

For control purposes, a method more discriminating than the present A.O.A.C. procedure is needed to serve as a basis for quality control for fertilizer manufacturers and for protection of the consumer.

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Literature Cited

- (1) Ando, J., *Bull. Chem. Soc. Japan* **31**, No. 2, 196 (1958).
- (2) Andrews, W. B., *J. Assoc. Offic. Agr. Chemists* **25**, 498 (1942).

- (3) Archer, J. R., Thomas, R. P., *J. Agr. Food Chem.* **4**, 608 (1956).
- (4) Assoc. Offic. Agr. Chemists, Washington, D. C., "Official Methods of Analysis," 8th ed., pp. 10-11, 1955.
- (5) Clark, K. G., Hoffman, W. M., Freeman, H. P., *J. Agr. Food Chem.* **8**, 2 (1960).
- (6) *Crops and Soils* **12**, No. 1, 12 (1959).
- (7) Hignett, T. P., Brabson, J. A., *J. Agr. Food Chem.* **9**, 272 (1961).
- (8) Kitson, R. E., Mellon, M. S., *Anal. Chem.* **16**, 379 (1944).
- (9) Lawton, K., Apostolakis, C., Cook, R. L., Hill, W. L., *Soil Sci.* **82**, 465 (1956).
- (10) Organisation for European Economic Cooperation, "Fertilizers—Methods of Analysis Used in O.E.E.C. Countries," Paris, pp. 81-3, 1952.
- (11) Rogers, H. T., Ensminger, L. E., *Chem. Farming* **3**, 6 (1961).

- (12) Rogers, H. T., Pearson, R. W., Ensminger, L. E., "Soil and Fertilizer Phosphorus in Crop Nutrition," W. H. Pierre and A. G. Norman, eds., Chap. VII, Academic Press, New York, 1953.
- (13) Ross, W. H., Adams, J. R., Hardesty, J. O., Whittaker, C., *J. Assoc. Offic. Agr. Chemists* **30**, 624 (1947).
- (14) Terman, G. L., Anthony, J. L., Mortensen, W. P., Lutz, J. A., Jr., *Soil Sci. Soc. Am. Proc.* **20**, 551 (1956).
- (15) Terman, G. L., Bouldin, D. R., Lehr, J. R., *Ibid.*, **22**, 25 (1958).
- (16) Wright, B., Lancaster, J. D., Anthony, J. L., *Mississippi State Univ. Agr. Expt. Sta. Tech. Bull.* **52** (1963).

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NUTRIENT CONSERVING AGENTS

The Loss of 2-Chloro-6-(trichloromethyl)pyridine from Soil

2-Chloro-6-(trichloromethyl)pyridine applied to soil as an intimate mixture is lost by two exponential processes. One is volatilization and the other is degradation to 6-chloropicolinic acid. Of four soils studied, the half time of the slowest degradation process is only 22 days at 20° C. The half time of the most rapid is 4 days at 20° C.

2-CHLORO-6-(trichloromethyl)pyridine (N-Serve, trademark of The Dow Chemical Co.), nutrient conservor, is a compound proposed for use as a nitrogen-conserving agent (2). When used in this manner, the compound would be applied to soil along with fertilizers containing ammonium ions to inhibit microbial oxidation and subsequent leaching loss. Hence, both volatilization from the soil and action of soil microflora might have a considerable effect on the length of time the plant was exposed to the chemical and on the residue levels which might subsequently be found in crop plants. To evaluate the relative importance of these different processes, the work described was initiated.

Reagents

6-Chloropicolinic Acid. Dissolve 10 grams (.045 mole) of 2-chloro-6-(trichloromethyl)pyridine in 50 grams (0.41 mole) of 80% (by weight) sulfuric acid and heat under reflux at 130° C. for 2 hours. During this time, hydrogen chloride is evolved freely by the solution. Cool the flask and contents to room temperature and add 100 grams

of crushed ice. Place the flask in a refrigerator maintained at 4° C. for several hours and then filter off the resulting precipitate.

Recrystallization to constant melting point from the minimum volume of hot 50% (by weight) methanol yields 4.5 grams (.029 mole) of 6-chloropicolinic acid melting at 194°-195° C. (dec.). Reported melting point, about 190° C. (7). Calculated for C₆H₄ClNO₂: C, 45.7%; H, 2.56%. Found: C, 45.8%; H, 2.77%.

