Time-Dependent Sorption of Imidacloprid in Two Different Soils

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Time-dependent sorption of imidacloprid [1-[(6-chloro-3-pyridinyl)-methyl]-*N*-nitro-2-imidazolidinimine] was investigated with two German soils (sandy loam and silt loam). Soil batches containing the active ingredient (0.33 mg/kg) were incubated for 100 days. After selected aging periods, imidacloprid desorbed by 0.01 M $CaCl_2$ (soluble phase) and by organic solvents (methanol and acetonitrile) and reflux extraction with acidified methanol (sorbed phase) was determined. Calculated sorption coefficients K_d and K_{oc} increased by a factor of 3.2−3.8 during 100 days of aging. Additionally, the time-dependent sorption was verified by a column leaching experiment with the aged soil. The amount of imidacloprid in column eluates (0.01 M $CaCl_2$) decreased compared to total recovered by a factor of ∼2. Sorption of imidacloprid thus increased with residence time in soil, making it more resistant to leaching. These results are further information to explain the low leaching potential of imidacloprid in the field, despite its high water solubility.

Keywords: *Imidacloprid; sorption; desorption; aging*

INTRODUCTION

Imidacloprid [1-[(6-chloro-3-pyridinyl)-methyl]-*N*-nitro-2-imidazolidinimine] is a member of a new chemical class called the chloronicotinyl insecticides. Imidacloprid controls sucking pests such as aphids, leafhoppers, planthoppers, thrips, and white flies and various coleopteran species (Elbert et al., 1990). Due to its systemicity, imidacloprid is used worldwide for seed treatment and soil and foliar application.

There is great public concern about the environmental fate of pesticides, particularly their leaching potential. Although the relatively high water solubility of imidacloprid (0.61 g/L at 20 °C) may indicate leaching potential in soil, field trials (Rouchaud et al., 1996a) and a lysimeter study (Hellpointner, 1998) did not indicate leaching behavior of the active ingredient in soil.

Sorption is one of the most important factors determining leaching potential in soil. A possible explanation for the lack of leaching of imidacloprid, despite its high water solubility, would be a larger sorption potential at lower concentration of 0.05 μg/mL (K_{oc} = 802−1560) compared to K_{oc} obtained from the Freundlich equation at higher concentration range from 0.05 to 250 μg/mL (K_{oc} = 323−378) (Cox et al., 1997). Desorption hysteresis should be also considered. In the general equilibrium batch method, some sorbed pesticides are difficult to desorb after the sorption step, giving higher desorption coefficients than sorption. This desorption hysteresis has already been reported for imidacloprid (Cox et al., 1997). Another explanation for the lack of leaching could be an increase in the sorption of imidacloprid in soil with time. This effect has been described for some pesticides (Walker et al., 1995), whereby at first the active ingredient is sorbed to the outer positions of the soil aggregates followed by sorption sites within the soil aggregates, which are diffusion limited and are reached only later. Other possible processes are the consolidation of initially weak bonds, a change of mechanism of sorption/binding, and a steric inclusion of the ingredient molecule into clay/humic matter complexes.

The degradation rate in soil should also be considered in the leaching potential. In a laboratory study, the half-life decreased significantly from 190 days in soil without groundcover to 45 days in soil with groundcover (Scholz and Spiteller, 1992). Similar half-lives were obtained in a field study under cropped conditions (Rouchaud et al., 1996b). These results indicated a contribution of the vegetation under natural field conditions.

In the present study the change of the sorption parameters K_d and K_{oc} as well as the change of the leaching potential of imidacloprid by means of an aqueous flow extraction procedure was investigated in two soils as affected by the aging period. In batch equilibrium tests, the contact times of the pesticide with the soil are considered to be very rapid (Cox et al., 1998c), whereas a limitation in transport of the active ingredient to the sorption sites occurs in soil column and field experiments. In batch equilibrium tests, therefore, this may not play a role owing to the complete dispersion of the soil particles. The soil column experiment may simulate more realistic leaching potential than K_{oc} value.

