ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY 16, 65–71 (1988)

Review of the Environmental Toxicity of Quaternary Ammonium Halides

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Received March 6, 1987

This paper summarizes all available information on the environmental toxicity of quaternary ammonium compounds (QACs). Ten-minute contact kills of bacteria occur at 50–333 mg/liter. These chemicals are acutely toxic at approximately 1 mg/liter to invertebrates and fish and toxicity is occasionally as low as 0.1 mg/liter; no-effect levels are generally 10 times lower than LC_{50} values. Toxicity to invertebrates and fish appears to be relatively independent of structure; the compounds studied, which have a large variety of structures, are all toxic at approximately the same order of magnitude. The QACs tested inhibited plant growth at 3–5 mg/liter. Predictions of toxicity to QACs are made based on knowledge of structure–activity relationships.

INTRODUCTION

Halides of quaternary ammonium compounds (QACs) are an important class of industrial chemicals with a wide range of commercial and consumer uses. U.S. production of QACs was estimated at 100 million pounds in 1979 (SRI, 1981). Much of the production (55–60 million pounds) is used in fabric softeners and in drilling muds (23 million pounds), with the remaining production used as biocides, sanitizers, disinfectants, hair conditioners in shampoos and cream rinses, emulsifying agents, and constituents of room deodorizers.

Most of the use of these chemicals is expected to lead to a release to the environment. While there has been an extensive review of the effects of these chemicals on wastewater treatment facilities (Boethling, 1984), it is surprising that there is no comprehensive review of the environmental toxicity of these chemicals. In addition, there appears to be sufficient literature to make predictions from structure about the potential toxicity of new members of this group. This paper reviews environmental toxicity of the QACs and presents a discussion of their structure–activity relations.

ENVIRONMENTAL TOXICITY

Effects of QACs on Microorganisms

Quarternary ammonium halides have the general formula $R_4N^+X^-$, where four organic groups are covalently bonded to nitrogen, and the positive charge is balanced by a halide ion. The antibacterial properties of QACs are well known and have been studied extensively (Sexton, 1963; Lawrence, 1970). Ten-minute contact kills occur

TABLE 2

COMPARISON OF SPECIES' SENSITIVITY TO HIGH-MOLECULAR-WEIGHT ALKYLDIMETHYLBENZYLAMMONIUM CHLORIDES (OR OTHER QACs AS NOTED)

Species (group)	Toxicity	Reference
Australorbis glabratus (mollusk)	10 mg/liter, 100% mortality	Pessoa (1952)
Culex quniquefasciatus (mosquito)	10 mg/liter, killed eggs and larvae; 1 mg/liter, "reduced" no. of larva	Taft and Strandtmann (1954)
Aedes aegypti (mosquito)	4 mg/liter, killed 80% of larvae and prevented maturity of the remainder	Taft and Strandtmann (1954)
Balanus (barnacle)	2.5 mg/liter, no effect; 25–100 mg/liter, interfered with development	Taft (1946)
Euglena (Protozoa)	20 mg/liter, 100% mortality in 19 hr	Taft (1946)
Rotifers	1 mg/liter, 100% mortality in 19 hr; 10 mg/liter, 100% mortality in 2 hr	Taft (1946)
Amphipoda	2.5–10 mg/liter, 100% mortality in a few hours	Taft (1946)
Cyprids (ostracods or "mussel-shrimp")	25 mg/liter, active after 5 hr	Taft (1946)
Planaria (flat worm)	10 mg/liter, 100% mortality in 1 hr	Taft (1946)
Ascaris (roundworm)	20 mg/liter, "alive" 18 hr later	Taft (1946)
Enchytrae albidus (Annelid)	1 mg/liter, 100% mortality in 4 hr or less	Taft (1946)
Asteroidea (starfish, Echinodermata)	2.5 mg/liter, 100% mortality in 24 hr	Taft (1946)
Crepidula (gastropod)	100 mg/liter, 100% mortality in 50 min	Taft (1946)
Australorbis glabratus (mollusk)	1 mg/liter, 0–80% mortality	Vallejo-Freire (1954)
Poecilia vivipara (guppy), *Lebistes reticulatus* (fish)	"The limit of activity is almost the same both for fish and molluscs"	Vallejo-Freire (1954)
Rasbora heteromorpha (harlequin fish), *Salmo truta* (brown trout), *Leciscus idus* (golden orfe, minnow), and *Carrasus auratus* (goldfish)	Mean LC_{50} values to cationic detergents 2.04–3.51 mg/liter	Reiff *et al.* (1979)

