Long-Term Fate of 4-Chloroaniline-^{14}C in Soil and Plants under Outdoor Conditions. A Contribution to Terrestrial Ecotoxicology of Chemicals

Dieter Freitag, Irene Scheunert,* Werner Klein, and Friedhelm Korte

4-Chloroaniline-^{14}C was applied to soil in a lysimeter, corresponding to about 1.25 ppm to a depth of 10 cm, and barley was sown. After 20 weeks, a total of 32.8% of the radiocarbon applied was recovered, in soil 32.4%, in plants 0.3%, and in leaching water 0.1%. The radioactivity in soil consisted of 30.8% unextractable residues and 1.6% soluble conversion products; that in plants consisted of 0.24% unextractable residues and 0.03% soluble metabolites (percent of applied ^{14}C). In the second and third year after the application, potatoes and carrots, respectively, were grown; total recoveries were 32.0% and 31.2%, respectively. The soluble radioactive fractions in soil and plants of the two first years contained 4-chloroformanilide (I), 4-chloroacetanilide (II), 4-chloronitrobenzene (III), 4-chloronitrosobenzene (IV), 4,4′-dichloroazoxybenzene (V), and 4,4′-dichloroazobenzene (VI). The radioactive substances unextractable in soil and those in leaching water were partially hydrolyzable and gave 4-chloroaniline.

Chlorinated anilines are known as widespread pollutants in agricultural soils. 4-Chloroaniline is part of the molecule of several herbicides (monolinuron, monuron, buturon) and may be formed from these in the environment. Therefore, the study of the environmental behavior of anilines—degradation and conversion in soil and plants and mobility and uptake of parent compounds as well as of conversion products by plants—is important from the ecotoxicological point of view as well as with respect to the quality of human food of vegetable origin. Numerous data are available on these questions under laboratory conditions, whereas publications on integrated research under actual environmental conditions are scarce.

Due to their high chemical reactivity, anilines undergo a multitude of reactions under environmental conditions, which have been reviewed recently (Parris, 1980). Laboratory experiments with 4-chloroaniline and microorganisms, soil, soil constituents, or enzymes revealed transformation to acylation products (4-chloroformanilide, 4-chloroacetanilide, 4-chloropropionanilide), ring-hydroxylated products (2-amino-5-chlorophenol, 2-acetamido-5-chlorophenol), N-oxidation products [(4-chlorophenyl)hydroxylamine, 4-chloronitrosobenzene, 4-chloronitrobenzene], various condensation products [4,4′-dichloroazobenzene, 4,4′-dichloroazoxybenzene, 1,3-bis(4-chlorophenyl)triazene, 7-chloro-2-amino-3*H*-3-phenoxazin-3-one, 7-chloro-2-amino-3*H*-hydroxyphenoxazine], and to complexes with soil constituents (Bartha et al., 1968; Bordeleau et al., 1972; Bordeleau and Bartha, 1972; Kaufman et al., 1973; Briggs and Walker, 1973; Hsu and Bartha, 1974; Bollag and Russel, 1976; Minard et al., 1977; Engelhardt et al., 1977; Bollag et al., 1978; Corbett et al., 1978; Anagnostopoulos et al., 1978; Corke et al., 1979; Fletcher and Kaufman, 1979; Corbett et al., 1979). The information on transformations in plants is very limited. Van der Trenck et al. (1981) demonstrated the copolymerization of 4-chloroaniline with coniferylalcohol into lignin by model experiments.

With the available knowledge on interactions of relevant factors, data from single-factor laboratory experiments are not sufficient to predict residue levels of chemicals in the environment. Interacting factors are, e.g., metabolism rates of all converting microorganisms present, abiotic reactions, degradation, mineralization, and volatilization of all conversion products formed. Therefore, an attempt was undertaken to examine the environmental relevance of the 4-chloroaniline metabolites reported in literature by a mass-balance study with ^{14}C-labeled 4-chloroaniline and soil–plant systems under fieldlike conditions (lysimeters) for 3 years. The extent of prediction of this methodology to the environment has been discussed on several examples by different groups (Scheunert et al., 1977; Guth, 1981; Jarczyk, 1983).

Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie, D-8042 Neuherberg, Federal Republic of Germany.

MATERIALS AND METHODS

Apparatus. Radioactivity measurements were performed in liquid scintillation counters Tri-Carb 3375 or 3380, Packard. Unextractable radioactivity in plant or soil samples was determined by combustion in an Oxymat-JA 101, Intertechnique, or a Packard oxydizer, Tri-Carb 306.

Column chromatography fractions were collected after passing through a glass scintillator cell from Berthold/Frieseke, Federal Republic of Germany.

Radioactive zones on thin-layer plates were located with a thin-layer scanner from Berthold/Frieseke, Federal Republic of Germany.

For gas–liquid chromatography (GLC), a gas chromatograph, Fractovap GI (Carlo Erba), with FID and a column 1 m × 4 mm packed with 1% XE-60 on Chromosorb W-AW-DMCS, 80–100 mesh, or a column 2 m × 4 mm packed with 1% OV-1 on Chromosorb were used; the carrier gas was nitrogen, 75 mL/min. Gas–liquid chromatography–mass spectrometry (GLC–MS) was performed with a GLC–MS combination LKB 9000 from LKB Produkter, Bromma, Sweden, using the same columns and conditions as for GLC; the carrier gas was helium, 40 mL/min. The mass spectra were compared with those of authentic reference compounds.

Reagents. 4-Chloroaniline-^{14}C was synthesized from benzene-^{14}C (Attar et al., 1973; radiochemical purity 99%; specific activity 2.77 mCi/mmol). Inactive 4-chloroaniline (Fluka, puriss., purity > 99%), 4-chloronitrobenzene (Fluka, puriss., purity >99%), and 4-chloronitrosobenzene (Fluka, pract., purity >97%) were commercially available. 4-Chloroformanilide (Slosson, 1895), 4-chloroacetanilide (Sidgwick and Rubie, 1921), 4,4′-dichloroazobenzene (Burns et al., 1928), and 4,4′-dichloroazoxybenzene (Burns et al., 1928) were synthesized according to well-known chemical methods.

Analysis of soil used was as follows: coarse sand 49.2%; fine sand 27.0%; silt 10.3%; clay 13.5%; humus 1.2%; pH 7.0.

For liquid scintillation counting of extracts and water, a scintillation liquid based on dioxane was used. For counting $^{14}CO_2$ from samples combusted in the Oxymat,

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Table I. Climatic Conditions for Crop Growing after Application of 4-Chloroaniline-^{14}C to Soil

growing period	crop	growing time, weeks	daily max air temp, range of av per week, °C	daily min air temp, range of av per week, °C	rainfall, mm
1	barley	20	13–33	−1–18	442
2	potatoes	14	20–35	5–18	174
3	carrots	23	11–32	5–16	410

a scintillation liquid based on toluene and containing phenethylamine was used; for those combusted in the oxydizer, Carbosorb–Permafluor V (8:12) from Packard was used.

For column chromatography, either silica gel 100 (Merck, Darmstadt) or two different gels (Bio-Beads S-X12, exclusion weight 400, or Merckogel PVA 500, exclusion weight 500) were used.

Thin- or thick-layer chromatography was carried out on plates self-coated with MN silica gel G (Fa. Macherey, Nagel & Co., Federal Republic of Germany) or ready-coated plates (PSC, silica gel without fluorescence indicator, 2 mm, Merck, Darmstadt, or aluminum oxide 60 E). All solvents used were analytical grade.

Application and Cultural Conditions. The experiments were carried out in a plywood box 60 × 60 × 60 cm under outdoor conditions. The bottom of the box contained holes permitting the drainage of excess water that was collected in a metal splash tray. The box was filled with soil and placed into a large pit such that the plants grew at the same level as the surrounding ground. This experimental setup previously had been shown to provide chemical residue data that are within the range limits of those from real field conditions (Scheunert et al., 1977).