MATERIALS AND METHODS

Chemicals. [*methylene*-^{14}C]Imidacloprid (specific radioactivity = 3.77 MBq/mg), nonlabeled imidacloprid (purity = 99.8%, cochromatography purpose only), imidacloprid-olefin [1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-1*H*-imidazol-2-amine] (97.2%), imidacloprid-nitrosimine [1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-*N*-nitroso-1*H*-imidazol-2-amine] (99.0%), and 6-chloronicotinic acid (>97%) [structure, see Scholz and Spiteller (1992) and Cox et al. (1997)] were synthesized by Bayer AG (Leverkusen, Germany) and certified spectroscopically. These substances were dissolved in acetonitrile and stored at ∼ −18 °C. The radiochemical purity of ^{14}C-imidacloprid was determined by thin-layer chromatography (TLC) prior to (99.1%) and after (99.4%) the application.

Soils. Two German soils, Laacher Hof "field plot AXXa" (LH AXXa) (Typic Cambudoll sandy, mixed, mesic) and Laacher

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Table 1. Physical and Chemical Characteristics of the Soils Used in the Study

	LH AXXa	LH A2
texture analysis (USDA)	sandy loam	silt loam
sand (2000−50 μm) (%)	72.4	36.9
silt (50−2 μm) (%)	22.6	51.1
clay (<2 μm) (%)	5.0	12.0
pH		
in H_2O	7.0	8.1
in 0.01 M $CaCl_2$	6.4	7.3
organic C (%)	1.8	0.9
cation exchange capacity (mequiv/100 g)	8	8
particle density (g/mL)	2.5	2.6
max water holding capacity (WHC_{max}) (%)	34.4	36.4

Hof "field plot A2" (LH A2) (Typic Argudarf loamy, mixed, mesic), from Monheim/Rheinland were used in this study. The characteristics of these soils are shown in Table 1. The soils were freshly collected from the 0−30 cm depth of the field plots, air-dried for 1 day, sieved through a 2 mm sieve, and stored at room temperature for 4 days prior to the experiments. The residual moisture was determined by drying at 105 °C and was taken into consideration correspondingly when the soils were weighed. The biomass of the test soil was determined by Dr. Anderson (Bayer AG, PF-E/Ecobiology) on the air-dried and sieved soil at the beginning and the end of the experiments (Anderson and Domsch, 1978). The organic C was determined by combusting the soil at >900 °C according to the international standard method ISO/CD 10694. The cation exchange capacity was determined according to German standard method DIN 19684. The particle density (Blake and Hartge, 1986) and texture (Gee and Bauder, 1986) was analyzed according to a USDA method. Soil pH was determined in a 1:2.5 (w/w) soil/deionized water and 0.01 M $CaCl_2$ solution. The maximum water holding capacity was determined according to the method of Schaller (1988).

Imidacloprid Application. An aliquot (685 μL) of ^{14}C-imidacloprid solution was dispensed with a microsyringe onto a subsample of 50 g of moist soil (premixture). After the organic solvent had been evaporated, this soil was thoroughly mixed with a spatula and then added to the major soil portion (2976.3 g of moist soil for LH AXXa and 2997.3 g for LH A2) to give the intended imidacloprid concentration [0.33 mg of active ingrediend (ai)/kg of dry soil], which corresponds to its maximum application rate (200 g of ai/ha) considering a soil depth of 5 cm and a bulk density of 1.2 kg/dm^3. The spiked soils were thoroughly mixed in a tumbling mixer, and aliquots equivalent to 100 g of dry soil (113.3 g of wet soil for LH AXXa and 114.1 g for LH A2) were placed into 300 mL Erlenmeyer flasks. Prior to incubation, the soil was adjusted to the soil moisture of 40% of the maximum water holding capacity (WHC_{max}) by adding water (1.3 mL for LH AXXa and 0.5 mL for LH A2).

Aging Study. Spiked soils were incubated at 20 ± 1 °C in the dark for up to 100 days. A glass tube (14.5 cm long, 2.2 cm diameter), which contained, in order, a polyurethane plug to trap volatile compounds, 10 g of soda lime for adsorption of $^{14}CO_2$ emanating from soil, ∼1 cm glass wool layer, and 4 g of soda lime for adsorption of atmospheric CO_2, was attached on the top of each Erlenmeyer flask. The top of the glass tube was not covered to allow oxygen diffusion to the flask. Soils were sampled for batch and column experiments at 0, 2, 7, 14, 28, 42, 56, and 100 days after application. Sampling was duplicated at 0 and 28 days after application.

