Bull. Environm. Contam. Toxicol. 21,849-854 (1979)

Acute Toxicity of Dechlorinated DDT, Chlordane and Lindane to Bluegill *(Lepomis macrochirus)* and *Daphnia magna*[1]

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The disposal of cancelled or surplus organochlorine insecticides poses a serious threat to the environment. A major approach in detoxifying these materials has been through chemical degradation (MUNNECKE et al. 1976). DENNIS and COOPER (1975, 1976, 1977) extensively dechlorinated several technical grade insecticides in an alcohol medium by the catalytic action of nickel boride, Ni_2B, with an excess of sodium borohydride, $NaBH_4$. Dechlorination of *p,p*'DDT yielded a product mixture consisting principally of: 1,1-bis(*p*-chlorophenyl)-2-chloroethane; 1,1-bis-(*p*-chlorophenyl)-ethane; 1-*p*-chlorophenyl-1-phenylethane; and 1,1-diphenylethane. Technical grade chlordane yielded a mixture of partially dechlorinated products: the major one was 4,5,6,7,8-pentachloro-2,3,3a,4,7,7a-hexahydro-8-antihydromethanoindene, which contains five chlorine atoms. Lindane was completely dechlorinated to a mixture of benzene, cyclohexene and cyclohexane.

The purpose of the present study was to test the effectiveness of Ni_2B-catalyzed dechlorination in reducing the acute toxicity of DDT, chlordane and lindane to bluegill and daphnia.

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[1] The opinions or assertions contained herein are the private views of the authors and are not to be construed as official or as reflecting the views of the Department of the Army or the Department of Defense.

[2] This paper describes research that was completed by the senior author as partial fulfillment of the requirements for the M.A. degree, Hood College, Frederick, MD.

0007-4861/79/0021-0849 $01.20

MATERIALS AND METHODS

The following technical grade insecticides and formulations were studied: technical standard DDT (99+% *p,p'*DDT); emulsifiable concentrate DDT (25% DDT); Technical chlordane (60% chlordane, 40% related compounds); emulsifiable concentrate chlordane (72% active); technical standard lindane (100% lindane) and lindane dusting powder (1% lindane).

Stock solutions of technical grade chlorinated insecticides were prepared in acetone and formulations were suspended in water. Dechlorinated insecticides were prepared by first stirring together the insecticide or formulation, methanol and nickel chloride until all ingredients were dissolved; an aqueous solution of 8.7 molar sodium borohydride was then added dropwise over a period of 10-15 minutes while stirring continued. Insecticide, nickel chloride and sodium borohydride were used at a molar ratio of 1.0:0.5:26. Thirty milliliters of methanol were used per millimole of insecticide (DENNIS and COOPER 1975, 1976, 1977). Approximately 50 minutes after addition of sodium borohydride the reaction mixture was bioassayed. The pH of each mixture was approximately 10.7. In order to determine the toxicity of the $Ni_2B/NaBH_4MeOH$ system alone, a reaction mixture containing no pesticide was prepared.

Each insecticide was bioassayed before and after catalytic dechlorination. Bluegill and daphnia were exposed to five or more concentrations of each material in a static system. Toxicants were diluted with well water having a total hardness, as $CaCO_3$, of 192 mg/l; total alkalinity, as $CaCO_3$ of 138 mg/l; and pH of 8.2. Prior to each bioassay, test solutions containing high concentrations of dechlorinated insecticide were adjusted to pH 8.2-8.5 by addition of H_3PO_4. For daphnia bioassays, 60 animals (12 replicates x 5 animals) < 24 hr old were exposed for 48 hr to each test concentration at 20 ± 1°C. For bluegill assays, 20 animals (2 replicates x 10 fish) with average weight of 0.26 g and age of < 1 year were exposed for 96 hr to each test concentration at 19 ± 1°C. At the end of each exposure the concentration at which 50% of the animals survived (48 hr EC50 for daphnia, 96 hr LC50 for bluegill) was calculated (APHA 1971, FINNEY 1971, HARRIS 1959). A detoxification factor was determined for each dechlorinated insecticide by dividing the LC50 or EC50 of the dechlorinated insecticide by the LC50 or EC50 of the respective parent (untreated) insecticide.

RESULTS AND DISCUSSION

DDT

Catalytic dechlorination significantly reduced the toxicity of technical standard DDT and emulsifiable concentrate DDT to both species (Table 1). Greatest detoxification was achieved with the technical standard, probably due to the absence of emulsifiers. Of the two species, the greatest toxicity reduction was observed with bluegill.

On the basis of EC50's and LC50's, dechlorinated DDT was "moderately" (LC50 of 1-10 mg/l) to "highly" toxic (LC50 $<$ 1 mg/l) (HANN and JENSON 1973). However, nickel boride-catalyzed dechlorination might be useful if combined with other treatment processes, such as biodegradation. Biodegradability of the reaction mixtures could readily be determined by bench-scale activated sludge studies or by manometric techniques, and the degradation products bioassayed.

Chlordane

The toxicities of technical grade and emulsifiable concentrate chlordane (Table 1) were considerably reduced by dechlorination. With bluegill, technical chlordane was about 1.5 times more toxic than the emulsifiable concentrate. The same relationship was observed between the dechlorinated technical grade and the dechlorinated emulsifiable concentrate. Detoxification factors for technical grade and emulsifiable concentrate were almost identical. With daphnia, the same patterns were repeated. Detoxification factors were considerably lower than those achieved with DDT (Table 1). Dechlorinated chlordane was considered "highly" toxic (HANN and JENSON 1973). However, as with the DDT mixtures, the chlordane reaction mixtures should be tested for biodegradability in order to determine whether the reaction products would be amenable to biological treatment processes.

