The relative (to amounts applied) volatility of TCDD exceeded that of the herbicides. Previously, we observed that volatilization was an important route of dissipation for persitent, but relatively nonvolatile compounds (Nash et al., 1977). On the basis of these and previous results (with TCDD applied to turf and DDT applied to cotton both in an emulsifiable concentrate), apparently TCDD was about three-fourths as volatile as DDT. Furthermore, it appears that volatilization is a major pathway of TCDD dissipation, with subsequent photochemical dechlorination probably occurring.

Since the grass (from the emulsifiable concentrate treatment), thatch, roots (or subthatch), and soil surface were all major repositories for TCDD, the soil thatch interface would appear to be the major repository of TCDD before it is volatilized when applied as a contaminant of silvex or 2,4,5-T. The soil thatch interface is a very active zone. Approximately 8% of the emulsifiable concentrate was removed from the chambers with the grass clippings. This would amount to 5 ng of TCDD/kg of grass if the initial silvex contained 0.1 ppm. The amounts of TCDD leached through 15 cm of soil and in earthworms were negligible.

The total amount of ^3H accounted for was 90% for the emulsifiable concentrate and 70% for the granular formulation (treatment 3). The total amounts accounted for at the end of treatment 2 were low because we did not sample the thatch and roots. The total amounts accounted for are probably reasonably good for a fairly stable compound like TCDD. Accounting for 2,4-D and silvex would be impossible in experiments with this length of time without the use of radioisotopes and CO_2 traps.

ACKNOWLEDGMENT

LITERATURE CITED

Beall, M. L., Jr., Nash, R. G., Kearney, P. C., Proceedings of the EPA Conference on Environmental Modeling and Simulation, Cincinnati, OH, April 19–22, 1976, p 790.
Crosby, D. G., Wong, A. S., *Science.* **195**, 1337 (1977).
Crosby, D. G., Wong, A. S., Plimmer, J. R., Woolson, E. A., *Science* **173**, 748 (1971).
Grover, R., *Weed Sci.* **23**, 529 (1975).
Grover, R., *Weed Sci.* **24**, 26 (1976).
Helling, C. S., *Soil Sci. Soc. Am. Proc.* **35**, 737 (1970).
Helling, C. S., Isensee, A. R., Woolson, E. A., Ensor, P. D. J., Jones, G. E., Plimmer, J. R., Kearney, P. C., *J. Environ. Qual.* **2**, 171 (1973).
Higginbotham, G. R., Huang, A., Firestone, D., Verrette, J., Campbell, A. D., *Nature (London)* **220**, 702 (1967).
Hilton, J. L., Bovey, R. W., Hull, H. M., Mullison, W. R., Talbert, R. E., "Herbicide Handbook", 3rd ed, Weed Science Society of America, 1974 pp 359–362.
Hummel, R. A., *J. Agric. Food. Chem.* **25**, 1049 (1977).
Kearney, P. C., Woolson, E. A., Ellington, C. P., Jr., *Environ. Sci. Technol.* **6**, 1017 (1972).
Kearney, P. C. Woolson, E. A., Isensee, A. R., Helling, C. S., *Environ. Health Perspect.*, 273 (1973).
Nash, R. G., Beall, M. L., Jr., *J. Agric. Food Chem.*, in press (1980).
Nash, R. g., Beall, M. L., Jr., Harris, W. G., *J. Agric. Food Chem.* **25**, 336 (1977).
Poland, A., Glover, E., *J. Biol. Control.* **251**, 4936 (1976).
Poland, A. P., Smith, D., Metter, G., Possick, P., *Arch. Environ. Health* **22**, 316 (1971).
Stewart, D. K. R., Gaul, S. O., *Bull. Environ. Contam. Toxicol.* **18**, 210 (1977).
Turner, B. C., Glotfelty, D. E., *Anal. Chem.* **43**, 7 (1977).

Sorption–Desorption of Lindane by Anaerobic and Aerobic Soils

P. A. Wahid and N. Sethunathan*

In a study on the sorption of pesticides by three soils, soils prereduced by flooding sorbed less lindane (γ-hexachlorocyclohexane) than the aerobic soils. This difference was particularly striking in the soil with lowest organic matter content and was probably masked in the other two soils by higher organic matter content. The decreased sorption of lindane by anaerobic soils low in organic matter content is attributed to the decrease in inorganic surface area caused by the reduction of ferric to ferrous ion and the high state of hydration attained by ferric oxides upon flooding. Desorption of lindane was not affected by soil anaerobiosis.

