do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Registry No. Fluvalinate, 69409-94-5; chlorpyrifos, 2921-88-2; captan, 133-06-2; chlorothalonil, 1897-45-6.

LITERATURE CITED

Adamis, Z.; Antal, A.; Fuzesi, I.; Molnar, J.; Nagy, L.; Susan, M. Occupational exposure to organophosphorus insecticides and synthetic pyrethroid. *Int. Arch. Occup. Environ. Health* **1985**, *56*, 299–305.

Gehan, E. A.; George, S. L. Estimation of human body surface area from height and weight. *Cancer Chemother. Rep.* **1970**, *54*(4), 225–235.

Nigg, H. N.; Stamper, J. H. Exposure of spray applicators and mixer-loaders to chlorobenzilate miticide in Florida citrus groves. *Arch. Environ. Contam. Toxicol.* **1983**, *12*, 477–487.

Nigg, H. N.; Stamper, J. H.; Queen, R. M. Dicofol exposure to Florida citrus applicators: effects of protective clothing. *Arch. Environ. Contam. Toxicol.* **1986**, *15*, 121–134.

U.S. Environmental Protection Agency, Washington, D.C. Development of statistical distributions or ranges of standard factors used in exposure assessments. No. 600-8-85-010. Office of Research and Development, 1985.

Wojeck, G. A.; Price, J. F.; Nigg, H. N.; Stamper, J. H. Worker exposure to paraquat and diquat. *Arch. Environ. Contam. Toxicol.* **1983**, *12*, 65–70.

Leaching of Conversion Products of [14C]Buturon from Soil during 12 Years after Application

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14C-Labeled buturon [N-(4-chlorophenyl)-N'-methyl-N'-isobutynylurea] was applied to wheat and soil in lysimeters under outdoor conditions. In one approach, labeling was uniformly in the ring; application was in two successive years (2.98 kg/ha each). In a second approach, labeling was at the N'-methyl group; application was once (2 kg/ha). Leached water containing radioactivity was collected for 12 years. In water from the experiment with ring-labeled [14C]buturon, 14C calculated as buturon after 12 years amounted to 2.14% of total 14C applied, with a concentration peak in the second year. After 12 years, the radioactivity in water comprised 4-chloroaniline, methyl N-(4-chlorophenyl)carbamate, and conjugated 4-chloroaniline, as identified by gas chromatography/mass spectrometry. In water from the experiment with [N'-methyl-14C]buturon, 14C after 12 years was 1.66% of 14C applied, with decreasing leaching rates after 6 years. No chlorinated radioactive products were detected, indicating that the N'-methyl group was incorporated into natural substances.

The phenylurea herbicide buturon [N-(4-chlorophenyl)-N'-methyl-N'-isobutynylurea] is widely used since 1962 under the commercial name of Eptapur. It is classified among the less persistent pesticides. Various studies report its rapid degradability and tendency to form conversion products in the terrestrial environment. Studies on its abiotic transformation dealt with its conversion by UV irradiation (Kotzias et al., 1973, 1974). Studies with the fungus *Rhizopus japonicus* reported an elimination of the isobutynyl group from the molecule (Wallnöfer et al., 1973). The metabolism in algae, *Chlorella fusca* var. rubra (Tsorbatzoudi et al., 1976), was also examined. In plants and soil, numerous conversion products were identified (Schuphan and Ebing, 1977; Ebing and Schuphan, 1979; Haque et al., 1976, 1977; Constenla et al., 1984).

In recent years, the occurrence of pesticide residues in groundwater has become a topic of major concern (Milde and Friesel, 1987). Among the pesticides detected in trace amounts in groundwater, there were also phenylurea herbicides; e.g., isoproturon was detected in the raw water of some German drinking water production plants (Industrieverband Pflanzenschutz e.V., 1987). In order to test the leaching behavior of buturon, a 40 kg/ha dose was applied to a lysimeter, 1.35-m height and 1-m² diameter (Herzel and Schmidt, 1979). After 4 months, traces of buturon were detected in the leachate (mean concentration 55 ng/L). Although the results of this study cannot be extrapolated to agricultural field conditions due to the very high application rate, they show the potential of this pesticide to be vertically mobile. The leaching behavior of conversion products was not studied.