In springtime, the soil was fertilized with 6.9 g of calcium ammonium nitrate and 10 g of KH_2PO_4, and 106 summer barley grains were sown (5-cm intervals, 3-cm depth). After 23 days, 50 mg of 4-chloroaniline-^{14}C (corresponding to 1.25 ppm in soil to a depth of 10 cm) were dissolved in a minimum amount of acetone. The solution was mixed with 250 mL of acidified water (0.3% HCl). This solution was applied on the soil between the young plants, incorporated, and leached into the soil by irrigation with 2 L of water. The next day, 250 mL of a solution of 1% $Ca(OH)_2$ in water was poured on the soil, followed by irrigation with 2 L of water. No change in soil pH was detectable after this procedure. The soil was kept at outdoor conditions for 3 years.

In the two following years, the soil was refertilized, and four potato tubers ("Attica", intervals 20 cm, depth 8–10 cm) or 2 rows of carrot seeds ("Nantaise", intervals 20 cm, depth 2–3 cm), respectively, were planted. Climatic conditions for the three vegetation periods are listed in Table I. The leaching water at the bottom of the box was collected during the entire experimental time and checked for radioactivity.

Extraction and Radioactivity Measurements. At harvest time, the crops were separated into various parts. Weeds growing between the crops were collected and analyzed also in order to obtain a complete mass balance. Soil samples were taken at different depths (0–10, 10–20, 20–30, 30–50, or 30–40 cm).

The plant samples were homogenized with an Ultra-Turrax in chloroform and then extracted with chloroform in a Soxhlet for 60 h. Soil samples were also extracted with chloroform in a Soxhlet for 60 h. The radioactivity of plant and soil extracts was determined by counting aliquots of 100–500 μL in a liquid scintillation counter. The unextractable radioactivity in soil and plant samples was determined by combustion of aliquots of the extracted samples (100–300 mg) followed by liquid scintillation counting of the $^{14}CO_2$.

Table II. Gas Chromatographic Retention Times of 4-Chloroaniline and Its Metabolites in Soil and Plants

substance	column with 1% OV-1[a] temp, °C	R_t, min	column with 1% XE-60[a] temp, °C	R_t, min
4-chloroaniline	90	5.6	68	0.6
4-chloroformanilide	180	1.4	140	2.1
4-chloroacetanilide	180	1.7	140	2.6
4-chloronitrobenzene	90	6.8	68	2.5
4-chloronitrosobenzene	90	2.0	68	4.3
4,4′-dichloroazobenzene	180	9.6	140	1.5
4,4′-dichloroazoxybenzene	180	21.7	140	5.8

[a] For further experimental details, see Apparatus.

The plant and soil extracts were evaporated to dryness in a rotary evaporator (condenser −20 °C) and dissolved in a few milliliters of methanol. In order to determine conversion rates, aliquots of the concentrated extracts were applied on self-coated thin-layer plates and developed with dichloromethane. Zones of 1 cm were scraped from the plates, extracted with scintillation liquid based on dioxane in scintillation vials, and counted in a liquid scintillation counter. Three major radioactive fractions were observed in all samples and were determined quantitatively.

Isolation and Identification of Conversion Products. *Conversion Products in Soil.* For isolation of conversion products of 4-chloroaniline in soil, the concentrated soil extracts of all soil layers of the first and second vegetation period were combined. The combined extract was applied on self-coated preparative silica gel layer plates (20 × 20 cm) and chromatographed with dichloromethane. Three major fractions were obtained. Each fraction was extracted with methanol from the silica gel, concentrated, and rechromatographed on self-coated silica gel layer plates with ethyl acetate to remove the major part of biological soil coextractives. The front fraction (3) was then separated and repurified several times on ready-coated TLC plates with hexane; the metabolites V and VI were obtained and identified by GLC and GLC–MS and authentic reference compounds.

