Bull. Environm. Contam. Toxicol. 22,800-806 (1979)

Uptake and Excretion of Fenitrothion by Clams and Mussels

D. W. McLeese, V. Zitko, and D. B. Sergeant

Fisheries and Environmental Sciences, Fisheries and Oceans Canada, Biological Station, St. Andrews, New Brunswick E0G 2X0, Canada

This paper describes the uptake and excretion of fenitrothion by soft-shelled clams (Mya arenaria), mussels (Mytilus edulis) and freshwater clams (Anodonta cataractae). Fenitrothion has a relatively low uptake and a relatively high excretion rate constant and, consequently, a low accumulation coefficient in these species. The data indicate no danger of shellfish contamination from a normal application of fenitrothion.

The fate of organophosphate pesticides in aquatic biota has received little attention. Results of some laboratory studies are summarized in Table 1. Only for two cases (BENDER 1969, TAKIMOTO and MIYAMOTO 1976) was it possible to calculate the uptake and excretion rate constants according to the "one compartment model" of BRANSON et al. (1975), for comparison with the values given in this paper.

As can be seen from Table 1, the accumulation coefficients are relatively low, and the excretion rate constants are high, corresponding to half-lives of 0.3-8 days ($t_{1/2} = \ln 2/K2$).

These laboratory observations are supported by field studies. From the data of LUDWIG et al. (1968), the maximum accumulation coefficient of chlorpyrifos in oysters is about 77 and only traces of the compound are detectable after 2 days. Data of KINGSBURY (1978) show a decrease of the accumulation coefficient of fenitrothion in trout from 400 at 12 h after application to 84 at 72 h, when fenitrothion was applied to a small lake.

Accumulation coefficients calculated from field data have to be considered with caution, since a steady-state might not have been established (NEELY and BLAU 1977) but, in such a case, the coefficients would be over- rather than underestimated.

In addition to organophosphorus pesticides listed in Table 1, ethion and diazinon were detected in fish from areas with a high agricultural usage of these compounds (MILES and HARRIS 1978). Foschlor (STUDNICKA 1970), trichlorfon and DDVP (TELEUGALIEV and NURZHANOV 1973) were found in fish exposed in the laboratory. Residues of parathion, methyl parathion, carbophenothion, and ethion were occasionally detected in juvenile fish from estuaries in the United States (BUTLER and SCHUTZMANN 1978).

0007-4861/79/0022-0800 $01.40
© 1979 Springer-Verlag New York Inc.

Table 1. Uptake (K1) and excretion (K2) rate constants and accumulation coefficients (K1/K2) of organophosphate pesticides in aquatic fauna.

Pesticide	Species	K1[a]	K2[a]	K1/K2	Reference
Malathion	carp	1.07	0.08[b]	13	BENDER 1969
Methyl parathion	"			6[c] 1[c]	CHIGAREVA 1973
Parathion				325 70[d] 32[d]	YU and SANBORN 1975 HARSTED 1976
Fenitrothion	motsugo rainbow trout	88	0.4	170 220	KANAZAWA 1975 TAKIMOTO and MIYAMOTO 1976
Diazinon	motsugo			246 68[e] 9[f]	KANAZAWA 1975 " 1978 " 1978
Chlorpyrifos	rainbow trout			468	NEELY and BLAU 1977
Dimethoate				26	METELEV et al. 1977
Trichlorometaphos[g]				4	"
Methylnitrophos[h]				29	"

[a] in day^{-1}
[b] calculated from uptake data. Excretion data in the same paper give K2 = 1.26
[c] lipids and muscle, resp.
[d] liver, kidney and muscle, resp.
[e] fish
[f] invertebrates
[g] O-ethyl O-methyl O-(2,4,5-trichlorophenyl) phosphorothioate
[h] fenitrothion in mixture with the O-(5-methyl-2-nitrophenyl) isomer

The reviewed data as well as results presented in this paper support the recent conclusion that "organophosphates do not accumulate to any appreciable extent in any of the organisms present in the aquatic environment" (GREENHALGH 1978).

METHODS

Exposure and excretion experiments

Clams and mussels with valve lengths of about 6.5 and 5.0 cm, respectively, were exposed in sea water at 15°C to fenitrothion at average concentrations of 0.00018, 0.00043, and 0.013 mg/L in flow-through systems for 14 days. The animals were then transferred to another tank with clean flowing water for 28 days. Freshwater clams, valve length of about 7.0 cm, were exposed in fresh water at 12°C to fenitrothion at 0.00083 mg/L. To follow fenitrothion uptake, 3-5 animals were sampled at 0, 1 or 2, 4, 7, and 14 days. After transfer to clean water they were sampled at 1, 4, 7, 21 and 28 days.

Fenitrothion, provided by Forest Protection Ltd., Fredericton, N.B., placed in an 800-mL gas wash bottle was volatilized by bubbling compressed air. The air was conducted into a 20-L fibreglas tank containing sea water and 45 clams and 60 mussels or fresh water and 45 freshwater clams. Water flow to the tank was maintained at 0.5 L/min and fenitrothion concentration in the water was adjusted by regulating the amount of air bubbling through fenitrothion. Following the exposure, water flow was maintained at 3 L/min.