Due to their higher water solubility, the leaching potential of polar conversion products of pesticides should be higher than that of parent compounds. However, information on the leaching of pesticide metabolites is very limited. In a lysimeter study with [14C]atrazine, seven conversion products were identified in leachate in addition to the parent compound (Schiavon, 1988). In the present study, both ring-labeled and N'-methyl-labeled [14C]buturon were applied to soils in different lysimeters, in order to study the long-term leaching behavior of conversion products formed in soil. Ring-labeled [14C]buturon was applied under the viewpoint of persistence. Buturon labeled at the N'-methyl group was applied to examine to what degree this functional group is biologically available or is incorporated into natural soil constituents. The results obtained from the analysis of soil and leachate of the experiment with ring-labeled buturon after one growing period have been published previously (Haque et al., 1977). Three months after application, about 50% of the applied radiocarbon was recovered. Of the radioactivity recovered in soil, 50% was extractable. Between one- and two-thirds

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of the radioactivity extractable from soil was unchanged buturon; eight conversion products were identified. In leached water, three conversion products were isolated (Haque et al., 1977). These were 4-chloroformanilide, methyl N-(4-chlorophenyl)-N-methylcarbamate, and an N-(hydroxyphenyl)-N'-methyl-N'-isobutynylurea. The same soil was reexamined after 6.5 years (Constenla et al., 1984). In soil extracts, three conversion products including 4-chloroaniline were identified. Bound residues were characterized by their association with certain soil fractions.

The present study reports the results of analysis of leachate of both experiments after 12 years.

MATERIALS AND METHODS

Apparatus. Determination of radioactivity in liquid samples was performed in liquid scintillation counters, Betaszint 5000/300 or Betaszint 8000, with external standardization, from Berthold. Combustion of solid radioactive samples was done with a Packard sample oxidizer, Tri-Carb 306. Radioactivity on thin-layer chromatograms was localized with a thin-layer scanner from Berthold-Frieseke. For high-pressure liquid chromatography (HPLC), the following system was used: pump, Gynkotek Model 300B; gradient former, Model 250B; UV detector, Knauer variable-wavelength monitor; ^{14}C detector, Berthold LB 504.

Gas chromatography (GC) was performed with a Hewlett-Packard 5880A or a Hewlett-Packard 5790A with flame ionization detectors (FID). For the identification of isolated conversion products, two gas chromatography/mass spectrometry (GC/MS) systems were used: (a) Finnigan system 8222; (b) Hewlett-Packard 5995A.

Reagents. Ring-labeled [^{14}C]buturon was synthesized by Attar et al. (1973) (radiochemical purity 99.2%, specific activity 5 mCi/mmol); for further details, see Haque et al. (1977). [N'-methyl-^{14}C]Buturon was commercially available (specific activity 5.9 mCi/mmol, purity 95%). The origin of reference compounds for the conversion products was as given by Haque et al. (1977).

The soil used was a regional sandy soil. The analysis was as follows: 76.2% sand, 10.3% parasilt, 13.5% clay; 1.2% organic matter; pH 7.0.

Radioactivity of aqueous samples was measured in Hydroluma (Baker), that of extracts in organic solvents in a cocktail consisting of 8 g of Permablend (Packard), 100 g of naphthalene, 100 mL of methanol, and 800 mL of 1,4-dioxane (all from Merck). The radioactivity in solid samples was combusted; ^{14}CO$_2$ was absorbed and measured in a cocktail containing 12% Permafluor (Packard) and 8% Carbosorb (Packard).