Fraction 2 was separated and purified on ready-coated TLC plates with different solvents [hexane, benzene, dichloromethane, benzene–ethyl acetate (3:1), and ethyl acetate] to obtain the metabolites III and IV, which were identified by GLC and GLC–MS and authentic reference compounds.

The polar fraction 1 was concentrated and applied on a gel permeation chromatography column with Merckogel PVA 500. After elution of the radioactive substances with acetone, they were purified by repeated TLC on ready-coated plates with various solvents (dichloromethane; benzene–ethyl acetate, 3:1; ethyl acetate). Final purification and separation of the metabolites I and II were performed on an aluminum oxide TLC plate with hexane–ethyl acetate, 1:1, as the solvent. They were identified by GLC and GLC–MS using authentic reference compounds. Further radioactive products in the polar fraction 1 were present but could not be identified. GLC retention times for 4-chloroaniline and metabolites I–VI are listed in Table II.

The unextractable ^{14}C residue in soil was characterized by refluxing an aliquot of the extracted soil in 50% NaOH

Table III. Recovery of Radioactivity in the Soil-Plant System, One to Three Growing Periods after Application of 4-Chloroaniline-^{14}C to Soil under Outdoor Conditions (in Percent of Initially Applied Radioactivity)

sample	after 1 growing season	after 2 growing seasons	after 3 growing seasons
soil, 0–10-cm depth	29.96	23.15	24.40
soil, 10–20-cm depth	1.51	1.85	3.92
soil, 20–30-cm depth	0.43	1.88	0.88
soil, 30–40-cm depth	0.46	4.39	1.04
soil, total	32.36	31.27	30.24
plants of 1st growing period (barley)	0.24	0.24	0.24
plants of 1st growing period (weeds)	0.03	0.03	0.03
leaching water of 1st growing period	0.15	0.15	0.15
plants of 2nd growing period (potatoes)		0.04	0.04
plants of 2nd growing period (weeds)		<0.01	<0.01
leaching water of 2nd growing period		0.30	0.30
plants of 3rd growing period (carrots)			0.02
plants of 3rd growing period (weeds)			<0.01
leaching water of 3rd growing period			0.21
sum of recovered residues	32.78	32.03	31.23
loss to the atmosphere	67.22	67.97	68.77

for 3 h. After centrifugation, half of the radioactivity bound in the sample was detected in the solution, and 10% could be extracted from the solution with ether. After purification on ready-coated TLC plates (solvent: dichloromethane), this substance was found to be 4-chloroaniline by GLC and GLC–MS.

The radioactive products in the soil after three vegetation periods were not isolated but characterized by one-dimensional comparative TLC. The chromatograms were very similar to those of the soils from the previous years.

Conversion Products in Plants. Since the plants contained only very low amounts of radioactive substances, the concentrated extracts of all plant roots and tops of the first and second vegetation period were combined and chromatographed 2 times in a gel permeation column filled with Bio-Beads S-X-12 and with benzene as the solvent. A radioactive fraction was obtained that was largely free of higher molecular weight plant coextractives. This fraction was concentrated and separated on a silica gel column with solvents of increasing polarity [*n*-hexane, *n*-hexane–ethyl acetate (5:1), benzene–ethyl acetate (3:1), and ethyl acetate]. Three major radioactive fractions were obtained, which were further purified like the corresponding soil extract fractions; the metabolites identified by GLC and GLC–MS and authentic reference compounds (I–VI) were identical with those isolated from soil.

The radioactive products in the plants of the third growing period (carrots) were not isolated but characterized by TLC. The chromatograms were very similar to those of the barley and potato extracts.

Conversion Products in Leaching Water. The radioactivity detected in the leaching water collected at the bottom of the box was not extractable from water by any organic solvent. Therefore, an aliquot of the water was concentrated in a rotary evaporator and then freeze-dried. The residue was dissolved in 50% NaOH and refluxed for 3 h. Then the solution was subjected to steam distillation. A total of 16% of the radioactivity present in the water could be detected in the distillate, which was extracted with dichloromethane. The radioactive substance in the concentrated dichloromethane extract was purified by TLC (solvent: dichloromethane) and identified as 4-chloroaniline by GLC and GLC–MS; thus, 16% of the radioactivity in leaching water was conjugated 4-chloroaniline.