During the exposure period, water samples (100 mL) were taken at 1-3 day intervals. Fenitrothion was extracted by the method of PETERSON and ZITKO (1974). Extracts were dried by passing through 10 g anhydrous sodium sulfate, evaporated and brought to final volume in pesticide-grade acetone. Gas chromatographic analyses of fenitrothion were carried out on a Varian Model 3700 gas chromatograph equipped with an Aerograph ^{63}Ni pulsed electron-capture detector. The column was packed with 4% SE-30 on Chromsorb W and instrument temperatures were 170°, 156° and 300°C for injector, column and detector, respectively.

Analysis of bivalves

The clams or mussels were thawed, shucked and the excess water was drained off. The specimens were then ground with 6 times their weight of anhydrous sodium sulfate and 5-10 g of Ottawa sand in a mortar until homogeneous. The homogenate was transferred to a glass extraction thimble and extracted for 1 h with ethyl acetate in a Soxhlet. The extract was dried with sodium sulfate and reduced to 2-3 mL volume on a rotatory evaporator. Cyclohexane (10 mL) was added and the volume was again reduced to 2-3 mL. The extract was then transferred to a centrifuge tube and methylene chloride was added so that the extract

was 50:50 in methylene chloride-cyclohexane. The extract was transferred to a 2.5 x 32-35 cm Bio-Beads SX-3 (BioRad Laboratories) column, swollen overnight in a 50:50 mixture of methylene chloride and cyclohexane. The centrifuge tube was washed with 5 mL of this solvent. The column was percolated with the solvent mixture, collecting the first 80 mL of effluent as fraction A, and the subsequent 110 mL as fraction B. These fractions contain lipids and fenitrothion, respectively.

The amount of lipid in the extract was determined by evaporating solvent from fraction A on a rotatory evaporator and weighing the residue. Fraction B was evaporated to 2-3 mL on a rotatory evaporator, transferred to a 15-mL centrifuge tube, evaporated under a stream of nitrogen to 0.5 mL, and an aliquot was analyzed by gas chromatography.

A Perkin-Elmer 990 gas chromatograph with a Melpar flame photometric detector was used for the analyses. The detector was modified by the method of BURGETT and GREEN (1974) to prevent solvent flame-out. Two columns were used interchangeably for sample analysis and confirmation. A 3% OV-101 column was operated at 180°C and a 11% OV-17/QF-1 was operated at 200°C. Other chromatographic conditions were: injector point 200°C, detector manifold 250°C, and gas flow rates for the carrier, hydrogen, air and oxygen were 60-65, 200, 50 and 25 mL/min, respectively.

The average recovery of fenitrothion from spiked samples was 94%.

Fenitrothion was confirmed in some samples by gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

The concentration of fenitrothion in water during the exposure phase of the experiments remained reasonably constant, with a relative standard deviation of about 20% at 0.0133 mg/L and 35% at 0.00018 mg/L. Between 7 and 14 days of the experiment at 0.00043 mg/L, the dosing system malfunctioned. This was not detected by water analyses, but samples of clams and mussels, taken after 14 days of exposure, contained very high concentrations of fenitrothion (699 and 93.5 μg/g, respectively).

The concentration of fenitrothion in individual bivalves varied considerably during the exposure and clearance phases of the experiments (Fig. 1). These variations may be due partly to analytical errors, but the major cause is likely due to biological factors.

The uptake and excretion rate constants (K1 and K2, Table 2) indicate a relatively slow uptake and a high excretion rate, respectively. As a result, the accumulation coefficients (K1/K2) are relatively low.

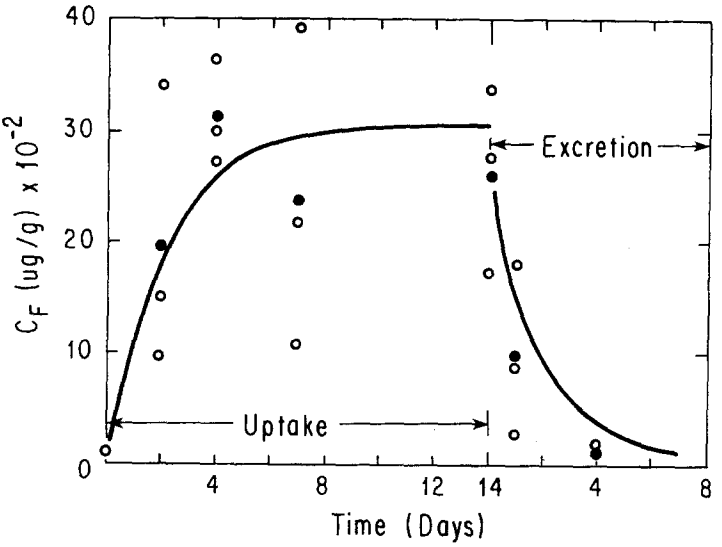

Fig. 1. Uptake and excretion of fenitrothion by clams. Individual analyses (○) and means (●) are indicated. The equation of the fitted curve is $C_F = 0.30 (1-\exp(-0.46t))$, where C_F = concentration of fenitrothion in clams, $\mu g/g$; t = time (days). Concentration of fenitrothion in water, C_W = 0.0133 mg/L, uptake rate constant, K1 = 10.34.