6-Chloropicolinic-C¹⁴ Acid. To a solution of 1 mmole of *n*-butyllithium in 6 ml. of dry ether at -40° to -35° C., add rapidly and with stirring a solution of 361 mg. (2.44 mmoles) of 2,6-dichloropyridine. Stir the mixture at this same temperature for 5 minutes. Carbonate with 1 mmole of carbon-C¹⁴ dioxide at -78° C. and continue stirring at this temperature for 2 more hours.

Permit the reaction mixture to warm to room temperature and add 20 ml. of water. Separate the aqueous phase from the ether phase and wash the aqueous with three equal portions of ether. Transfer the remaining aqueous phase to a small liquid extractor, saturate with sodium chloride, and adjust

the pH to 2.2 with 6*N* hydrochloric acid. Extract with chloroform for 2 hours, and evaporate the chloroform extract to dryness on a steam bath to obtain 132 mg. of product (85%) melting at 191°-192° C. The infrared spectrum is identical to that of 6-chloropicolinic acid prepared by the hydrolysis of 2-chloro-6-(trichloromethyl)pyridine.

2-Chloro-6-(trichloromethyl)-C¹⁴pyridine. Seal 132 mg. (0.85 mmole) of 6-chloropicolinic-C¹⁴ acid in a 6-inch borosilicate-glass test tube with 1 gram of phosphorus pentachloride and heat at 170° C. for 32 hours. Cool the reaction mixture to room temperature and pour onto 5 grams of crushed ice. Make alkaline with 6*N* sodium hydroxide solution and extract with four successive 5-ml. portions of ethanol-free ether. Dry the ether extracts over anhydrous magnesium sulfate and assay for product by means of its ultraviolet absorption spectrum: λ_{max.} is 270 mμ; E_{max.} is 4190. The yield is approximately 183 mg., representing a 94% conversion of the 6-chloropicolinic-C¹⁴ acid.

The melting point of the product isolated from preliminary runs was 66°-68° C.; there was no depression of melting point when mixed with an authentic

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Table I. Properties of Soils Studied

Property	Soil C ₁	Soil A ₁	Soil 19	Soil R
Per cent silt	29	43	65	75
Per cent clay	25	41	31	17
Per cent organic matter	3.1	1.1	0.8	0.3
pH	7.8	7.5	7.3	5.5
Base exchange capacity	16.7	14.4	8.5	...
Conductivity, mmhos	2.2	1.9	14.3	...
Description	Loam	Loam	Sandy loam	Sandy loam
Source	So. Calif.	So. Calif.	Calif.	Calif.

Table II. R_f Values of Radioactive Material Extracted from Soil 19 Treated One Year Previously with 2-Chloro-6-(trichloromethyl)-C¹⁴-pyridine

Solvent System	R _f of Compound from Soil	R _f of 6-Chloro-picolinic Acid
<i>n</i> -Butanol saturated with 1.5 <i>N</i> NH ₄ OH	0.34	0.36
Benzene, propionic acid, water, 2:2:1 v./v.	0.74	0.74
<i>n</i> -Butanol, triethylamine, water, 5:1:2 v./v.	0.49	0.48

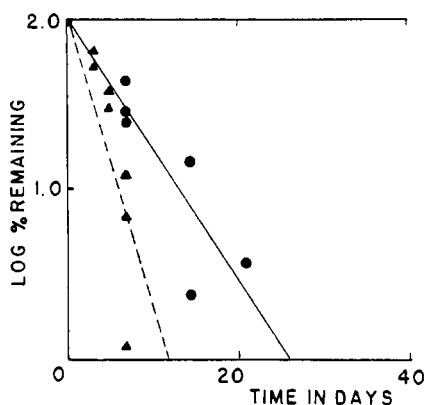


Figure 1. Loss of 2-chloro-6-(trichloromethyl)pyridine from 100 grams soil A₁ at 20° C.

