and Groffman, 1997). The mineralization of 2,4-D can involve several microbial species, which may act as a consortium so as cover different steps in the biodegradation process. Differences observed in our study between the different lag phases could be related to the size of the populations originally present in the soils. The sandy soil was more acidic (pH 5.8) and had a much lower organic matter content than the other two soils (Table 1). The sandy soil hence likely contained fewer bacteria, and/or at least one or more microbial species at a much lower density. Mineralization of 2,4-D may be via co-metabolism immediately after its application, and via metabolism after microorganisms able to use 2,4-D as carbon and energy sources have reached a critical level and become the main contributors to the mineralization process. Still, a large fraction of the 2,4-D was mineralized relatively rapidly (within 30 days) after application to all three soils, with a concomitant rapid decrease in its availability and hence susceptibility to leaching.

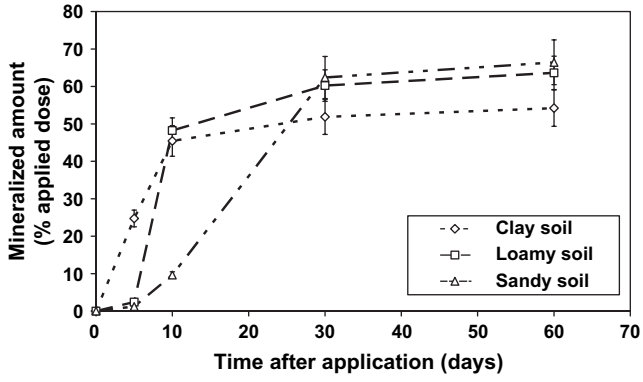

Fig. 1. Amounts of 2,4-D mineralized for the three soils during 60 days of incubation.

3.2. Release kinetics of 2,4-D

Fig. 2 shows the release kinetics of 2,4-D immediately after application (T0) and after contact times of up to 60 days (T10 to T60). Immediately after application, about 70% of the applied 2.4-D was quickly released (i.e., within 1 h) by the clay and loamy soils, while 80% was released by the sandy soil. The shapes of the release curves indicate that as long as large amounts of residue are available (from T0 to T10 days), the residues are able to rapidly re-enter the solution, with a quasi-equilibrium situation developing after only about 2 h (Fig. 2). This suggests that much of the 2,4-D will remain readily available for the first 10 days after application, and hence may be subject to possible advective transport and leaching with flowing water in the soil. With longer contact times ($T\geq 30$ days), the release kinetics show that only small amounts of 2,4-D will re-enter into the soil solution. The limited release after 30 days likely was caused mostly by the relatively rapid mineralization rates in our soils, as discussed previously. However, sorption kinetics probably also played a role. For example, the sandy soil released only small amounts of 2,4-D after 10 days of incubation (Fig. 2), even though mineralization at that time was still relatively low (Fig. 1). This suggests that the kinetic sorption process may have continued for quite some time after the initial application.

Other studies have shown that 2,4-D degradation may only be partial, and that the main degradation product (2,4-dichlorophenol) may be more strongly adsorbed to soils (Soulas and Fournier, 1981). After 10 incubation days, no additional residues were