For thin-layer chromatography (TLC), precoated silica plates (Merck) with a fluorescence indicator at 254 nm were used; they were cleaned by running in methanol and then activated. For HPLC, the stainless steel precolumn was filled with Perisorb RP 18, 30–40 μm (Merck); the stainless steel main column was 220 × 4.6 mm and packed with Perisorb RP, 18.5 μm (Merck). The mobile phase of 70% acetonitrile and 30% water had a flow rate of 0.7 mL/min.

The GC and GC/MS were equipped with 15 m × 0.32 mm capillary columns, Durabond DB 5, 0.25-μm film thickness.

Procedure. *Setup of Experiments and Application of* [^{14}C]*Buturon.* The experiments were carried out under outdoor conditions in boxes 60 × 60 × 70 cm, constructed from water-resistant plywood, filled with about 160 kg of soil, and placed in a large pit so that the surface of the soil was at the same level as the surrounding ground. The base

of the boxes contained holes to permit the drainage of excess water that was collected in a metal splash tray. Further details of the experimental setup have been reported previously (Haque et al., 1977).

In each of the first and second years of the experiment, 108.9 mg of ring-labeled [^{14}C]buturon was sprayed on winter or summer wheat, respectively, and on soil as an aqueous formulation. Each dose corresponded to 2.98 kg of active ingredient/ha; this was about twice the dose recommended for winter wheat in the field. For further details, see Haque et al. (1977). No further buturon treatment was carried out in the following years. In the third year, potatoes were grown in the same soil; in the next years, the soil was left fallow. Similarly, [N'-methyl-^{14}C]buturon was sprayed on winter wheat in the first year only (2 kg/ha, corresponding to 1.5-fold of the dose recommended in agriculture). In the following year, sugar beets were grown in the same soil without buturon reapplication. In the next years, the soil was left fallow. Precipitation was recorded throughout the experimental period. The leached water at the bottom of the boxes was collected for about 12 years, in 10- or 25-L portions at irregular intervals, dependent on the rate of precipitations. All portions were assayed for radioactivity. In cases when leachate was not collected immediately, further microbial changes, in addition to those occurring in the soil during past years, were not observed. This was confirmed by comparing total radioactivity, extractability of ^{14}C, and thin-layer chromatograms of immediately collected samples with those of samples kept in the tray for several days.

Preparation of Leachate. Leached water collected after 12 years was purified by running through glass wool and paper filters. Volume was reduced on a Rotavap with a cooled condensor (−20 °C). The concentrated water was extracted three times with 0.2 L of dichloromethane/L of water.

The extract from ring-labeled buturon was subjected to TLC in hexane/benzene/acetone (7:3:1). Radioactivity was located at R_f 0.37–0.54. In order to desorb the radioactive substances, the silica gel was scraped off, shaken vigorously with solvent, and sedimentated in a cooling centrifuge. The eluate was rechromatographed in toluene/chloroform/acetone (8:5:7), where a radioactive zone was at R_f 0.04–0.13. It was eluted and subjected to GC and GC/MS.

To hydrolyze organic conjugates and polymers, the extracted water was incubated with 6 N HCl at 100 °C for 6 h and extracted again. This extract was subjected directly to HPLC. The relative portions of several radioactive compounds in one sample were measured by the ^{14}C detector. This was also used to check whether the sample included no additional radioactive compounds. One fraction was collected containing 83.1% of the radioactivity in the extract. The radioactive substance was assayed by GC/MS. Of the radioactivity in the extract, 14% belonged to several other compounds that remained unidentified because of very low concentrations.

During TLC of the extract of [N'-methyl-^{14}C]buturon with various solvent systems, radioactivity was spread between the chromatogram's origin and the solvent front. Radioactivity was present in zones of different colors, fluorescent ones and nonfluorescent ones. For elution, the chromatogram was divided into zones of 1 cm. Of the 18 eluates, 7 were subjected to HPLC, but no distinct radioactive fractions could be separated.

