

Dissipation of 4-Chloroaniline and 4-Chlorophenol from Soils

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ABSTRACT

The release of 4-chloro[U-¹⁴C]aniline, 4-chloro[U-¹⁴C]phenol and their ¹⁴C-containing metabolites from Yangminshan loamy and Wufeng clay-loamy soils was determined after treatment with different concentrations. Only 1 to 2% of ¹⁴C in ¹⁴C-containing compounds from Yangminshan loamy soil and less than 8% of ¹⁴C in ¹⁴C-containing compounds from Wufeng clay-loamy soil were released by treatment with 4-chloro[U-¹⁴C]aniline for 40 days. The effect of the concentration of 4-chloroaniline on the susceptibility to degradation may be reflected in the activity of two different kinds of organisms: those tolerant to HgCl₂ toxicity active at a higher concentration (5,000 µg/g soil) and those susceptible to HgCl₂ toxicity active at a lower concentration (5 and 100 µg/g soil). 4-Chlorophenol itself is a microbial inhibitor at high concentration. Only a small amount of ¹⁴C in ¹⁴C-containing compounds was released at 5,000 µg/g soil of 4-chlorophenol during 40 days incubation when compared to the 5 and 100 µg/g soil of 4-chlorophenol added. 4-Chlorophenol was more susceptible to microbial degradation than was 4-chloroaniline.

Key Words: dissipation; 4-chloroaniline; 4-chlorophenol; soil.

I. Introduction

Many pesticides have been reported to convert to chlorobenzenes and their derivative compounds; for example, herbicide 2,3,6-trichlorobenzoate is degraded to a product of 3,5-dichlorocatechol by soil microorganisms (Horvath, 1971); the fungicide PCNB (pentachloronitrobenzene) degrades to PCP (pentachlorophenol), PCA (pentachloroaniline) and PCTA (pentachlorothioanisole) in anaerobic soils (Murthy and Kaufman, 1978); the herbicide 3',4'-dichloropropionanilide decomposes in soil to 3,4-dichloroaniline, and two molecules of 3,4-dichloroaniline condense to form 3,3',4,4'-tetrachloroazobenzene (Bartha and Pramer, 1967); the anilide herbicides, propanil (3,4-dichloro propionanilide) and dicryl [N-(3,4-dichlorophenyl)methacrylamide], are converted by soil microorganisms to 3,4-dichloroaniline (Bartha, 1969), and the phenylurea herbicides, diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], are converted to 3,4-dichlo-

roaniline in soil (Belasco and Pease, 1969); monuron [3, -(4-chlorophenyl)-1,1-dimethylurea] is converted to 4-chloroaniline by sunlight (Tang and Crosby, 1969). Because substituted chlorobenzene compounds are toxic pollutants, and some azobenzenes are known carcinogens, it is important to understand the release of these compounds from the soil after the use of pesticides in fields.

The present study was thus designed to determine the release of ¹⁴C-labelled 4-chloroaniline and 4-chlorophenol and their metabolites from different soils at different concentrations to evaluate the effects of these chemicals on the environment.

II. Materials and Methods

1. Materials

Uniform labelled (ring labelled) compounds, 4-chloro[U-¹⁴C]aniline and 4-chloro[U-¹⁴C]phenol, with a specific activity of 15.6 and 7.4 mCi/mmol

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and a radiochemical purity of more than 98%, respectively, were purchased from the Sigma Chemical Co. (St. Louis, USA). Unlabelled chemicals of more than 99% purity were purchased from the Tokyo Chemical Industrial Co. (Tokyo, Japan). The fundamental physical properties of the chemicals (Dean, 1987) are shown in Table 1.

Test soils were collected from Yangminshan of Taipei City and Wufeng of Taichung prefecture, Taiwan, ROC, and the soil textures were loam and clay loam, respectively. Some characteristics of the two soils are shown in Table 2.