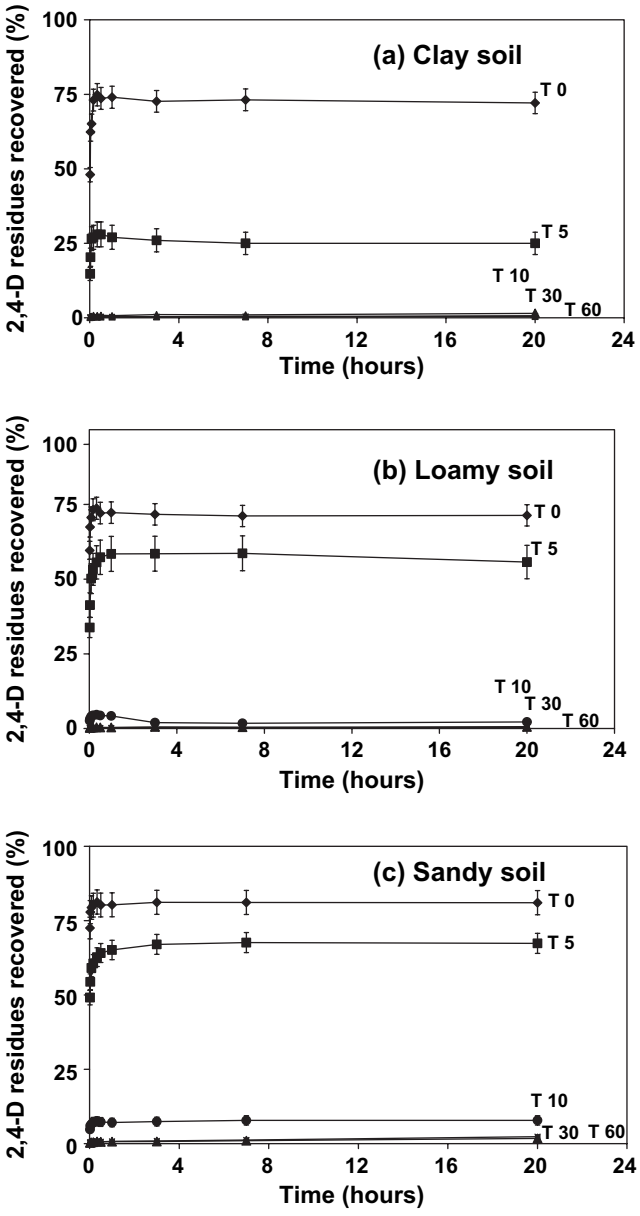

Fig. 2. Recovered residues of 2,4-D and its metabolites from (a) clay soil, (b) loamy soil, (c) sandy soil after different incubation periods (T0–T60 days). The recovery time studies were carried out with a 0.01 M calcium chloride solution.

recovered from our clay and loamy soils, while the amount recovered from the sandy soil was less than 8%. Thus, in spite of its high solubility, mineralization of 2,4-D and/or simultaneous increased sorption of the residues caused a substantial and rapid decrease (after 10 days) in the chemical availability for the three soils.

3.3. Amount and nature of extracted 2,4-D residues

We found that after the initial application of the chemical, more than 93% of the applied 2,4-D desorbed with water (0.01 M calcium chloride) from all three soils. This confirms that immediately after its initial application, 2,4-D sorption is reversible. This may be due in part to its large solubility in water. With longer contact times, the amounts of extracted residues dramatically decreased, and became less than 2% after 60 days incubation.

Accessibility to 2,4-D residues was higher in the sandy soil just after 2,4-D application and until 10 days of incubation (Table 2). 2,4-D mineralization was slower in this soil, which also showed less sorption because of its lower clay and organic matter contents. We observed that the amounts of 2,4-D residues extracted with methanol, following extractions with water (0.01 M calcium chloride), were very low immediately after application, reached a peak after 10 incubation days, and then decreased again. This would confirm that sorption of 2,4-D residues increases with longer contact times. This seems particularly true for the sandy soil, where 13% of the residues were desorbed with the methanol extractions after 10 contact days. The residues extracted in this way could have been the 2,4-D itself, and/or its degradation products that were more strongly sorbed to the soil and not available to water extraction (0.01 M calcium chloride).

Sorption of organic substrates has been shown to often decrease their availability to microorganisms. Sorbed 2,4-D therefore should be less rapidly mineralized than free 2,4-D (Benoit et al., 1998; Carrizosa et al., 2000). Increased sorption over time in the sandy soil, which means having less 2,4-D and its metabolites in solution, was expected to lead to less mineralization. This was contrary to our results, which showed that mineralization proceeded rapidly after the initial lag phase (Fig. 1). Because of this and the relatively low sorption rates in the sandy soils, we believe that the availability of the chemical and its degradation products was limited more by physical entrapment than by irreversible chemical bounding.

In soils, initial side chain cleavage can cause the formation of an important metabolite, 2,4-dichlorophenol (2,4-DCP), as well as small amount of various other degradation products (“Others” in Fig. 3) of lower molecular mass but generally with a higher polarity (results not shown). Analysis of the extracted products indicated that some of the metabolites were already present very soon after 2,4-D application. Rapid biotic and/or abiotic degradation may have generated these products. It has been shown that the carbon atom of the 2,4-D molecule can contribute to bacterial cellular protoplasm synthesis (Soulas, 1990). Neo-synthesis of the products (bioaccumulation), with a chemical structure that differs from 2,4-D, may lead to the immobilization of C from 2,4-D in the soils. The various molecules thus created, each having a different molecular mass, may combine to produce the ^{14}C signals (“Others”) recorded via β detection.