After extraction, the water of the experiment with [N'-methyl-^{14}C]buturon was also incubated with 6 N HCl. The extract of the hydrolyzed aqueous solution was sub-

Table I. ^{14}C in Leachate after Application of Ring-Labeled [^{14}C]Buturon to Wheat/Soil (Application Rate 2 × 2.98 kg/ha)

sampling period (yr since 1st applicn)	amt ^{14}C in leachate,[a] μg	^{14}C in leachate/ yr,[b] %	cum ^{14}C in leachate,[b] %
1st	465	0.21	0.21
2nd[c]	1588	0.72	0.93
3rd	267	0.12	1.05
4th	310	0.14	1.19
5th	486	0.22	1.41
6th	475	0.22	1.63
7th	395	0.18	1.81
8th	278	0.13	1.94
9th	153	0.07	2.01
10th	118	0.05	2.06
11th	98	0.04	2.10
12th	76	0.04	2.14

[a] Micrograms calculated as buturon. [b] Percent of total ^{14}C applied in both years. [c] Second application 13 months after first application.

Table II. ^{14}C in Leachate after Application of [N'-methyl-^{14}C]Buturon to Wheat/Soil (Application Rate 2 kg/ha)

sampling period (yr since applicn)	amt ^{14}C in leachate,[a] μg	^{14}C in leachate/yr,[b] %	cum ^{14}C in leachate,[b] %
1st	219	0.20	0.20
2nd	223	0.21	0.41
3rd	263	0.24	0.65
4th	209	0.19	0.84
5th	252	0.23	1.07
6th	234	0.22	1.29
7th	121	0.11	1.40
8th	92	0.08	1.48
9th	64	0.06	1.54
10th	54	0.05	1.59
11th	51	0.05	1.64
12th	20	0.02	1.66

[a] Micrograms calculated as buturon. [b] Percent of total ^{14}C applied.

jected to TLC in toluene/chloroform/acetone (8:5:7). Again, radioactivity was spread between R_f 0–1. The plate was separated into nine zones of 2 cm. GC/MS analysis of the eluates furnished no proof of chlorinated compounds.

Identification of Conversion Products. The identity of compounds was confirmed by comparing the GC retention times with those of authentic compounds, cochromatography, and comparison of mass spectra of samples with those of authentic substances.

The GC operating conditions were as follows: 5 min at 50 °C, 50–260 °C at 8 °C/min, 20 min at 260 °C. Carrier gas was H$_2$ (20 mL/min) for the first GC and N$_2$ (2 mL/min) for the second one. Burning gases were H$_2$ (50 mL/min) and synthetic air (400 mL/min). For GC/MS, carrier gas was helium (2 mL/min). Mass spectra were recorded at 70 eV.

RESULTS AND DISCUSSION

Radioactivity Measurements. The values obtained by the measurement of radioactivity in water leached from each experiment during 12 years are summarized in Tables I and II.

In the case of ring-labeled buturon (Table I), radioactivity in water amounted, after 12 years, to 2.14% of total ^{14}C applied. The lower amounts of radioactivity washed out in years 3 and 4 (Table I) obviously are due to low rainfall rates and, consequently, lower volumes of water collected in these years. Apart from this observation, correlation between the amounts of rainfall or volumes of water collected and the amounts of leached radioactivity

Table III. Conversion Products of [^{14}C]Buturon in Leachate 12 Years after Application to Wheat/Soil

compound	ratio of radioact (% in orig leachate)	ng/L[a]
4-chloroaniline	14.8	53.1
methyl N-(4-chlorophenyl)carbamate	2.9	10.4
conjugated 4-chloroaniline	9.5	34.1

[a] Nanograms calculated as buturon.

is very poor. The maximum of radioactivity in leachate observed in year 2 after the second buturon application is due to a maximum ^{14}C concentration in water, not to a maximum of volume of water collected. The radioactivity in leachate, both in terms of absolute amounts and of concentration, decreases continuously from this moment until the end of the experiment. Since the radioactivity in water is not due to one chemical compound only but to a mixture of conversion products formed in soil, leaching pattern of ^{14}C depends on formation site and formation rate of each conversion product in soil, on physicochemical properties of each conversion product, and on the ratios between the mixture components. Thus, leaching rates are not predictable from precipitation rates alone.