mg/liter, with some exceptions. Annelides and rotifers, for example, appear to be the most sensitive species and were killed in 4 hr or less and in 19 hr, respectively, at a concentration of 1 mg/liter. Assuming the dose/response toxicity curve is similar to that for other species (as demonstrated by data in Table 4), no-effect levels may occur at 0.01 mg/liter. Mysids and copepods were also sensitive (see below and Table 3). This sensitivity may be extremely important in the environment, since these species are important members of aquatic food chains. They may be lost due to chemical

TABLE 5

ACUTE TOXICITIES 96-hr (LC_{50} VALUES) TO BLUEGILL (*Lepomis macrochirus*) AND RAINBOW TROUT (*Salmo gairdneri*) OF PESTICIDAL QACs (ENGLER, 1982)

Chemical type	Mean toxicity	
	Bluegill	Trout
Alkyldimethylbenzylammonium chloride and dialkyldimethylbenzylammonium chloride	0.33	0.71
Alkyldimethylbenzyl- (and ethylbenzyl-) ammonium chloride	0.42	1.25
Alkyldimethylammonium chloride	0.51	0.56
Dialkyldimethylammonium chloride	0.59	1.10
Alkyldimethyldibenzylammonium chloride	0.64	2.45
Dialkyldimethylammonium chloride	0.59	1.10
Alkyldimethylbenzylammonium chloride	0.64	2.45
Alkyltrimethylammonim acetate	0.65	0.34
Alkyldimethylbenzyl- (and ethylbenzyl-) ammonium chloride	0.83	1.36
Alkyldimethyldichlorobenzylammonium chloride	0.84	—
Trimethylammonium chloride	0.96	1.32
Alkylbenzyltrimethylammonium chloride	1.20	—
Alkyldimethylbenzyl- and ethylbenzylammonium chloride	1.40	2.10
Alkyl- and dialkyldimethylammonium chloride	1.44	—
Substituted imidazolinium chloride	2.30	7.60
Alkyldimethylbenzylammonium chloride	2.35	7.80
Alkyldimethylnaphthylmethylammonium chloride	3.23	12.30
Alkylbenzyltrimethylammonium chloride	4.50	10.50
Dialkyldimethylammonium chloride	5.90	—
Alkyldimethylnaphthylmethylammonium chloride	—	5.10
Mean toxicity	1.65	3.80

QACs] is almost the same both for the fish and mollusk" that he tested (Table 2). Reiff *et al.* (1979) found that the mean values for the 48-hr LC_{50}'s of four species of fish were 2.06–3.51 mg/liter (Table 3). In these tests, the brown trout (*Salmo trutta*) was more sensitive than the golden orfe and harlequin fish, which were more sensitive than the goldfish (*Carrasius auratus*); mean 48-hr LC_{50} values were 1.69, 3.33, 3.58, and 6.75 (6-hr value), respectively.

A further approximation of the range of toxicity of quaternary compounds can be obtained in a study on cationic polyelectrolytes (Biesinger *et al.*, 1976). These compounds are high-molecular-weight cationic surfactants, a chemical class of which the QACs also are members. The four compounds studied exhibited LC_{50} values in the range 0.29–218 mg/liter (Table 4). Mysids and copepods were more sensitive than the fish and daphnid tested and had LC_{50} values of 0.50 and 0.29 mg/liter, respectively. However, as with other QACs tested, most LC_{50} values were over 1 mg/liter. No-effect levels for these species are expected to be near 0.05 and 0.029 mg/liter, respectively, since LC_{50} values for QACs are generally one order of magnitude higher than no-effect levels.

About 4000 QACs are registered under the auspices of United States FIFRA (pesticide) Act (Engler, 1982). It appears from a representative set of data for these compounds that the structure of these quaternary compounds does not appear to significantly affect their acute toxicity to fish (Table 5). A review of compounds with a large

ACKNOWLEDGMENT

I thank Elizabeth Dreyer for clerical assistance.

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