Batch Test. At each sampling period, the soda lime from the ^{14}C trap was dissolved in 60 mL of 18% hydrochloric acid. The liberated $^{14}CO_2$ was absorbed by a cocktail of Carbosorb and Permafluor E$^+$ (Packard Instrument Co.), and the radioactivity was determined by LSC. The polyurethane plug of each trap was extracted with 30 mL of methanol. Aliquots of the extract were used for radioactivity assessment. Each soil sample (100 g dry soil equiv) was transferred into a 1000 mL centrifuge tube and shaken with 500 mL of 0.01 M $CaCl_2$ solution for 24 h by means of an overhead shaker (25 ± 2 rpm). The tube was centrifuged at 4100 rpm (5000*g*), and the supernatant (desorption solution) was removed. The residual soil was extracted once with 80 mL of methanol and then three times with 80 mL of acetonitrile. For each extraction cycle, the soil was shaken for 30 min and filtered. The extracts were then combined (organic extract). The concentration of radioactivity in the desorption solution and organic extract was determined by LSC. Aliquots of the desorption solution and the organic extract were also analyzed by TLC. After organic extraction, the soil residue was weighed and homogenized. Aliquots of soil and the whole filter were combusted and the resulting $^{14}CO_2$ was measured by LSC (bound residue).

The nonextracted radioactive residues in soil were extracted in a Soxhlet apparatus. A subsample of 10 g of extracted soil was boiled under reflux for 1 h with 40 mL of methanol/water/concentrated HCl (80 + 20 + 0.5) (reflux extract). The volume of extract was measured and aliquots were radioassayed. Aliquots were also analyzed by TLC.

Column Leaching Test. Erlenmeyer flasks were sampled at 0, 2, 7, 14, 28, 42, 56, and 100 days after application. The $^{14}CO_2$ trapped with soda lime was measured in the same manner as for the batch test. The entire soil of one flask was placed into a 5 cm i.d. glass column, which had a glass wool plug and quartz sand at the bottom. The final height of the soil was ∼4.5 cm. Finally, the soil surface was covered by a glass frit.

To simulate a steady flow extraction of the aged soil, 500 mL of 0.01 M $CaCl_2$ solution was added dropwise on top of the soil within a period of 47−48 h. The resulting eluate was collected, the volume was measured, and aliquots were taken for ^{14}C measurement. After elution, the soil was analyzed in the same manner as described above for the batch test.

Determination of Radioactivity. Radioactivity in solution was determined by LSC using Quickszint 401 or Quicksafe A (Zinsser Analytic) scintillation cocktails. The samples were measured in Philips PW 4700, LKB/Wallac Rack Beta 1219, and Beckman LS 6500 instruments.

Radioactivity in soil was determined by combusting 1 g portions of each sample three times in an oxidizer (OX-500, Harvey Instrument Corp.) after the extracted soil was air-dried and milled. The liberated CO_2 was absorbed in a cocktail (Oxysolve C-400, Zinsser Analytic Co.) and measured by LSC. The filter papers used were cut into pieces, which were then pressed to tablets. The radioactivity was determined by combustion via an oxidizer. Oxysolve C-400 was used as absorption and scintillation cocktail.

Chromatographic Methods. The solutions were stored in the refrigerator (3−7 °C) for no more than 2 days before TLC analysis. Aliquots of $CaCl_2$ solutions (100 μL), organic extracts (200 μL), and reflux extracts (200 μL) were applied to TLC without any step of enrichment or conditioning. These aliquots were spotted on TLC plates (silica gel 60 F_{254}, layer thickness = 0.25 mm), 10 mm width bands using an automatic plate spotter (Linomat IV, Camag Co.), and developed with acetonitrile/dichloromethane (50:50, v/v) (system A) and acetonitrile/ethyl acetate/water (70:23:7, v/v) (system B). The R_f values were 0.77 in system A and 0.86 in system B for imidacloprid, 0.56 and 0.86 for imidacloprid-nitrosimine, 0.26 and 0.63 for imidacloprid-olefin, and 0.00 and 0.16 for 6-chloronicotinic acid. Radioactive zones of interest on the TLC plates were measured using a bioimaging analyzer, BAS 2000 (Fuji Co.).