In the case of [N'-methyl-^{14}C]buturon, radioactivity after 12 years reached a value of 1.66% of ^{14}C applied (Table II). No correlation between the amounts of ^{14}C leached within each year and rates of precipitations or volumes of water was observed. The amounts of ^{14}C leached per year remained more or less constant during the first 6 years and then decreased. It is assumed that the amounts of soluble and leachable products containing ^{14}C from the methyl group of buturon decreased slowly in soil after a 6-year period.

Identification of Conversion Products after 12 Years. From the experiment with *ring-labeled buturon*, 23.3% of the radioactivity present in water was extractable with dichloromethane. In this extract, 4-chloroaniline and methyl N-(4-chlorophenyl)carbamate were identified by GC/MS. Their quantitative ratio was 5.2:1. Both substances are known as conversion products of buturon in soil (Haque et al., 1977). 4-Chloroaniline had been detected also in soil 6.5 years after buturon application (Constenla et al., 1984). Hydroxylated and/or methoxylated derivatives of 4-chloroaniline had also been identified in soil. It is probable that they still existed in soil after 12 years but were too low in concentration to be identified in leachate. So far, methyl N-(4-chlorophenyl)carbamate was not considered to be persistent in soil. Possibly it existed as a reversible bound residue for years and was thus protected from intensive degradation. Its formation as an artefact (Haque et al., 1976, 1977) can be excluded as the material was never heated above 30 °C. Many examples for the release of bound pesticide residues in soil by various biotic processes are known (Fuhremann and Lichtenstein, 1978; Khan, 1980; Führ and Mittelstaedt, 1980; Khan and Iverson, 1981, 1982).

The existence of other radioactive compounds in the extract could be demonstrated; however, levels were too low for identification.

After extraction, the water was subjected to hydrolysis and extracted again. The extract contained 11.4% of the radioactivity in the original leachate. According to retention time in HPLC it was assumed that the extract contained 4-chloroaniline (83.1% of radioactivity in the extract). This was proved by GC/MS.

Table III shows the identified conversion products of [^{14}C]buturon and their ratios and concentrations in original leached water. All of them have in common the total
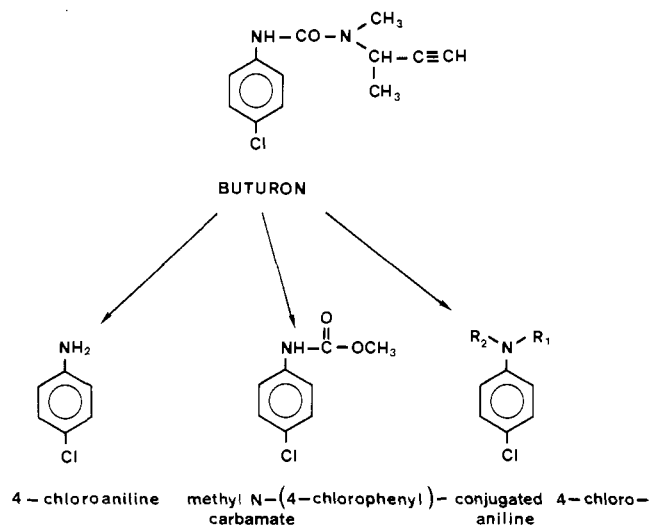
Figure 1. Conversion products of buturon found in leached water 12 years after application of buturon to soil.

elimination of the side chain. N-Dealkylation and N-dealkoxylation are main detoxification mechanisms of phenylurea herbicides. The remaining radioactivity in the water not listed in this table could not be identified. Figure 1 shows the identified conversion products of buturon in leached water. It can be seen that these products are not identical with those identified in leachate after one growing period [4-chloroformanilide, methyl N-(4-chlorophenyl)-N-methylcarbamate, and an N-(hydroxyphenyl)-N'-methyl-N'-isobutynylurea; Haque et al., 1977] but are products of further degradation.