RESULTS

Mass Balance Studies. The fate of 4-chloroaniline-^{14}C, one to three vegetation periods after application to soil in a concentration corresponding to about 1.25 ppm to a depth of 10 cm under outdoor conditions, is shown in Table III. The table shows that the total recovery is low, and that most of the radiocarbon recovered has remained at the application site, i.e., the upper soil layer. Uptake by plants, migration into soil layers deeper than 10 cm, and leaching into water at the bottom of the box were low, also. It may be concluded that most of the applied radioactivity had been lost to the atmosphere. Previous short-term tests in a closed laboratory ecosystem have shown that the major part of this loss is not due to volatilization of 4-chloroaniline or conversion products but to mineralization to carbon dioxide (Kloskowski et al., 1981). In the second and third growing season, additional residue losses were very small (0.8% each year) as compared to the first year (67.2%). The bioavailability of residues to plants decreased with time, whereas the amount in the leaching water reached a maximum in the second year.

Quantitative Determination of Conversion Products. Table IV shows the concentrations of extracted and unextractable residues as well as of total residues in plants and soil for the first growing period.

It is evident from Table IV that the total residues are smallest in the edible portion, the grains. By far the major portion of residues in all samples is unextractable: in soil 91–95% of residues present; in plants 74–91% of residues present. On the basis of applied radioactivity, this corresponds to 30.8% unextractable residues in soil and 0.24% unextractable residues in plants. This is in agreement with literature where high binding rates of 4-chloroaniline and other anilines to soil constituents have been reported (Hsu and Bartha, 1974; Bollag et al., 1978). The fraction of soluble radioactive substances was small; for soil, it constituted 1.6% of the radioactivity applied and for plants 0.03%.

Tables V and VI give respective data for the second and third year. In the potato plants, also, the smallest total residue is in the edible part, the peeled tuber. The carrot plants contained very low residues in tops as well as in roots. The data for all samples show low extraction rates, like in the first year.

Isolation and Identification of Conversion Products. For the *plant and soil extracts of the first and second year*, the radioactive substances in the TLC fractions shown in Tables IV and V were isolated and purified by chromatographic methods. Figure 1 presents the conversion products isolated and identified both from soil and plants.

TLC fraction 1 contained, besides unidentified highly polar compounds, 4-chloroformanilide (I) and 4-chloroacetanilide (II). TLC fraction 2 consisted of a mixture of 4-chloronitrobenzene (III) and 4-chloronitrosobenzene (IV), and TLC fraction 3 consisted of 4,4′-dichloroazoxybenzene (V) and 4,4′-dichloroazobenzene (VI). It is remarkable that neither in soil nor in plants any free unchanged 4-chloroaniline could be detected.

No attempts were made to isolate and identify the radioactive residues in the *samples of the third year.*

Table IV. Radioactive Residues in Soil and Barley Plants, One Growing Period after Application of 4-Chloroaniline-^{14}C to Soil (in μg/g equiv to 4-Chloroaniline; for Soil Based on Air-Dry Weight and for Plants Based on Fresh Weight)

sample	unextractable residues	extractable residues for TLC fractions[a]			total residues
		1, R_f 0-0.12 (metabolites I, II, and unidentified)	2, R_f 0.29-0.65 (metabolites III and IV)	3, R_f 0.71-0.94 (metabolites V and VI)	
soil, 0-10-cm depth	0.380	0.015	0.002	0.004	0.401
soil, 10-20-cm depth	0.018	0.001	<0.001	<0.001	0.020
soil, 20-30-cm depth	0.006	<0.001	<0.001	<0.001	0.006
soil, 30-50-cm depth	0.003	<0.001	<0.001	<0.001	0.003
barley roots	1.114	0.086	0.005	0.023	1.228
barley straw	0.576	0.057	0.009	0.002	0.644
barley husks	0.051	0.011	0.001	0.002	0.065
barley grains	0.010	0.002	<0.001	<0.001	0.013

[a] Solvent: dichloromethane.