2. Methods

0.50 g of 4-chloroaniline or 4-chlorophenol to 10 mL of acetone dissolved in a flask was used as the stock solution. Collected soils were air-dried, ground and sieved through a 2-mm sieve to remove debris or plant fragments. The soils were adjusted to a 70% moisture content of the field capacity with distilled water, and each 50 g of soil was taken and placed in a glass bottle. To the glass bottle, 5, 0.1 or 0.005 mL of stock solution together with its ^{14}C -labelled compound (0.5 μCi in 50 μL) was added to form 5,000, 100 or 5 $\mu\text{g/g}$ soil, respectively, and mixed. The purchased ^{14}C -labelled chemicals (100 μCi) were washed in a 10-mL volumetric flask with acetone, and acetone was filled to the mark. The ^{14}C -labelled chemicals corresponded to 5.32 μg (for 4-chloro[U- ^{14}C]aniline) or 8.69 μg (for 4-chloro[U- ^{14}C]phenol) per 50 μL of acetone. Each treatment was carried out in triplicate. A scintillation vial containing 1 mL of trapping solution (ethanolamine) (Jeffay and Alvarez, 1961) was shallowly and slantwise inserted into the

soil in a glass bottle (Fig. 1), and the glass bottle was covered with a Petri dish, sealed with paraffine and incubated at $20 \pm 2^\circ\text{C}$ in an incubator. The scintillation vial in a glass bottle was taken from each treatment for radioactivity determination every two days after treatment. A new scintillation vial containing trapping solution was used for replacement in coincident. The contrast experiment was performed by sterilizing the soil with 6 mg/g soil of HgCl_2 before the test chemical was treated. The radioactivity was determined in scintillation vials in 10 mL of a cocktail composed of 6 g PPO (2,5-diphenyloxazole), 60 g ethanolamine, 0.55 L toluene and 0.39 L ethylene glycol monoethyl ether (Jeffay and Alvarez, 1961). Radioactivity was measured with a Beckman LS-1801 liquid scintillation counter. The percentage of cumulative release of ^{14}C -containing compounds was obtained from the sum radioactivity of each sample before division by the original added radioactivity.

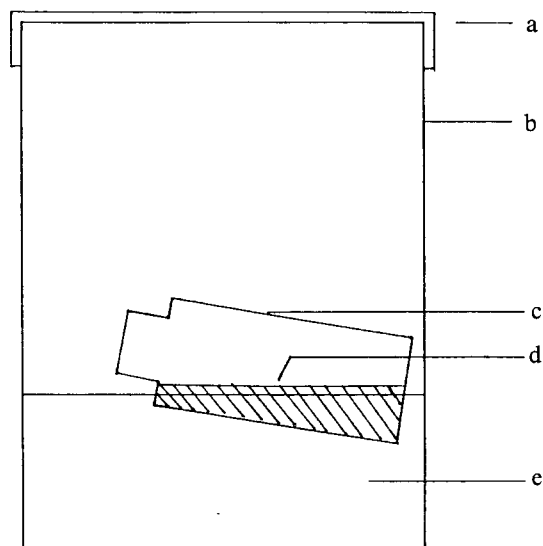


Fig. 1. Diagram showing the design of the apparatus which was used to determine the amount of ^{14}C -containing compound(s) released in the system (scale: 1cm in figure = 1.4 cm). (a) petri dish, (b) glass bottle, (c) scintillation vial, (d) trapping solution, and (e) soil.

Table 1. Physical Properties of 4-Chloroaniline and 4-Chlorophenol (Dean, 1987)

Reagent	Melting point ----- °C -----	Boiling point	Vapor pressure ---- mmHg ----
4-Chloroaniline	70-72	231-322	0.015
4-Chlorophenol	43	217	0.1

Table 2. Properties of the Two Test Soils

Soil	pH	Field capacity	Organic matter	mechanical analysis			Soil texture
				clay	silt	sand	
				----- % -----			
Wufeng	4.9	28.7	5.2	30.7	26.8	42.5	clay-loam
Yangminshan	4.1	50	20	11.0	41.3	47.7	loam