In rice culture, pesticides are either broadcast to the flood water or sprayed to the foliage and lower parts of the leaf sheaths of rice plants. A substantial portion of the pesticides applied to the standing crop as practiced in transplanted rice culture eventually shifts to the soil as residues. The chemical and biochemical transformations in soil upon flooding affect its organic and biochemical makeup qualitatively and quantitatively (Ponnamperuma,

Table I. Some Physicochemical Characteristics of the Soils Used

soil no.	soil type	pH[a]	org matter, %	clay, %	free Fe, %
1	alluvial	6.2	0.75	15.6	0.83
2	laterite	6.3	2.88	23.6	2.40
3	acid sulfate, saline[b]	5.2	5.52	45.6	1.38

[a] 1:2.5 soil-water slurry.   [b] Locally known as pokkali.

Central Rice Research Institute, Cuttack-753006, India (N.S.) and the College of Horticulture Vellanikara, Trichur, Kerala, India (P.A.W.).

1972). The impact of such transformations and soil anaerobiosis on sorption–desorption of pesticides has not
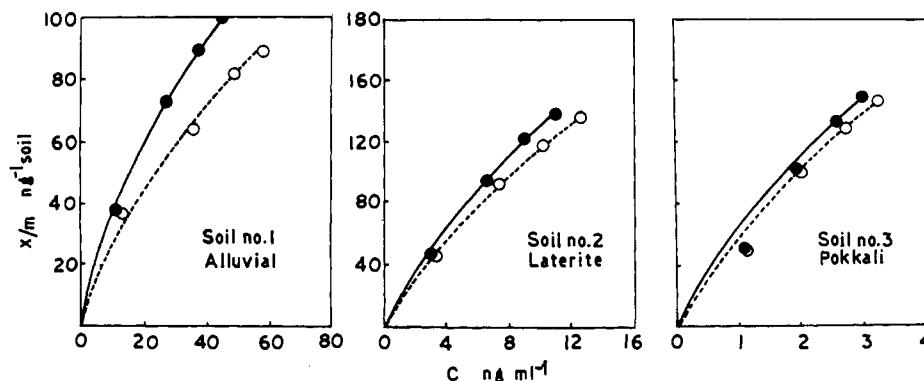
Figure 1. Sorption isotherms of lindane in aerobic (●) and anaerobic (○) soils.

been studied. This paper reports the sorption–desorption pattern of lindane (γ-hexachlorocyclohexane) by aerobic and anaerobic soils.

MATERIALS AND METHODS

Soils. The physicochemical characteristics of three soils used in the study are presented in Table I. The air-dried soils were sieved through a 2-mm mesh before use.

[^{14}C]Lindane. [^{14}C]Lindane (Radiochemical Centre, Amersham, England; sp act., 45 mCi/mmol) was dissolved in acetone. The purity of the material was confirmed as 98% by thin-layer chromatography.

Sorption Studies. Ten-gram portions of soil samples contained in round-bottomed, screw-capped glass tubes (30 by 120 mm, 30-mL capacity) were flooded with 10 mL of distilled water to provide about 2 cm of standing water. The tubes were closed, and the soils were incubated at room temperature (28 ± 4 °C) for 30 days to allow reduction. A polyethylene sheet was sandwiched between the mouth of the tube and the screw cap to prevent the contents from adhering to the cap during equilibration of the pesticide with the soil for sorption and subsequent centrifugation. To study sorption by batch adsorption methodology as described earlier (Wahid and Sethunathan, 1978a), 0.2 mL of acetone solution containing 0–1.5 μg of [^{14}C]lindane was added to 30-day flooded soil (anaerobic system), and the sealed system was equilibrated on a shaker for 30 min. Soils flooded just before the addition of the pesticide followed by a 30-min equilibration served as aerobic controls. A short equilibration period of 30 min was chosen because significant amount of the pesticide could be sorbed by the soils within 30 min (Wahid and Sethunathan, 1978b). After 30 min of equilibration of soil–pesticide system, the suspension was centrifuged at 5000g for 5 min, and the radioactivity in an aliquot of the supernatant was determined. The decrease in the radioactivity of the supernatant was attributed to sorption.

To study desorption of lindane by anaerobic soils, the supernatant in the sorption experiment was discarded and lindane sorbed by the soils was desorbed by equilibrating with 10 mL of distilled water on a shaker for 30 min. The suspension was then centrifuged and the radioactivity in an aliquot of the supernatant was assayed.

Measurement of Redox Potential. The redox potential of the soil–water suspension was measured before and after equilibration with the pesticide using a portable redox meter (Model RM-IF, TOA Electronics Ltd., Tokyo) fitted with a compound calomel–platinum electrode. The potentials were not corrected for hydrogen electrode or pH 7.