Table 2
2,4-D residues extracted from the three soils studied after different incubation times

	2,4-D residues extracted (% total applied) after incubation time (days) of				
	0	5	10	30	60
Clay soil					
$CaCl_2$ (0.01 M)	96 (±2)	24 (±2)	2 (±2)	2 (±1)	1 (±1)
MeOH	0.2 (±0.1)	2 (±1)	1.5 (±1)	0.1 (±0.2)	0.1 (±0.1)
Loamy soil					
$CaCl_2$ (0.01 M)	93 (±2)	70 (±2)	2.5 (±1)	2 (±2)	1.5 (±0.2)
MeOH	0.1 (±0.1)	1.5 (±1)	2 (±1)	0.2 (±0.1)	0.1 (±0.05)
Sandy soil					
$CaCl_2$ (0.01 M)	98 (±2)	75 (±3)	46 (±3)	2.5 (±1)	2 (±4)
MeOH	0.1 (±0.1)	2 (±1)	13 (±2)	0.3 (±0.1)	0.05 (±0.03)

Extractions were performed with water (0.01 M calcium chloride) followed by methanol. Standard deviations are given in parentheses.

Fig. 3 shows that 2,4-D was still the main chemical being extracted from all three soils after 5 days, while the proportion of degradation products was relatively low. In the sandy soil, a large proportion of the extracted residues after 10 incubation days consisted of 2,4-DCP. The relative prevalence of this metabolite indicates that the size of at least one population, and perhaps more, of the consortium responsible for 2,4-D mineralization was relatively small. Moreover, it supports the assumption of a significant contribution of non-specific microorganisms for an extended period before the development of more efficient degraders.

3.4. Dynamics of 2,4-D bound residues formation in soil

Bound residues were already detected immediately after application of the chemical, as shown in Fig. 4. This may have been due to strong sorption, including cation-bridging with bivalent metals (Dubus et al., 2001). Bound residues in the clay and loamy soils increased rapidly after 5 days of incubation, while less bound residues were generated in the sandy soil. The fraction of bound residues formed in the sandy soil was found to be significantly lower statistically ($p<0.05$) than in the two others soils.

Bound residue formation has been linked to the presence of soil organic matter because of its large number of sorption-specific sites (Pignatello, 1998). Bounding of the residues may have contributed to the observed decrease in the mineralization rates after 10 days contact time for the loamy and clay soils. Nevertheless, no long-term quasi-equilibrium state was ever reached. Fig. 4 shows that the fraction of bound residue increased until approximately 10 incubation days in the three soils, and then decreased again ($p<0.05$). This means that parts of these residues were still potentially available. We previously noted that 2,4-D degradation produced several degradation products of different molecular mass. Also, ^{14}C from 2,4-D may have been temporally immobilized by being incorporated into the protoplasm of some of the soil microorganisms. In addition to chemical bounding and physical entrapment, which both should contribute to the formation of bound residue (Boivin et al., 2004), incorporation into the constitutive parts of microorganisms (bioaccumulation) could lead to overestimation of bound residue formation. Still, the neosynthesis compounds have a chemical structure that differs from 2,4-D, and

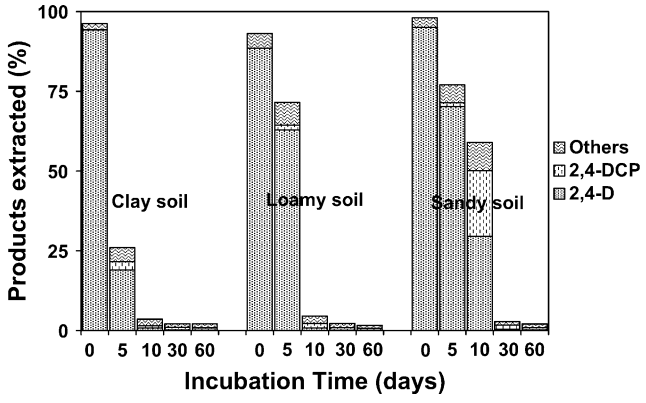

Fig. 3. Products (% of applied dose) recovered using methanol extraction. Three groups of chemicals were examined: 2,4-D, 2,4-DCP and "Others", the latter being the sum of all recorded weak β signals. The standard deviation of each fraction was less than 5%.