III. Results and Discussion

The percentages of cumulative release of ^{14}C -containing compound(s) from Yangminshan loamy and Wufeng clay-loamy soils after treatment with 4-chloro[U- ^{14}C]aniline are shown in Figs. 2 and 3. Only 1 to 2% of ^{14}C -containing compound(s) from Yangminshan loamy soil and less than 8% of ^{14}C from Wufeng clay-loamy soil were released after treatment with labelled chemicals for 40 days. Bartha (1971) also reported that only low percentages of ^{14}C -containing compound(s) were lost due to mineralization and volatilization of chloroanilines; his results showed that 2.0% of ^{14}C (1.5% in the form of CO_2 and 0.5% in the form of dichloroaniline) for propanil (3',4'-dichloropropionanilide) and 2.2% of ^{14}C (2.1% in the form of CO_2 and 0.1% in the form of 4-chloroaniline) for 4-chloroaniline evolved from soil when treated with 5 $\mu\text{g/g}$ of labelled chemicals. Almost no release of ^{14}C (less than 0.21%) from sterilized soil was observed at 5 and 100 $\mu\text{g/g}$ concentrations of ^{14}C -labelled 4-chloroaniline in both Yangminshan loamy and Wufeng clay-loamy soils, but some of the ^{14}C -containing compounds were released from sterilized soil at a 5,000 $\mu\text{g/g}$ concentration (Figs. 2 and 3). The effect of chemical concentration on the susceptibility of 4-chloroaniline to degradation in both Yangminshan loamy and Wufeng clay-loamy soils may reflect the activity of two different kinds of organisms; the

microorganism that was active at a higher concentration (5,000 $\mu\text{g/g}$) of 4-chloroaniline was tolerant to HgCl_2 toxicity, and the microorganism that was active at a lower concentration (5 or 100 $\mu\text{g/g}$) of 4-chloroaniline was susceptible to HgCl_2 toxicity, as described by Rubin *et al.* (1982).

According to Rubin *et al.* (1982), the rate of phenol mineralization is a linear function of concentration at levels below 1 $\mu\text{g/mL}$, falls off between 1 and 100 $\mu\text{g/mL}$, and is again high at levels above 100 $\mu\text{g/mL}$. They suggested that their results may reflect the activity of two different kinds of organisms: oligotrophs active at lower concentrations and eutrophs active at higher concentrations. The susceptibility of an organic chemical to microbial destruction in nature may be attributable to environmental factors or to the structure of the chemical itself (Boethling and Alexander, 1979). Evidence from Wang *et al.* (1984) indicated that the herbicide IPC (isopropyl N-phenylcarbamate) may be mineralized at one concentration and apparently cometabolized, or at least converted in high yield into solely organic products, at another concentration. The possible influence of the chemical concentration and type of environment on the susceptibility of several pesticides to mineralization and cometabolism was assessed by Wang *et al.* (1985), and their results showed that a pesticide may be cometabolized at one concentration or in samples from one type of environment and mineralized at a lower

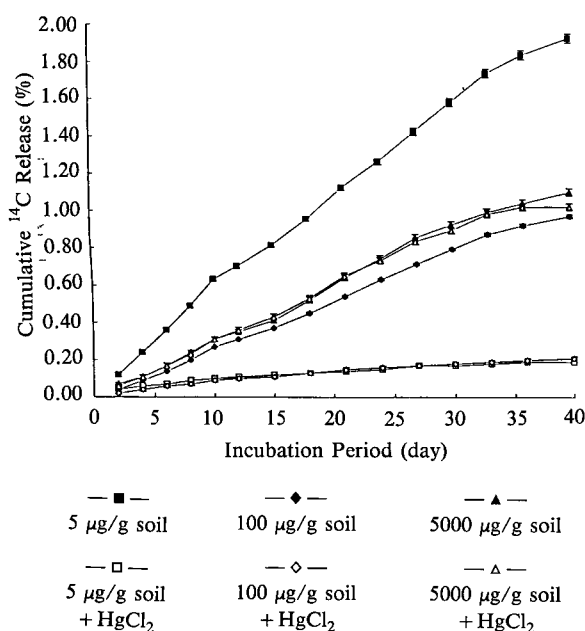


Fig. 2. Cumulative release of ^{14}C -containing compound(s) from Yangminshan loamy soil after treatment with 4-chloro[U- ^{14}C]aniline.