Radioactivity Measurement. To determine the radioactivity, 0.5 mL of the supernatant in sorption and desorption experiments was mixed with 5 mL of liquid

scintillator which consisted of 60 g of naphthalene, 4 g of PPO (2,5-diphenyloxazole), 0.2 g of POPOP [1,4-bis(2,5-phenyloxazolyl)benzene], 100 mL of methanol, 20 mL of ethylene glycol, and dioxane to make the volume to 1 L. The radioactivity was measured in a liquid scintillation system (Electronics Corporation of India Ltd., Hyderabad, India). The variations in the radioactivity within duplicate estimations were less than 5%.

Ferrous Ion Estimation. Ferrous ion in flooded soils was extracted and estimated by the method of Motomura and Yokoi (1969) as modified by Howeler and Bouldin (1971). The flooded soils incubated in test tubes were transferred to a 250-mL Erlenmeyer flask with 100 mL of 1 N sodium acetate (pH 2.8) and shaken for 1 h on a shaker. The suspension was centrifuged and Fe^{2+} was estimated by treating an aliquot of the supernatant with 1 mL of 0.3% orthophenanthroline (Black, 1965). The resulting red color was measured at 510 nm in a Spectronic 20. By this method, variations in Fe^{2+} content within duplicate estimations were less than 3%.

RESULTS AND DISCUSSION

Sorption of lindane by aerobic soils and by soils prereduced by 30-day flooding was studied. Potential measurements showed convincingly that all the three soils were reduced after 30 days of flooding. Thus, the redox potentials decreased from 230 to −60 mV in soil no. 1, from 260 to −160 mV in soil no. 2, and from 200 to −220 mV in soil no. 3. No increase in soil potentials occurred following 30 min of equilibration of anaerobic soils with lindane in the sealed system used. The sorption isotherms of lindane added to anaerobic and aerobic soils in 0.2 mL of acetone are given in Figure 1. The extent of sorption of the pesticide by anaerobic and aerobic soils differed appreciably, particularly in soils with low organic matter content. Thus, anaerobic soils sorbed relatively less lindane than the aerobic soils. The difference in sorption between anaerobic and aerobic soils widened gradually with decrease in organic matter content; the alluvial soil (no. 1) having the least organic matter content showed the largest difference, followed by laterite soil (no. 2) and organic-matter-rich pokkali soil (no. 3) in that order.

The decrease in the sorption of lindane following soil reduction needs further explanation. It must be mentioned here that both clay and free iron oxides have been implicated in the sorption of lindane in aerobic soils with comparatively low organic matter content and in soils pretreated with H_2O_2 (Wahid and Sethunathan, 1979). The most important chemical change in the soil following flooding is probably the reduction of iron (Ponnamperuma, 1972) since iron generally exceeds the total amount of other redox elements by a factor of 10 or more in most tropical soils (Patrick and Reddy, 1978). Whether the decrease in
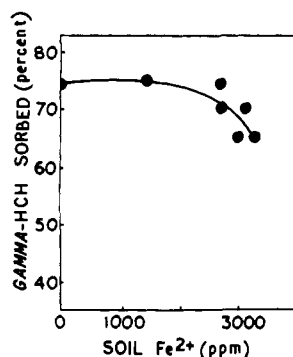
Sorption–Desorption of Lindane

J. Agric. Food Chem., Vol. 28, No. 3, 1980 **625**

Figure 2. Relationship between lindane sorption and Fe^{2+} in flooded soil amended with glucose.

the sorption of lindane by reduced soils was related to the dissolution of ferric oxides upon flooding was, therefore, examined.

Only alluvial (no. 1) was chosen for this purpose in view of the pronounced difference in sorption of lindane between aerobic and anaerobic samples of this soil. Ten-gram portions of this soil were incubated with 10 mL of 0.5% glucose solution to expedite Fe^{3+} reduction (Yamanaka and Motomura, 1959) up to 20 days. At desired intervals after incubation with glucose, duplicate soil samples were tested for their ability to sorb lindane at an initial concentration of 100 ng/g of soil. Simultaneously, ferrous ion in another set of soil samples was also assayed. The data presented in Figure 2 revealed that Fe^{2+} increased with incubation, but sorption of lindane was not affected until Fe^{2+} concentration reached the 2500-ppm level. However, at concentrations above this level, sorption of lindane decreased considerably from an initial level of 74 to 64%. Undoubtedly, a relationship existed between lindane sorption and Fe^{2+} accumulation in flooded soil. But the level of Fe^{2+} affecting the sorption in alluvial soil (no. 1) was above 2500 ppm with glucose (Figure 2) and below 1000 ppm without glucose (Figure 1). The reason for this discrepancy is not clear. Perhaps, microorganisms stimulated by the readily available carbon source, glucose, accumulated the insecticide, masking the role of iron oxides. Microorganisms are known to sorb and bioconcentrate chlorinated hydrocarbon pesticides (Ko and Lockwood, 1968; Wurster, 1968; Ware and Roan, 1970).