Table V. Radioactive Residues in Soil and Potato Plants, Two Growing Periods after Application of 4-Chloroaniline-^{14}C to Soil (in μg/g equiv to 4-Chloroaniline; for Soil Based on Air-Dry Weight and for Plants Based on Fresh Weight)

sample	unextractable residues	extractable residues for TLC fractions[a]			total residues
		1, R_f 0-0.12 (metabolites I, II, and unidentified)	2, R_f 0.29-0.65 (metabolites III and IV)	3, R_f 0.71-0.94 (metabolites V and VI)	
soil, 0-10-cm depth	0.289	0.018	0.003	0.006	0.316
soil, 10-20-cm depth	0.022	0.002	0.001	<0.001	0.025
soil, 20-30-cm depth	0.023	0.002	0.001	<0.001	0.026
soil, 30-50-cm depth	0.024	0.004	0.001	0.001	0.030
potato roots	0.088	0.042	0.008	0.003	0.141
potato haulm	0.100	0.037	0.007	0.001	0.145
potato peels	0.015	0.002	<0.001	<0.001	0.017
potato tubers, peeled	0.002	0.001	<0.001	<0.001	0.003

[a] Solvent: dichloromethane.

Table VI. Radioactive Residues in Soil and Carrot Plants, Three Growing Periods after Application of 4-Chloroaniline-^{14}C to Soil (in μg/g equiv to 4-Chloroaniline; for Soil Based on Air-Dry Weight and for Plants Based on Fresh Weight)

sample	unextractable residues	extractable residues for TLC fractions[a]			total residues
		1, R_f 0-0.12 (metabolites I, II, and unidentified)	2, R_f 0.29-0.65 (metabolites III and IV)	3, R_f 0.71-0.94 (metabolites V and VI)	
soil, 0-10-cm depth	0.266	0.030	0.001	0.008	0.305
soil, 10-20-cm depth	0.044	0.004	<0.001	0.001	0.049
soil, 20-30-cm depth	0.010	0.001	<0.001	<0.001	0.011
soil, 30-40-cm depth	0.012	0.001	<0.001	<0.001	0.013
carrot tops	0.008	0.002	0.001	0.001	0.012
carrot roots	0.002	0.001	<0.001	0.001	0.004

[a] Solvent: dichloromethane.

However, since the TLC patterns were very similar to those of the previous years, it is probable that the conversion products were qualitatively the same as those from the first and second year.

The *unextractable residue fraction in soil* was partly hydrolyzable by strong alkali and yielded 4-chloroaniline (10% of unextractable residue or 3.1% of applied ^{14}C).

The radioactivity in the *leaching water* consisted of fully water soluble compounds. Part of them (16%) were hydrolyzable to 4-chloroaniline by strong alkali treatment.

DISCUSSION

The two major pathways of 4-chloroaniline disappearance in the soil–plant system lead to total degradation (mineralization) and incorporation into soil or plant macromolecules. Free 4-chloroaniline was not detectable after one growing season (20 weeks), neither in plants nor in soil.

According to our knowledge, no metabolites of 4-chloroaniline in plants have been isolated and identified thus far. The metabolites identified in this study, which occur in small concentrations, seem to play only a minor role in the residue behavior of 4-chloroaniline in the environment. The same applies to the soluble soil metabolites identified. Although, after hydrolysis of residues bound in soil or of water-soluble residues in leaching water, only 4-chloroaniline could be identified, the soluble conversion products isolated also might be intermediates in the formation of unextractable residues. Due to their low concentrations and their chemical instability, their identification in unextractable residues after alkali hydrolysis probably will not be possible.