Covered jars, ●—●; uncovered jars, ▲ - - - ▲

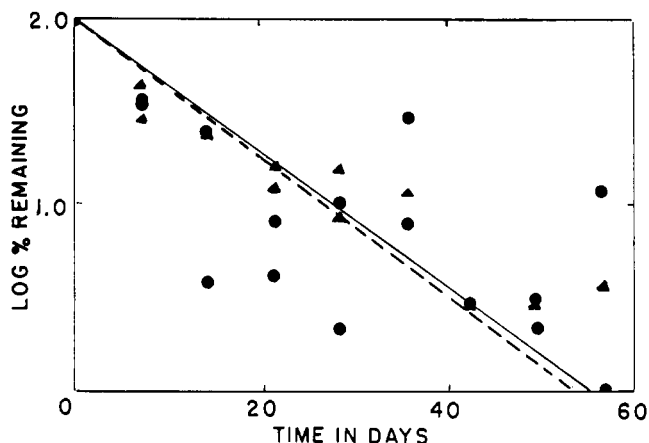


Figure 2. Loss of 2-chloro-6-(trichloromethyl)pyridine from 100 grams of soil C₁ at 20° C.

Covered jars, ●—●; uncovered jars, ▲ - - - ▲

sample of 2-chloro-6-(trichloromethyl)pyridine. The infrared spectrum was identical to that of a known sample of 2-chloro-6-(trichloromethyl)pyridine.

Procedure

Soils Studied. To obtain an estimate of the importance of soil type on the decomposition rate of 2-chloro-6-(trichloromethyl)pyridine, four different soils were studied. The composition of each of these types is presented in Table I.

Treatment of Soil Samples. A solution of 30 mg. of 2-chloro-6-(trichloromethyl)pyridine in 3 ml. of methanol was mixed dropwise with mortar and pestle into 200 grams of sifted and air-dried soil. The resulting concentrated sample of treated soil was subsequently added to 2.8 kg. of the same type soil contained in a 5-gallon wide-mouthed glass jar, sealed with a cap lined with Teflon, and milled on a roller mill for 2 hours. Immediately at the end of the milling process, 100-gram samples of the soil containing approximately 10 p.p.m. 2-chloro-6-(trichloromethyl)pyridine were weighed into individual 8-ounce jars and moistened to field capacity with distilled water.

One half of each set of jars was permitted to remain uncovered. The other half was securely covered with screw caps lined with Teflon. Both covered and uncovered jars were placed in a greenhouse maintained at 20° C., where they remained until sampled.

Analytical Method. At each sampling time, four jars, two covered and two uncovered, were randomly selected from the group for each soil type.

For each jar, the entire contents plus distilled water washings from the jar and lid were placed in a 1-liter round-bottomed flask having a neck length of 17 cm. Two-hundred milliliters of distilled water were added, and the flask was attached to a semimicro Kjeldahl nitrogen apparatus and steam-distilled until 50 ml. of distillate had collected.

The concentration of 2-chloro-6-(trichloromethyl)pyridine in the distillate was estimated by measuring the absorbance at 270 mμ with a spectrophotometer. The distillate from a 100-gram sample of untreated soil was used as a solvent blank.

Tracer Experiment. To determine whether a material derivable from 2-chloro-6-(trichloromethyl)pyridine might remain in the soil after most of the 2-chloro-6-(trichloromethyl)pyridine had

vanished, a tracer experiment was conducted.

Two round, 3-gallon metal cans measuring 9½ inches in diameter were filled to within 2 inches of the top with a mixture of equal volumes of soil 19 and Sponge Rock soil modifier. Ten milligrams (0.22 mc.) of 2-chloro-6-(trichloromethyl)-C¹⁴-pyridine coated on 1 gram of fertilizer was added at the bottom of a 3-inch deep furrow along a diameter of the pot. The furrow was then filled, the pot planted to *New York Special* lettuce, and the crop maintained in the greenhouse until harvested.

One year later, 260 grams of soil were removed from the top 2 inches of the pot and stirred up with a suspension of 1 gram of sodium bicarbonate in a solution of 500 ml. of methanol and 100 ml. of water. Next the extract was filtered off with suction and vacuum-evaporated to dryness. The residue was subsequently taken up in enough 1.5*N* hydrochloric acid to lower the pH to 2 and shaken out with two successive 3-ml. portions of ethyl acetate. The combined ethyl acetate extracts were evaporated to incipient dryness under a gentle air stream, transferred to strips of Whatman No. 1 filter paper, and developed with the solvents indicated in Table II.