Apart from the decline in inorganic surface area concomitant with the transformation of ferric oxides to soluble Fe^{2+}, the hydration of ferric oxides in waterlogged soils (Oades, 1963; Gotoh and Patrick, 1974) may repel the nonionic lindane molecule from being sorbed as could be inferred from its hydrophobic nature. However, in soils rich in organic matter (Figure 1), sorption would be little affected by these processes as sorption of lindane occurs almost exclusively on organic matter (Wahid and Sethunathan, 1979).

Lindane is known for its instability in anaerobic systems (Sethunathan, 1973). Whether lindane was degraded during 30 min of equilibration with anaerobic soils in sorption experiments was, therefore, tested. [^{14}C]Lindane was equilibrated with anaerobic and aerobic soils on a shaker. The residues in the soils after 1-h equilibration were extracted by shaking first with 30 mL of acetone and 25 g of Na_2SO_4 for 15 min and then with 50 mL of hexane for 45 min. The hexane layer was removed to a beaker and evaporated at room temperature, and the residues were redissolved in 2 mL of methanol. The thin-layer chromatograms of the residues were exposed to Kodak X-ray

Table II. Desorption of Lindane by Aerobic and Anaerobic Soils

soil no.	lindane desorbed, %	
	aerobic	anaerobic
1	27.18	27.15
2	7.86	7.42
3	2.26	2.79

film. The radioautograph of lindane residues from anaerobic and aerobic soils showed only lindane and no breakdown products, indicating its stability under the experimental conditions. This was further confirmed by a recovery of 84–86% of added lindane by elution from thin-layer chromatograms, followed by assay by liquid scintillation.

To study desorption, lindane sorbed by 30-day flooded soils during 30 min of equilibration was desorbed by equilibrating with water for 30 min. During equilibration for desorption, the redox potentials increased from –60, –160, and –220 mV to 120, –10, and –220 mV in soil 1, 2, and 3, respectively; but these potentials were certainly lower than those of the respective aerobic soils with values ranging from 200 to 260 mV. Results showed (Table II) that no appreciable difference in desorption occurred despite the state of redox conditions of the soils. As in aerobic soils, an inverse relationship between organic matter and desorption of lindane was evident in anaerobic soils as well with least desorption from organic-matter-rich pokkali soil. These results suggest that the reduction of the soil following flooding does not affect its pesticide desorbing power.

The decreased sorption of lindane by anaerobic soils may have significant implications from the standpoint of its bioactivity and environmental transport, especially in many tropical rice growing areas with soils low in organic matter content and high in iron oxides.

LITERATURE CITED

Black, C. A., "Methods of Soil Analysis", Part 2, Am. Soc. Agron. Inc., Madison, WI, 1965.
Gotoh, S., Patrick, W. H., Jr., *Soil Sci. Soc. Am. Proc.* **38**, 66 (1974).
Howeler, R. H., Bouldin, D. R., *Soil Sci. Soc. Am. Proc.* **35**, 202 (1971).
Ko, W. H., Lockwood, J. L., *Can. J. Microbiol.* **14**, 1075 (1968).
Motomura, S., Yokoi, H., *Soil Sci. Plant Nutr.* **15**, 28 (1969).
Oades, J. M., *Soils Fert.* **26**, 69 (1963).
Patrick, W. H., Jr., Reddy, C. N., in "Soils and Rice", International Rice Research Institute, Los Banos, Philippines, 1978, pp 361–379.
Ponnamperuma, F. N., *Adv. Agron.* **24**, 29 (1972).
Sethunathan, N., *Residue Rev.* **47**, 143 (1973).
Wahid, P. A., Sethunathan, N., *J. Agric. Food Chem.* **26**, 101 (1978a).
Wahid, P. A., Sethunathan, N., *Soil Sci.* **126**, 56 (1978b).
Wahid, P. A., Sethunathan, N., *J. Agric. Food Chem.* **27**, 1050 (1979).
Ware, G. W., Roan, C. C., *Residue Rev.* **33**, 15 (1970).
Wurster, C. F., *Science* **159**, 1474 (1968).
Yamanaka, K., Motomura, S., *Soil Plant Food* **5**, 134 (1959).