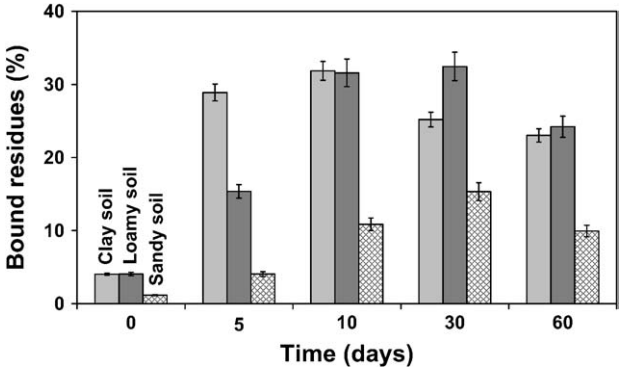

Fig. 4. Bound residues (% of applied dose) derived from 2,4-D during 60 days of contact time.

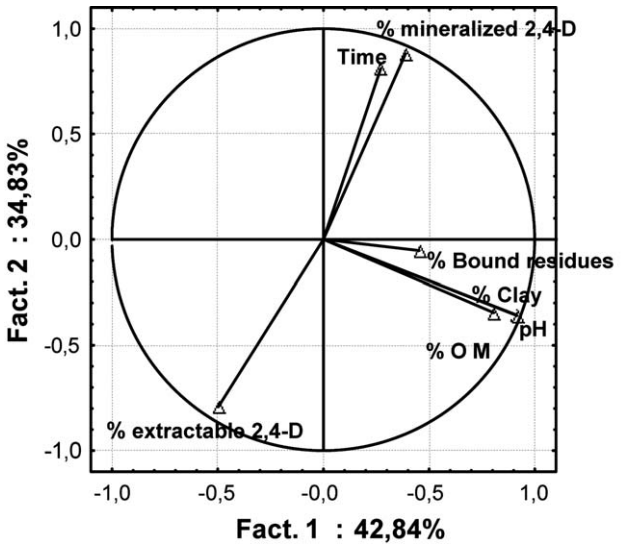

Fig. 5. Results of a principal component analysis using Statistica® (projection on 1, 2 planes) for the incubation experiments using selected soil characteristics; 77.7% of the total variability was explained by the two selected principal component axes.

hence should not be a threat to the contamination of water resources.

3.5. Statistical approach of 2,4-D behavior

A principal component analysis was carried out to identify the main factors affecting 2,4-D availability. Fig. 5 shows that incubation time was the most important factor influencing 2,4-D availability, which reflects the fact that mineralization and sorption are both highly dynamic. The statistical results indicate that with longer contact times, 2,4-D availability decreases considerably due to its mineralization. No significant relationships were found between soil characteristics (% organic matter, % clay, soil pH) and 2,4-D mineralization. We earlier showed that 2,4-D was readily mineralized irrespective of soil type, and that the only difference between the three soils was the longer lag phase for the sandy soil. By contrast, bound residue formation was found to be correlated with soil type. The amount of bound residue in the sandy soil was significantly lower than that in the two other soils. Contact time was not found to have a significant effect on bound residue formation, in part likely because of bioaccumulation which may have caused some overestimation of the amount of bound residue after long incubation times.

The above results show that the effects of aging on 2,4-D and its residues in soils is a complex process. Overall, we found that the amount of total extractable 2,4-D residue (i.e., extractions with 0.01 M calcium chloride, following by methanol) decreased with contact time, while bound residue formation was probably overestimated because of bioaccumulation.

4. Conclusions

2,4-D in the three soils was found to be readily mineralized by microorganisms. Mineralization appeared to be the main process limiting the availability of this chemical. Hence, while this herbicide is one of the most mobile pesticides, its very rapid mineralization (50% of the applied dose in 10 days) lessens some of its potentially adverse effects on the environment (groundwater and surface water contamination). Bound residues were found to be formed quickly in the three soils, with the amounts slowly decreasing again near the end of the 60-day incubation experiments, possibly due to some overestimation of the amount of 2,4-D or metabolites being taken up by soil microorganisms (bioaccumulation). Pesticides presenting a chemical structure similar to natural products are biodegradable, and their use therefore seems a reasonable compromise between crop protection and environmental concerns.

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