4-Chloroaniline tends to form conjugated and bound residues in soil. 4-Chloroaniline applied to a similar lysimeter experiment formed high amounts of bound residues in soil; 4-chloroaniline conjugated with water-soluble soil constituents was washed out into water within 3.5 years (Freitag et al., 1984).

From the experiment with [N'-methyl-¹⁴C]buturon, 33% of the radioactivity present in leachate was extractable with dichloromethane. In none of the TLC eluates nor HPLC fractions were chlorinated compounds found by GC/MS. Thus, it can be concluded that all or at least most of the ¹⁴C in the extract was incorporated into unchlorinated natural substances. The same applied to a second extract obtained after hydrolysis, which contained 7.6% of total ¹⁴C present in water.

CONCLUSION

The behavior of the radioactive material in the extracts of leached water from the experiment with [¹⁴C]buturon labeled at the side chain indicates a large number of radioactive substances that can be regarded as natural compounds. After being split off, the N'-methyl group was assimilated to natural products. Dechlorination of the benzene ring (which would explain why no chlorinated chemicals had been found) as an alternative to side-chain elimination could not be demonstrated by these experiments. The data obtained from ring-labeled buturon demonstrate a marked persistence of some conversion products, although buturon itself is not persistent. According to their chemical structure, they must be classified as xenobiotics.

It may be concluded that various conversion products of buturon having xenobiotic character may be leached out during a 12-year period. The higher application rate, as compared to agricultural practice, and the soil type, which was a very sandy one, suggest that these results cannot be extrapolated to each field situation. However, they show

that these products, in principle, have the potential to be transported vertically. In the European community, a concentration limit of 0.1 μg/L for a pesticide or "a similar product" in drinking water has been established (Hässelbarth, 1987). This very low level requires that even very low amounts of chemical products that could reach groundwater should not be neglected, especially in vulnerable soils. For nonpersistent chemicals in soil, the behavior of potential metabolites has to be regarded.

LITERATURE CITED

Attar, A.; Ismail, R.; Bieniek, D.; Klein, W.; Korte, F. Beiträge zur Ökologischen Chemie LXV. Synthese radioaktiv markierter Umweltchemikalien aus Benzol-¹⁴C (Imugan, Buturon, Monolinuron und PCB-Isomere). *Chemosphere* **1973**, *2*, 261–266.

Constenla, M.; Moza, P.; Scheunert, I.; Haque, A.; Klein, W. Fate of Buturon-¹⁴C in Soil during Seven Seasons of Exposure under Outdoor Conditions. *J. Agric. Food Chem.* **1984**, *32*, 208–211.

Ebing, W.; Schuphan, I. Studies on the Behaviour of Environmental Chemicals in Plants and Soil Quantitatively Investigated in Closed Cultivating Systems. *Ecotoxicol. Environ. Saf.* **1979**, *3*, 133–143.

Freitag, D.; Scheunert, I.; Klein, W.; Korte, F. Long-Term Fate of 4-Chloroaniline-¹⁴C in Soil and Plants under Outdoor Conditions. A Contribution to Terrestrial Ecotoxicology of Chemicals. *J. Agric. Food Chem.* **1984**, *32*, 203–207.

Führ, F.; Mittelstaedt, W. Plant Experiments on the Bioavailability of Unextracted Carbonyl-¹⁴C-Methabenzthiazuron Residues from Soil. *J. Agric. Food Chem.* **1980**, *28*, 122–125.

Fuhremann, T.; Lichtenstein, E. P. Release of Soil-Bound Methyl-¹⁴C-Parathion Residues and Their Uptake by Earthworms and Oat Plants. *J. Agric. Food Chem.* **1978**, *26*, 605–610.

Hässelbarth, U. Zur Erfassung und Bewertung von Pflanzenbehandlungs- und Schädlingsbekämpfungsmitteln in Trinkwässern entsprechend der Novelle der Trinkwasserverordnung. In *Grundwasserbeeinflussung durch Pflanzenschutzmittel*; Milde, G., Friesel, P., Eds.; Gustav Fischer Verlag: Stuttgart, New York, 1987.