Evaluation. For the batch test, desorption coefficients K_d were obtained from single-dose experiments and calculated from the concentration of imidacloprid in desorption ($CaCl_2$) solution and the concentration of sorbed imidacloprid recovered from organic extract (methanol plus acetonitrile) and reflux extract.

RESULTS AND DISCUSSION

Material Balance and Distribution of Imidacloprid. A radioactivity balance was established for each flask at each sampling interval. The total recovered

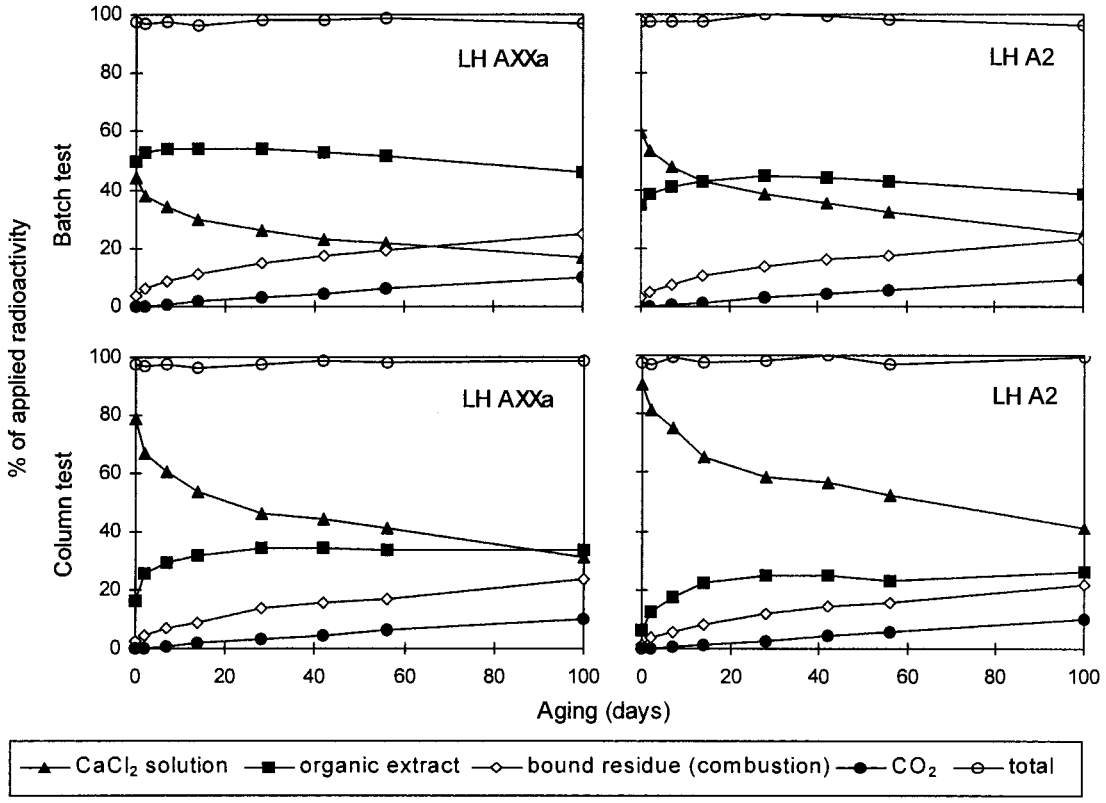

Figure 1. Distribution of radioactivity at each sampling interval in batch test (top) and column test (bottom).

radioactivity expressed as the percent of the applied radioactivity and the distribution of radioactivity in desorption solution (batch test) or eluate (column extraction test), and organic extracts (methanol and acetonitrile), bound residue (combustion), and CO_2 are shown graphically in Figure 1. The total recovery of radioactivity ranged from 96.3 to 100.1% of the applied amount. In both soils, the radioactivity in desorption solutions (batch test) and eluates (column test) decreased with time, whereas radioactivity in bound residues increased with time. The amount of radioactivity in the organic extract increased a little and then decreased slowly in the batch test, whereas it increased during the first two weeks and then became steady in the column test. Mineralization was very similar in both soils and reached ~10% of the application after 100 days.