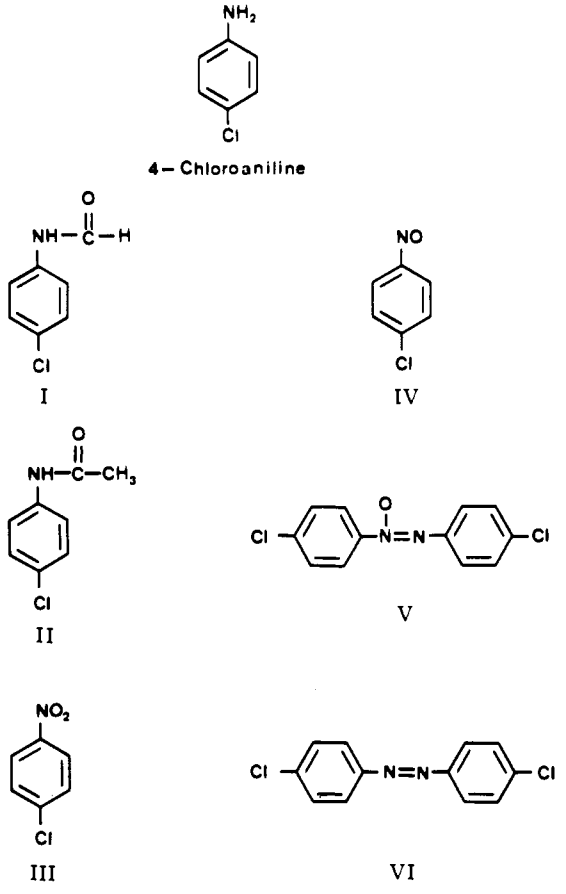

Figure 1. Conversion products of 4-chloroaniline isolated from soil and plants under environmental conditions.

Out of the metabolites identified from laboratory experiments and reported in literature, in this outdoor study acylation products, N-oxidation products, condensation products, and products bound to natural macromolecules were detected. One group of metabolites reported in the literature could not be detected under outdoor conditions: ring- or N-hydroxylated compounds (phenols, hydroxylamines) (detection limit: 0.1% of the total residue present in the respective sample). This gap might be due to the chemical instability of these substances, resulting in short life spans in outdoor samples and in susceptibility to decomposition during sample analysis which is more complex and time consuming for environmental samples in the ng/g range than for laboratory samples with higher concentrations.

Out of the condensation products reported, only 4,4′-dichloroazobenzene and 4,4′-dichloroazoxybenzene could be identified in outdoor soil and plant samples; the formation of a triazene or of a phenoxazine was not observed. The formation of these products was reported to occur only at concentrations that were by far higher (80–100 ppm in the culture medium; Engelhardt et al., 1977; Minard et al., 1977) than those applied in this outdoor study; thus, these condensation products probably do not have any environmental significance.

It may be concluded that 4-chloroaniline in a free unchanged form is not persistent in soil; it is subjected to various acylation and oxidation reactions and finally to total biodegradation and to incorporation into natural soil or plant constituents. Those 4-chloroaniline molecules or conversion products that have become part of the molecule of a natural soil or plant constituent will be at least as persistent as the respective natural molecule (e.g., humic acid or lignin).

Since the conversion rate of 4-chloroaniline to soil-bound residues is very high (>90% of total residues present in soil after one growing period), this conversion process apparently is so fast that only small amounts of parent compound are able to migrate into deeper soil layers. Therefore, soil mobility studies in the laboratory, which normally have much higher leaching rates and shorter time spans than those under environmental conditions, are not suitable to predict the long-term environmental behavior of this chemical.

Registry No. 4-Chloroaniline, 106-47-8; 4-chloroformanilide, 2617-79-0; 4-chloroacetanilide, 539-03-7; 4-chloronitrobenzene, 100-00-5; 4-chloronitrosobenzene, 932-98-9; 4,4′-dichloroazoxybenzene, 614-26-6; 4,4′-dichloroazobenzene, 1602-00-2.

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