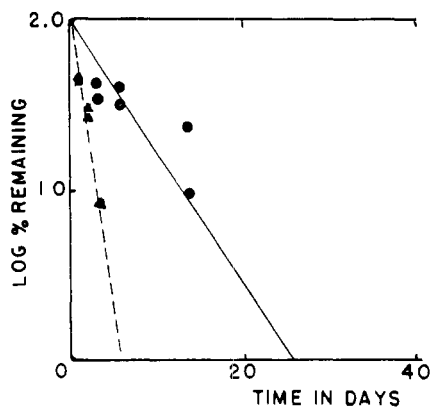


Figure 3. Loss of 2-chloro-6-(trichloromethyl)pyridine from 100 grams of soil 19 at 20° C.

Covered jars, ●—●; uncovered jars, ▲ - - - ▲

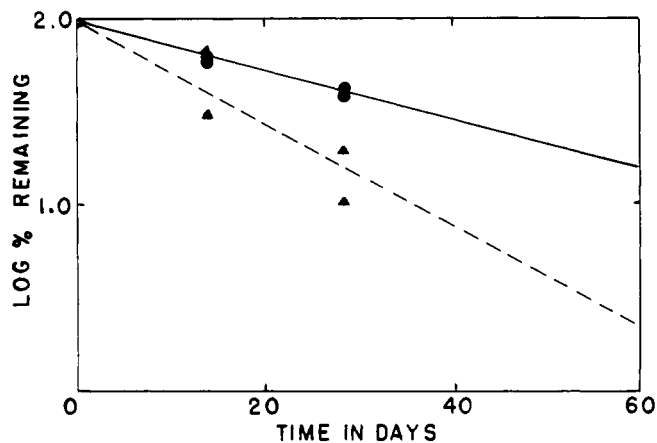


Figure 4. Loss of 2-chloro-6-(trichloromethyl)pyridine from 100 grams of soil R at 20° C.

Covered jars, ●—●; uncovered jars, ▲ - - - ▲

The R_f values indicated were measured by scanning the chromatograms with a strip flow counter and measuring the position of the peak radioactivity on the resulting scans.

Results

Loss Rate Data. Investigation showed that aqueous solutions of 2-chloro-6-(trichloromethyl)pyridine dissolved in water obeyed Beer's law at the wavelength of maximum absorbance, 270 $m\mu$.

Recoveries from the steam distillation were not quantitative, primarily because of the slow hydrolysis of 2-chloro-6-(trichloromethyl)pyridine at 100° C. However, the recoveries were better than 75% and fairly consistent for a given soil.

To make the rate data more meaningful, the different soils were all sampled and analyzed at zero time. The experimental value found at zero time was then used as a basis of calculating the percentage of 2-chloro-6-(trichloromethyl)pyridine remaining at the other sampling times.

The rates of loss of 2-chloro-6-(trichloromethyl)pyridine from the four soils examined are shown in Figures 1 through 4 for both the covered and the uncovered jars.

Examination of these data reveals several facts. The 2-chloro-6-(trichloromethyl)pyridine remaining in the soil is an exponential function of time. The loss rate varies from soil to soil, the half time of the degradation process being 22 days at 20° C. in soil R but only 4 days at 20° C. in soil 19. The loss is more rapid from uncovered jars than from covered, indicating that volatilization may be an important source of loss.

For one soil, however, the loss rate is comparatively slow, and little difference exists between the covered and the uncovered jars. This soil is the one richest in organic matter.

Tracer Data. The data in Table II show that only one radioactive compound was found in the soil 1 year after treatment with labeled 2-chloro-6-(trichloromethyl)pyridine. The R_f values of this one compound in three different

solvent systems are in good agreement with those for 6-chloropicolinic acid.

In view of the ease of hydrolysis of 2-chloro-6-(trichloromethyl)pyridine to 6-chloropicolinic acid, it is almost certain that the degradation process that occurred in the covered jars of soil was chiefly the hydrolytic conversion to 6-chloropicolinic acid.

Hence, application of 2-chloro-6-(trichloromethyl)pyridine to soils as an agronomic practice will probably result in the presence of minute residues of 6-chloropicolinic acid in the soil.

Acknowledgment

The authors are indebted to Cleve Goring of this laboratory for the data concerning the properties of the soils studied.

Literature Cited

- (1) Fischer, E., Hess, K., Stahlschmidt, A., *Ber.* **45**, 2461 (1912).
- (2) Goring, C. A. I., *Soil Sci.* **93**, 211 (1962).

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