The amount of radioactivity corresponding to imidacloprid in desorption solutions (batch test) or eluate (column test) and organic extracts and reflux extract was calculated based on analysis by TLC. The reflux extract was determined to be 56.0−88.4% of the bound residues. Graphical presentation of imidacloprid distribution is shown in Figure 2. Because the radioactivity corresponding to metabolites was low (only 15% of ai after 100 days), distribution of the imidacloprid was similar to that of the total radioactivity except for imidacloprid in reflux extract. Increase of imidacloprid in reflux extract was slower than that of bound residue (combustion). The increase of bound imidacloprid and/or its metabolites may indicate that they are irreversibly bound and not bioavailable. On the other hand, the amount of imidacloprid that was extractable with organic solvent was either stable or decreased, although a high amount of imidacloprid was still present in the $CaCl_2$ soluble phase. This likely indicates that the organic extractable imidacloprid is still reversibly bound and bioavailable. The difference in the bioavailability of imidacloprid among $CaCl_2$ solution, organic extract, and bound residue is an interesting theme to be investigated.

Half-lives were calculated by the best fit method using the mathematical procedures described by Timme et al. (1986). The half-lives calculated on the basis of the time course of extractable active ingredient (sum of desorption solution or eluate and organic extract) were ~180 days in both soils, values similar to that of a former study (190 days under aerobic laboratory conditions) (Scholz and Spiteller, 1992).

The microbial biomass decreased to ~80% of the initial biomass after 100 days, that is, from 401 to 307 mg of microbial C/kg of soil dry weight in LH AXXa and from 380 to 307 mg of microbial C/kg of soil dry weight in LH A2. The biomass was also investigated with the soil spiked with imidacloprid; however, no influence was shown on the biomass. The rate of degradation of imidacloprid and its mineralization to CO_2 remained constant during the experiment (Figures 1 and 2), indicating that the microbial biomass responsible for its metabolism also remained constant.

K_d and K_{oc} Values as a Function of Time from Batch Test. The K_d values were calculated on the basis of the amount of imidacloprid desorbed into $CaCl_2$ solution (solution concentration) and that of sorbed imidacloprid (sum of amount in organic extract and reflux extract). The resulting K_d values obtained at day 0 were 4.82 mL/g in soil LH AXXa and 2.24 mL/g in soil LH A2. At the end of incubation (day 100), K_d values increased to 15.6 mL/g in the LH AXXa soil and to 8.6 mL/g in the LH A2 soil.

In general, organic matter in soil is the most important fraction to bind organic chemicals. Therefore, the sorption coefficients (K_d) are frequently correlated with the C content of the soils for a better comparison of the