Haque, A.; Weisgerber, I.; Kotzias, D.; Klein, W.; Korte, F. Contributions to Ecological Chemistry CXII. Balance of Conversion of Buturon-¹⁴C in Wheat under Outdoor Conditions. *J. Environ. Sci. Health* **1976**, *BII*, 211–223.

Haque, A.; Weisgerber, I.; Kotzias, D.; Klein, W. Conversion of [¹⁴C]Buturon in Soil and Leaching Water under Outdoor Conditions. *Pestic. Biochem. Physiol.* **1977**, *7*, 321–331.

Herzel, F.; Schmidt, G. *Prüfung des Versickerungsverhaltens von Pflanzenschutzmitteln an Lysimetern und Kleinsäulen*; WaBoLuBerichte 3, Dietrich Reimer Verlag: Berlin, 1979.

Industrieverband Pflanzenschutz e.V. *Pflanzenschutzwirkstoffe und Trinkwasser*; IPS: Frankfurt/Main, 1987.

Khan, S. Plant Uptake of Unextracted (Bound) Residues from an Organic Soil Treated with Prometryn. *J. Agric. Food Chem.* **1980**, *28*, 1096–1098.

Khan, S.; Ivarson, K. Microbiological Release of Unextracted (Bound) Residues from an Organic Soil Treated with Prometryn. *J. Agric. Food Chem.* **1981**, *29*, 1301–1303.

Khan, S.; Ivarson, K. Release of Soil-Bound (Nonextractable) Residues by Various Physiological Groups of Microorganisms. *J. Environ. Sci. Health* **1982**, *B17*, 737–749.

Kotzias, D.; Klein, W.; Korte, F. Beiträge zur Ökologischen Chemie LVII. Reaktionen des Buturons bei UV-Bestrahlung. *Chemosphere* **1973**, *2*, 87–90.

Kotzias, D.; Klein, W.; Korte, F. Beiträge zur Ökologischen Chemie LXXIX. Reaktionen von Buturon und Monolinuron in fester und flüssiger Phase bei UV-Bestrahlung. *Chemosphere* **1974**, *3*, 161–166.

Milde, G.; Friesel, P. *Grundwasserbeeinflussung durch Pflanzenschutzmittel*; Gustav Fischer Verlag: Stuttgart, New York, 1987.

Schiavon, M. Studies of the Leaching of Atrazine, of its Chlorinated Derivatives, and of Hydroxyatrazine from Soil Using ¹⁴C Ring Labelled Compounds under Outdoor Conditions. *Ecotoxicol. Environ. Saf.* **1988**, *15*, 46–54.

Schuphan, I.; Ebing, W. Zum Metabolismus von Phenylharn-stoff-Herbiziden VII. Metabolismus-Aufklärung und Bilan-zierung des Verbleibs von Buturon-^{14}C nach Anwendung bei Winterweizen. *Weed Res.* **1977**, *17*, 181–189.

Tsorbatzoudi, E.; Vockel, D.; Korte, F. Beiträge zur Ökologischen Chemie CXI. Metabolismus von Buturon-^{14}C in Algen. *Chemosphere* **1976**, *5*, 49–52.

Wallnöfer, P. R.; Safe, S.; Hutzinger, O. Microbial Demethylation and Debutynylation of Four Phenylurea Herbicides. *Pestic. Biochem. Physiol.* **1973**, *3*, 253–258.