Lindane

Detoxification factors in Table 1 show that, with bluegill, the toxicity of technical standard lindane and of lindane dust was significantly reduced. Technical standard lindane was slightly more toxic than the dust formulation. Dechlorinated technical standard was similar in toxicity to dechlorinated dust.

TABLE 1

Acute Toxicity of Chlorinated and Dechlorinated Insecticides to Bluegill and *D. magna*

Insecticide	Species	Formulation	LC50 (μg/l)[a] and 95% Confidence Limits: Chlorinated	LC50 (μg/l)[a] and 95% Confidence Limits: Dechlorinated	Detoxification Factor[b]
DDT	Bluegill	Technical	3.4 (2.6-4.1)	3472 (2966-4065)	1021
		25% EC[c]	9.0 (7.4-10.6)	1519 (1283-1800)	169
	Daphnia	Technical	1.1 (1.0-1.3)	170 (157-185)	155
		25% EC	1.7 (1.5-1.8)	101 (94-108)	59
Chlordane	Bluegill	Technical	41 (35-49)	582 (550-612)	14
		72% EC	62 (53-72)	800 (600-1000)	13
	Daphnia	Technical	97 (87-107)	813 (750-872)	8
		72% EC	156 (142-171)	1174 (1087-1268)	8
Lindane	Bluegill	Technical	57 (52-61)	82,065 (73,189-92,018)	1440
		1% Dust	138 (120-155)	69,000 (55,980-93,300)	500
	Daphnia	Technical	516 (480-551)	19,342 (17,956-20,835)	37
		1% Dust	6442 (5597-7415)	13,054 (10,734-15,372)	2

[a] 96-hr LC50 for bluegill, 48-hr EC50 for daphnia; calculated on basis of insecticide present in formulation.

[b] $\text{Factor} = \frac{\text{LC50 dechlorinated}}{\text{LC50 chlorinated}}$.

[c] EC = Emulsifiable Concentrate.

With daphnids, the acute toxicity of untreated technical standard lindane (EC50 = 516 μg/l) was reduced 37-fold. The acute toxicity of the untreated dust formulation was relatively low (EC50 = 6442 μg/l), hence the low (2-fold) reduction in toxicity shown in Table 1. Actually, dechlorination reduced the toxicity of both materials to approximately the same level.

The toxicities of dechlorinated lindane reaction mixtures were closer to those of the $Ni_2B/NaBH_4/MeOH$ system itself than were the toxicities of DDT and chlordane mixtures (Table 2). However, some residual toxicity was apparently caused by lindane degradation products. Compared to the $Ni_2B/NaBH_4/MeOH$ system, the lindane reaction mixtures were approximately two times more toxic to bluegill and three times more toxic to daphnids.

TABLE 2
Toxicity of the $Ni_2B/NaBH_4/MeOH$ System Compared with Toxicity of Dechlorinated Insecticide Reaction Mixtures

Dechlorinated Insecticide Reaction Mixture	Median Lethal Concentration (ml/l)	
	Bluegill[a]	*D. magna*[b]
DDT Technical Standard	0.4	0.48
DDT Emulsifiable Concentrate	0.21	0.014
Technical Chlordane	0.14	0.20
Chlordane Emulsifiable Concentrate	0.20	0.29
Lindane Technical Standard	8.7	2.0
Lindane Dust	12.3	2.2
$Ni_2B/NaBH_4MeOH$ system	21.0	6.0

[a] 96-hr LC50.
[b] 48-hr EC50.

Dechlorinated lindane was considered "slightly" toxic (i.e., LC50's 10-100 mg/l) (HANN and JENSON 1973). Due to the presence of a small amount of benzene, the reaction mixture should be disposed of by burning or landfilling (FEDERAL REGISTER 1977).

CONCLUSIONS

The acute toxicity of DDT and chlordane formulations was considerably reduced by nickel boride-catalyzed dechlorination. However, the reduction in toxicity was not sufficient to warrant the use of this method for the ultimate disposal of these pesticides. The dechlorination of lindane by this method appears to have potential as a chemical disposal procedure.

REFERENCES

APHA: Standard Methods for the Examination of Water Wastewater. 13 ed. New York: American Public Health Assoc. 1971.

DENNIS, W.H. and W.J. COOPER: Bull. Environ. Contam. Toxicol. 14, 738 (1975).

DENNIS, W.H. and W.J. COOPER: Bull. Environ. Contam. Toxicol. 16, 425 (1976).

DENNIS, W.H. and W.J. COOPER: Bull. Environ. Contam. Toxicol. 18, 57 (1977).

FEDERAL REGISTER: 42, 22517 (1977).

FINNEY, D.J.: Probit Analysis. London: Cambridge U. Press 1971.

HANN, R.W., JR. and P.A. JENSON: Water Quality Characteristics of Hazardous Materials. Texas A&M University: Civil Engineering Dept. Circa 1973.

HARRIS, E.K.: Biometrics 15, 424 (1959).

MUNNECKE, D., H.R. DAY and H.W. TRASK: Review of Pesticide Disposal Research. SW-527. U.S. Environmental Protection Agency, Cincinnati, OH (1976).