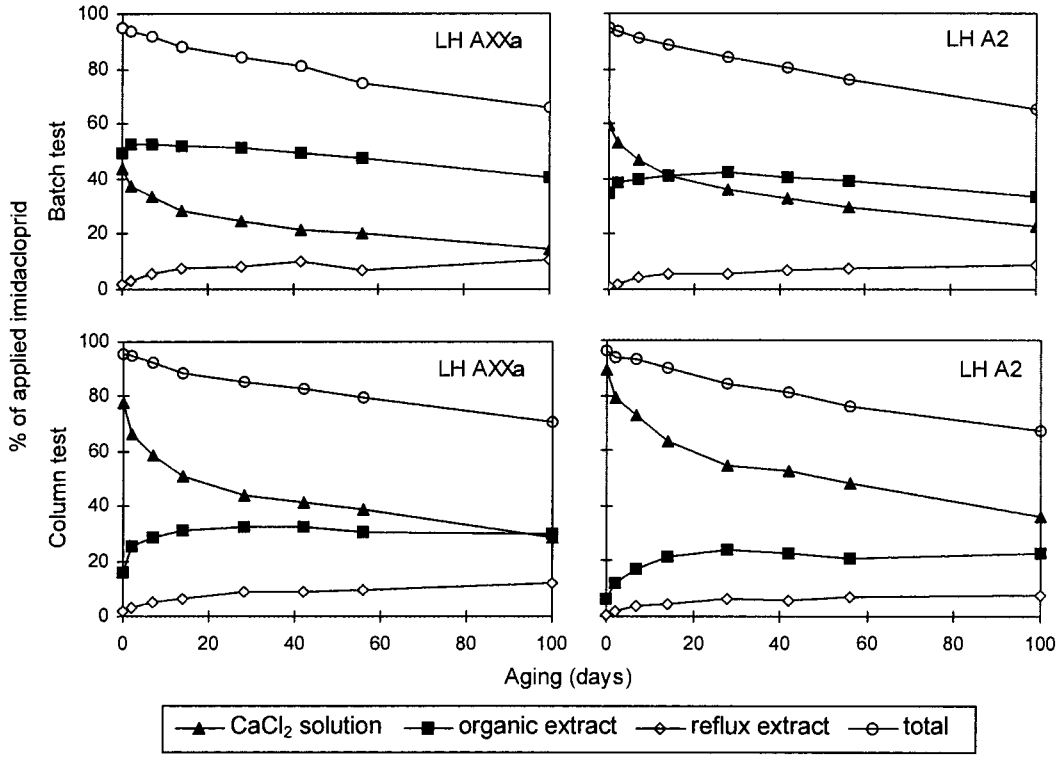

Figure 2. Distribution of imidacloprid at each sampling interval in batch test (top) and column test (bottom).

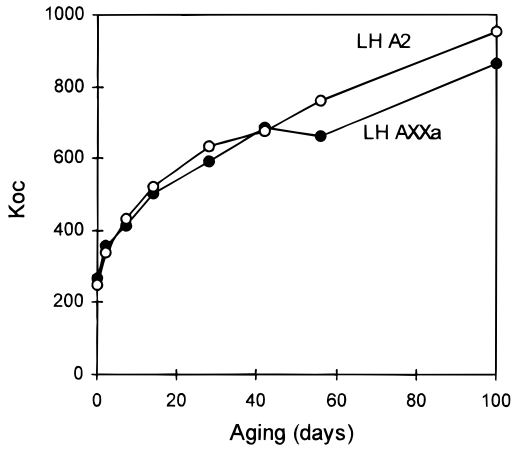

Figure 3. Increase of K_{oc} values with time in batch test.

sorption behavior in different soils (Cox et al., 1998a). Thus, the K_d values were converted into K_{oc} values (Figure 3). Both soils showed similar K_{oc} values and kinetics. The time course of K_{oc} showed a steady increase with time with the most rapid increase in the first two weeks. The values increased by a factors of 3.2 (LH AXXa) to 3.8 (LH A2) by 100 days after application. Cox et al. (1998b), however, found that both organic matter and mineral surface of soil clay can be important components affecting sorption of imidacloprid.

An increase of K_{oc} value is not surprising, because time-dependent sorption processes have been demonstrated for cyanazine and metribuzin (Boesten and Van der Pas, 1983), picloram (McCall and Agin, 1985), linuron, isoxaben, and propyzamide (Walker, 1987), isoproturon (Blair et al., 1990), and metsulfuron-methyl and alachlor (Walker et al., 1995). Similar results were obtained in a recent work (Cox et al., 1998c) in which imidacloprid was aged for 16 weeks in three soils from Minnesota: K_d values increased by a factor of 2.7−2.9 over this aging period. The soils used in this study have higher pH values, lower clay contents, and different organic C contents compared to those used by Cox et al. (1998c). Despite the different characteristics of soils, a time-dependent sorption was observed in this study. The consolidation of sorption/binding of imidacloprid to organic matter and mineral surfaces of soil clay and a steric inclusion of imidacloprid into clay/organic matter complexes are possible explanations of the time-dependent sorption of imidacloprid.

Normalizing K_d values with the organic C content of the soils rendered K_{oc} values of 249−268 (day 0) and 869−960 (day 100). According to the classification of Briggs (1973) for the estimation of the mobility of plant protectants in soil based on K_{oc} values, the mobility potential of imidacloprid changed from low mobility at day 0 to immobile at day 100.

Rouchaud et al. (1996b) showed that recent organic fertilizer treatments slowed imidacloprid, aldicarb, and thiofanox biodegradation in soil. Although the treatments may be expected to enhance microbial activity, the decrease in biodegradation is likely due to the increased sorption of the compounds onto soil.