Table 2. Uptake (K1) and excretion (K2) rate constants and accumulation coefficients of fenitrothion in bivalves.

Species	Concentration (mg/L)	K1	K2	K1/K2
Clam (*Mya arenaria*)	0.013	10	0.46	22
	0.00043	19	0.55	35
	0.00018	12	0.62	19
Mussel (*Mytilus edulis*)	0.013	47	0.60	78
	0.00018	52	0.40	130
Freshwater clam (*Anodonta cataractae*)	0.00083	3	0.35	9

This result is not unexpected. The accumulation coefficient of fenitrothion in rainbow trout (Salmo gairdneri), calculated according to CHIOU et al. (1977) is 240, which agrees well with the experimental data of TAKIMOTO and MIYAMOTO (1976).

Because of the low accumulation coefficients in bivalves, concentrations of fenitrothion in water of about 0.01 mg/L or less are not likely to result in a significant contamination. On the other hand, an accidental spill of fenitrothion may cause considerable contamination.

Fenitrothion was excreted from clams, by accident highly contaminated in the laboratory, with a rate constant K2 = 1.39, but the excretion from mussels was biphasic with excretion rate constants K2 = 1.39 and K2 = 0.10, respectively. These data indicate that, even at high levels of contamination, fenitrothion is excreted relatively rapidly.

Following a spill in the field, pools of fenitrothion in sediments may maintain high concentrations of fenitrothion in a body of water for some time. As a result, the contamination of aquatic fauna would be longer lasting than indicated by the described experiments, but certainly would not be as persistent as contamination by some organochlorine compounds.

ACKNOWLEDGMENTS

We thank Messrs. C. Metcalfe, L. Burridge, and J. Pike for technical assistance. Mrs. Brenda McCullough typed the manuscript, Messrs. W. McMullon and F. Cunningham prepared the figure. Mrs. Ruth Garnett and Drs. D. Wildish and R. Peterson commented on the text.

REFERENCES

BENDER, M. E.: Prog. Fish-Cult. 31, 155 (1969).

BRANSON, D. R., BLAU, G. E., ALEXANDER, H. C., NEELY, W. B.: Trans. Am. Fish. Soc. 104, 785 (1975).

BURGETT, C. A., GREEN, L. E.: J. Chromatogr. Sci. 12, 356 (1974).

BUTLER, P. A., SCHUTZMANN, R. L.: Pestic. Monit. J. 12, 51 (1978).

CHIGAREVA, O. I.: Tr., Vses. Nauchno-Issled. Inst. Vet. Sanit. 46, 102 (1973); CA 84, 1015 (1976).

CHIOU, C. T., FREED, V. H., SCHMEDDING, D. W., KOHNERT, R. L.: Environ. Sci. Technol. 11, 475 (1977).

GREENHALGH, R.: J. Assoc. Offic. Anal. Chem. 61, 841 (1978).

HARSTED, B.: Nordforsk. Miljoevardssekr. Publ. 471 (1976); CA 87, 128390.

KANAZAWA, J.: Bull. Environ. Contam. Toxicol. 14, 346 (1975).

KANAZAWA, J.: Bull. Environ. Contam. Toxicol. 20, 613 (1978).

KINGSBURY, P. D.: Rept. FPM-X-13, Forest Pest Management Institute, Sault Ste. Marie, Ontario (1978).

LUDWIG, P. D., DISHBURGER, H. J., McNEILL, J. C., IV, MILLER, W. O., RICE, J. R.: J. Econ. Entomol. 61, 626 (1968).

METELEV, V. V., BRICHKO, V. F., KORZHEVENKO, G. N.: Veterinariya (Moscow) 100 (1977); CA 87, 926 (1977).

MILES, J. R. W., HARRIS, C. R.: J. Econ. Entomol. 71, 125 (1978).

NEELY, W. B., BLAU, G. E.: Pesticides in Aquatic Environments, M. A. Q. Khan, Editor, Plenum Press, New York, p. 145-163 (1977).

PETERSON, R. H., ZITKO, V.: Fish. Res. Board Can., Tech. Rep. 439, 40 p. (1974).

STUDNICKA, M.: Pol. Arch. Wet. 13, 107 (1970); CA 75, 73072 (1971).

TAKIMOTO, Y., MIYAMOTO, J. J.: J. Pesticide Sci. 1, 261 (1976).

TELEUGALIEV, T. M., NURZHANOV, I.: Vestn. Sel'sko-Khoz. Nauki Kaz. 109 (1973); CA 80, 2359 (1974).

YU, C. C., SANBORN, J. R.: Bull. Environ. Contam. Toxicol. 13, 543 (1975).