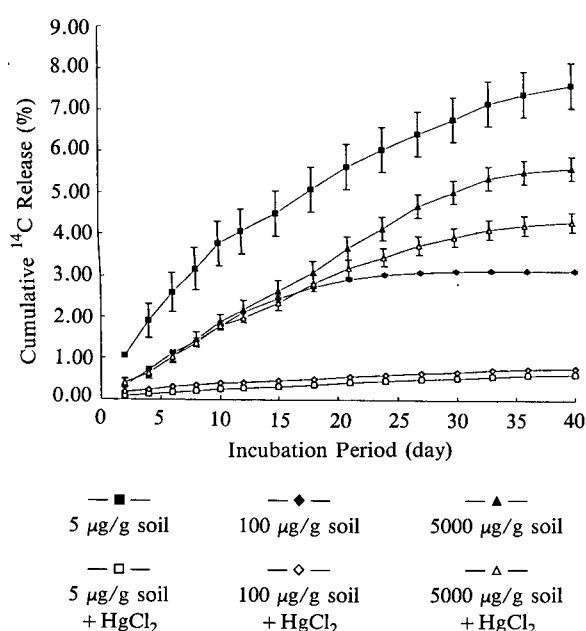


Fig. 3. Cumulative release of ^{14}C -containing compound(s) from Wufeng clay-loamy soil after treatment with 4-chloro[U- ^{14}C]aniline.

concentration or in samples from a different type of environment.

In Wufeng clay-loamy soil (Fig. 3), the percentages of the release of ^{14}C -containing compound(s) from ^{14}C -labelled 4-chloroaniline ($5,000\ \mu\text{g/g}$ soil) in the system of sterilized soil and non-sterilized soil was 4.3 and 5.6%, respectively, after 40 days. The difference between them may have been because micro-organisms that were active at a higher concentration of 4-chloroaniline were inhibited by HgCl_2 during the early period.

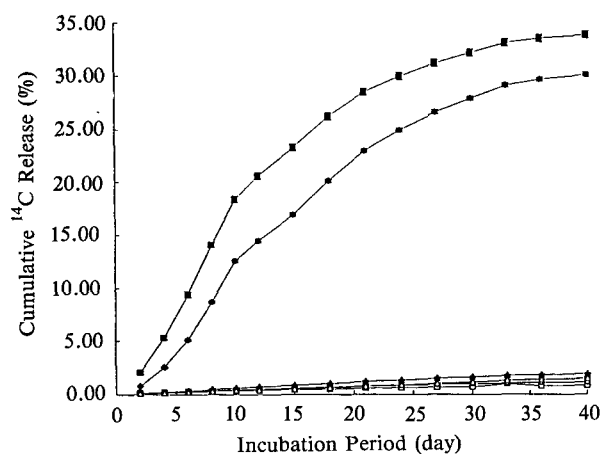
The dissipation of 4-chloro[$\text{U-}^{14}\text{C}$]phenol from Yangminshan loamy and Wufeng clay-loamy soil was caused by microbial degradation (Figs. 4 and 5). In non-sterilized soil, 35 and 30% of ^{14}C in ^{14}C -containing compound(s) were released from Yangminshan loamy soil and 44 and 19% from Wufeng clay-loamy soil following treatment with 5 and $100\ \mu\text{g/g}$ concentrations, respectively. The negligible release of ^{14}C from both soils following treatment with a higher concentration of $5,000\ \mu\text{g/g}$ was attributable to 4-chlorophenol itself being a microbial inhibitor. The extremely small amounts of ^{14}C in ^{14}C -containing compound(s) released from both sterilized soils were attributable to the 4-chlorophenol, which could not be attacked by microbes in the sterilized conditions (Figs. 4 and 5). Dec and Bollag (1988) reported that most of the radioactivity of trichlorophenol (54.7 to 88.9%) remained bound to synthetic humic acid, suggesting that

once chlorophenols were incorporated into humus, their release was very slow and unlikely to adversely affect the environment. Thus, the incorporation of 4-chloro[$\text{U-}^{14}\text{C}$]phenol into humus of both sterilized soils may have also occurred in this study.