Potential Bioavailability in Column Leaching Test. The effect of aging on sorption of imidacloprid on the two soils was also determined by using a column leaching test, whereby an increase in sorption constant should retard the leaching of imidacloprid. It is expected that a portion (or concentration) of imidacloprid that was leached out from the aged soil by adding $CaCl_2$ solution should decrease as a function of incubation time.

The ratio of radioactivity recovered from $CaCl_2$ eluates to the total radioactivity recovered from soil (sum of eluate, organic extract, and bound residue) decreased with incubation time by a factor of ~2, whereas radioactivity in the bound residue increased with time (Figure 1). The imidacloprid distributed in the eluates, organic extracts, and reflux extracts from bound resi-

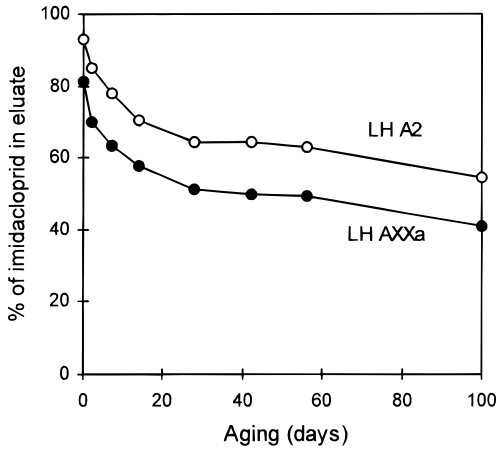

Figure 4. Decrease in the amount of imidacloprid in the eluate as a portion of the total imidacloprid recovered in column leaching test.

dues was determined by TLC. The imidacloprid recovered from eluates decreased with time in both soils (Figure 2). Concomitantly, there was an increase in the imidacloprid recovered in the methanol/HCl reflux extracts. This reflects a change from reversible to more irreversible sorption of imidacloprid with increasing aging time. It was shown that the proportion of imidacloprid recovered from the bound ^{14}C residue increased by a factor of 5−10 after 100 days. The percentage of imidacloprid in eluates compared with the total recovered imidacloprid in eluate, organic extract, and reflux extract decreased from 81.3% (day 0) to 41.0% (day 100) in soil LH AXXa and from 92.8% (day 0) to 54.4% (day 100) in soil LH A2 (Figure 4). The decrease of the proportion of eluted imidacloprid with incubation time reflected the increase of K_{oc} value; that is, the proportion of eluted imidacloprid decreased rapidly during the first two weeks, followed by a steady decrease.

Sorption of Metabolites. Although the maximum amount for single metabolite was only ∼3% of applied radioactivity at 100 days, the four major radioactive zones were cochromatographically correlated with imidacloprid and its known soil metabolites (Scholz and Spiteller, 1992; Klein, 1994), imidacloprid-nitrosimine (M1), imidacloprid-olefin (M2), and 6-chloronicotinic acid (M3), respectively. M2 was detected in both $CaCl_2$ solution and organic extract, for which the K_{oc} value for M2 increased from ∼270 (28 days) to ∼360 (100 days). The amounts of M1 and M3 detected in organic extract at 100 days were ∼2% and ∼0.5% of applied radioactivity, respectively. In the $CaCl_2$ solution, only M1 was detected in LH A2 (0.75% at 100 days), corresponding to a K_{oc} value of ∼1500. M3 was not detected in the $CaCl_2$ solution (<0.5% of application). The sorption coefficient for the radiolabeled metabolites were previously investigated by Cox et al. (1997): imidacloprid-guanidine and imidacloprid-guanidine-olefin showed much higher K_{oc} values (>2000) and imidacloprid-urea lower K_{oc} value (∼200) compared to the imidacloprid. However, these metabolites were not major (<1% of application) in the $CaCl_2$ solutions and the organic extracts of this study, although a few unknown metabolites were found in the reflux extracts.

Conclusions. Decrease of leaching potential of imidacloprid with residence time in soil was shown by two methods, batch and column leaching tests. It is concluded that increasing K_{oc} values are mainly due to change in the sorption process leading to stronger sorption to soil, thereby persistence in soil. These results are further information to explain the gap between the estimated leaching potential of imidacloprid from conventional laboratory experiments and field data. These factors should be taken into account when the potential mobility of imidacloprid in soil is evaluated.

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