Abiotic Reduction of Nitro Aromatic Pesticides in Anaerobic Laboratory Systems

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Rapid abiotic reduction of nitro aromatic pesticides occurs in homogeneous solutions of quinone redox couples, which were selected to model the redox-labile functional groups in natural organic matter. The kinetics of methyl parathion disappearance are first order in methyl parathion and first order in the monophenolate form of the hydroquinone. The concentration of the monophenolate was calculated from electrode measurement of Eh and pH of the model system and thermodynamic data. The second-order rate constant at 25 °C is 31.1 ± 4.9 L min^{-1} mol^{-1} in a solution where the quinone–hydroquinone redox system consists of partially reduced indigo disulfonate and is $(3.80 ± 0.65) \times 10^4$ L min^{-1} mol^{-1} in redox systems based on anthraquinonedisulfonate. Reduction of methyl parathion is negligible above about –50 mV; this is the apparent reduction potential of methyl parathion under the conditions used in this study. In indigodisulfonate model systems, the disappearance of profluralin is also second order but with a rate constant equal to 79.0 ± 8.6 L min^{-1} mol^{-1}.

Environmental reduction reactions of organic pollutants that may be abiotic include dehalogenation, nitro reduction, dealkylation, azo reduction, and sulfoxide reduction (Macalady et al., 1986; Sethunathan, 1973; Tsukano, 1986). Nitro reduction is the most easily effected and, we believe, the most likely to occur abiotically in the environment, so it was selected as the focus of this work. Nitro reduction of the phosphorothioate insecticides fenitrothion, methyl parathion, and parathion to their amino analogues is known to occur rapidly in anaerobic soils and sediments and is considered to be largely an abiotic process (Adhya et al., 1981a,b; Gambrell et al., 1984; Wahid et al., 1980; Wahid and Sethunathan, 1979; Wolfe et al., 1986). However, currently, the rate of abiotic nitro reduction in the environment cannot be predicted because the pathways and associated kinetics are not known.

Speculation regarding the agents responsible for abiotic reduction of organic pollutants most commonly emphasizes ferrous ion or complexes of ferrous ion (Macalady et al., 1986). However, it is a common generalization that natural organic matter is a strong reducing agent (Crosby, 1970; Stevenson, 1982; Thurman, 1985; Waite, in press), and organic matter will reduce metals that can, in turn, reduce organic pollutants. Presumably, organic matter can also reduce organic pollutants directly. Studies to date have not identified the reducing site(s) on natural organic matter though they are likely to be associated with polyphenols, especially those with para orientation, i.e. hydroquinones (Waite, in press). The reactions that we report here are all direct reductions of nitro groups to amines by hydroquinones.

We have determined the effects of Eh, pH, and other reaction conditions on the kinetics of nitro reduction by hydroquinones. Despite the severe difficulties with measurement and interpretation of electrode potentials in natural materials (Bohn, 1971; Hostettler, 1984; Lindberg, 1983; Whitfield, 1969), they continue to be widely reported as qualitative indicators of redox conditions. Part of the environmental significance of this project derives from the use of measured electrode potentials as a predictor variable. However, in this work poised model systems are used rather than soil or sediment samples in part because potentiometry in comparatively ideal laboratory solutions is much more satisfactory than in natural materials. The model systems were homogeneous poised solutions based on quinone–hydroquinone redox couples.

EXPERIMENTAL METHODS

Model Redox Systems. A 5 mM aqueous solution of indigodisulfonate (used as received from Fisher, certified grade, and from Aldrich) was used as the basis of a model system in the manner described in Experimental Procedures. Similarly, anthraquinonedisulfonate (used as received from Aldrich) was prepared in 5 mM aqueous mixtures, but these were slightly cloudy. Gas chromatographs of the isooctane extract of the anthraquinonedisulfonate mixture showed a large impurity peak that was shown to be anthraquinone. The impurity peak was reduced but not eliminated by filtering all anthraquinone disulfonate mixtures at 0.22 μm. Subsequently, it was shown that anthraquinone had no measurable effect on the rate of reduction of methyl parathion. Model systems were also based on 5 mM solutions of quinhydrone (used as received from Eastman) and dihydroquinone (used as received from Mallinckrodt, photopurified grade, and Aldrich, Gold Label grade). Fulvic acid was extracted by the traditional alkaline/acid method from a black, sulfurous, organic-rich sediment collected at Chatfield Reservoir (Douglas County, CO).

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