Bartha (1971) reported that 73% of propanil ring-carbon became bound to the soil at a $5\ \mu\text{g/g}$ application rate, and that only 54% was immobilized at a $500\ \mu\text{g/g}$ concentration, where the immobilized residues consisted of intact chloroanilines that were chemically bonded to humic substances. 4-Chloroaniline and 4-chlorophenol are similar in the essential skeletons of their chemical structures. The lower amounts of 4-chloroaniline and its degraded products that were lost from both soils, as shown in Figs. 2 and 3, may thus be attributable to the lower vapor pressure of the chemical itself (Table 1) and to the absorption by clay minerals and soil organic matter.

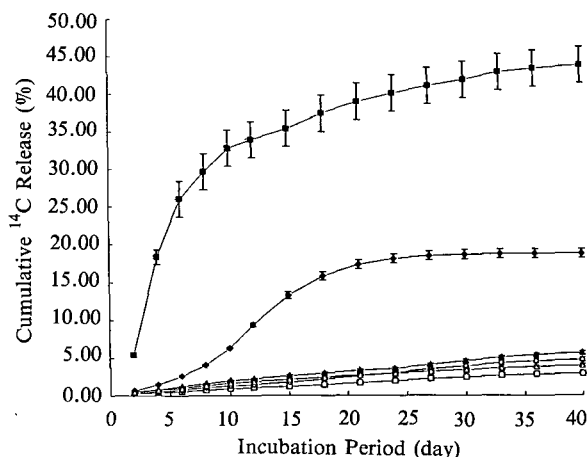
IV. Conclusions

4-Chloroaniline and 4-chlorophenol were principally released in the form of microbial degraded products, and only a small amount was volatilized in the form of original material. Because 4-chlorophenol itself is a microbial inhibitor at high concentrations, the behavior of the release rate in soil at a high concentration ($5,000\ \mu\text{g/g}$) was the same as that for HgCl_2 added. 4-Chlorophenol was more susceptible



—■— 5 $\mu\text{g/g}$ soil
—◆— 100 $\mu\text{g/g}$ soil
—▲— 5000 $\mu\text{g/g}$ soil
—□— 5 $\mu\text{g/g}$ soil + HgCl_2
—◇— 100 $\mu\text{g/g}$ soil + HgCl_2
—△— 5000 $\mu\text{g/g}$ soil + HgCl_2

Fig. 4. Cumulative release of ^{14}C -containing compound(s) from Yangminshan loamy soil after treatment with 4-chloro[$\text{U-}^{14}\text{C}$]phenol.



—■— 5 $\mu\text{g/g}$ soil
—◆— 100 $\mu\text{g/g}$ soil
—▲— 5000 $\mu\text{g/g}$ soil
—□— 5 $\mu\text{g/g}$ soil + HgCl_2
—◇— 100 $\mu\text{g/g}$ soil + HgCl_2
—△— 5000 $\mu\text{g/g}$ soil + HgCl_2

Fig. 5. Cumulative release of ^{14}C -containing compound(s) from Wufeng clay-loamy soil after treatment with 4-chloro[$\text{U-}^{14}\text{C}$]phenol.

to microbial degradation than was 4-chloroaniline at a low concentration. Chloroaniline, which was reported to chemically bond easily to soil humic substances, may have been transformed to chloroazobenzene by bimolecular condensation. The dissipation rate of ^{14}C -containing compounds from soil was lower than that of 4-chlorophenol when the ^{14}C -labelled chemical was introduced.

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4-氯苯胺與4-氯酚自土壤中之消散

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摘 要

本研究在探討不同濃度之4-氯苯胺與4-氯酚及其代謝產物在陽明山壤土及霧峰黏壤土中之釋放情況。以帶有放射活性之4-氯苯胺加入土壤中40天，則總共僅有1-2%之放射活性自陽明山壤土中釋出而僅有少於8%之放射活性自霧峰黏壤土中釋出。4-氯苯胺之濃度，對於其被降解之效應不同可歸因於二種不同微生物之活性，耐受 HgCl_2 毒性之微生物可作用於高濃度（5,000 μg / 每克土壤）4-氯苯胺之分解，而對 HgCl_2 毒性敏感之微生物則作用於低濃度（5 及 100 μg / 每克土壤）4-氯苯胺之分解。4-氯酚在高濃度下，本身為微生物抑制劑，故在5,000 μg / 每克土壤，40天後僅有很少之放射活性釋出。4-氯酚比4-氯苯胺更容易受微生物分解。