Simazine Residue Dynamics in Small Ponds

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Herbicides are important aids in enhancing sport fishing, fish removal, and other recreational uses of lakes and ponds. Simazine, 2-chloro-4,6-bis(ethylamino)-s-triazine, has been tested for several years as an experimental aquatic herbicide and has been shown to be effective in controlling aquatic plants in many different situations (FLANAGAN, 1960; SNOW, 1964; SUTTON et al., 1965; WALKER, 1964; and WILE, 1967). The present federal registration proposal states that "ponds should be treated before 10 to 20% of the surface is covered with pond scum (algae mats) and/or while submerged aquatic weeds are actively growing and before they reach the surface of the water." However, the application of herbicides before aquatic vegetation begins growing in the spring, minimizes problems associated with the biological oxygen demand of dying plants. Simazine residues disappear rapidly when aquatic plants are present (SUTTON, 1965), but before this systemic herbicide can be registered for pre-emergent aquatic vegetation use, its residual effects in aquatic ecosystems must be evaluated. Therefore, we monitored and evaluated simazine residues in the substrate (mud), water, benthic invertebrates, and fish for more than 2 years after the herbicide was applied at four rates in early spring.

Materials and Methods

Five physically and biologically similar 0.1-ha (0.25 acre) ponds at the Fish-Pesticide Research Laboratory, near Columbia, Missouri, were used in the study. The maximum pond depth was 1.5 m, and the pond bottoms were primarily clay with a thin layer (about 1 to 2 mm) of organic detritus. Each pond was drained and refilled with well water having the following characteristics: alkalinity, 260 mg/l as $CaCO_3$; pH, 8.4; dissolved oxygen, 12 mg/l; and transparency, 1.5 m (maximum pond depth). Because the ponds were relatively sterile, each was fertilized with 44 kg cottonseed meal per ha (240 lbs/acre) on March 21, 1970. Each pond was then stocked with 250 sub-adult bluegills (Lepomis macrochirus).

An 80% wettable powder formulation of simazine (Princep^R 80W, Ciba-Geigy Corp.) was applied for pre-emergent control of aquatic

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vegetation to four of the ponds on March 29, 1970, and April 2, 1971; the fifth pond was the control. No aquatic vegetation was observed on the first application date, but an alga (Rhizoclonium hieroglyphicum) was present in all but the most heavily treated pond on the second application date. The chemical was thoroughly mixed with the pond water to give estimated simazine (active ingredient) concentrations (µg/ml) of 0.1, 0.3, 1.0 or 3.0 in the four treated ponds. The application concentrations recommended by the manufacturer range from 0.5 to 2.5 µg/ml.

Samples of mud, water, benthic invertebrates, and fish were obtained at intervals irregularly spaced over about a 2 year period. Mud (a core 7.6 cm long x 5.1 cm wide) was collected with a core sampler described by HOLZ et al. (1972); water samples (600 ml) were taken just below the water surface with B.O.D. bottles; benthic invertebrates were collected with an Eckman dredge (15.2 x 15.2 cm); and fish were sampled either by trapping or angling. The samples of mud, invertebrates, and fish were preserved by freezing for later chemical residue analysis. Water samples were analyzed immediately after collection.

Residues were analyzed largely by methods suggested by HESSELBERG and JOHNSON (1972) and JOHNSON (1972). Water samples were extracted with methylene dichloride and the extracts were dried with anhydrous sodium sulfate. Toluene was added to each extract and then evaporated to 1-5 ml for analysis. Samples of mud, invertebrates, and fish were ground, weighed, and mixed with four times their weight of anhydrous Na_2SO_4. The mixture was poured into a glass extraction column plugged with glass wool at the base, and the simazine was extracted with diethyl ether. The extracts were evaporated to about 2 ml and transferred in benzene to a Florisil column, eluted with diethyl ether in petroleum ether, and evaporated to a small volume. Benzene was added to give the desired volume for analysis by gas-liquid chromatography with an alkali flame ionization detector. The GLC column used was 2.1 m x 2 mm ID, packed with 80-100 mesh Chromasorb W.H.P. coated with 3% OV-225. The GLC column temperature was 200 C and the helium carrier flow was 30 ml/min. The minimum detection limits for mud, water, invertebrates, and fish were 1.0 ng/g. 10 ng/ml, 10 ng/g, and 1.0 µg/g, respectively.

Results

The amount of simazine in the pond mud was directly related to application rates (Table 1). Simazine residues declined in all treated ponds after the 1970 application, but were still present in reduced quantities after 346 days. The concentrations plateaued in 29 to 45 days after application of 1 and 3 µg/ml simazine. At about equal post-treatment intervals, concentrations were 2 to 8 times higher after the 1971 treatment than after the 1970 treatment. Simazine concentrations appeared to plateau at 40 days after the 1971 application. Residues were still detectable in all of the treated ponds 456 days after the 1971 application.

Table 1. Concentration of simazine residues (µg/g) in mud from four ponds at successive intervals after treatment with simazine at 0.1, 0.3, 1.0, or 3.0 µg/ml on March 29, 1970 and April 2, 1971. (ND = not detectable. Simazine was not detectable in any sample taken from an untreated control pond during the 27-month period.)

Time after treatment (days)	Treatment concentration (µg/ml) 0.1	0.3	1.0	3.0
-2	ND	ND	ND	ND
March 29, 1970----Simazine applied----				
1	ND	0.18	0.45	3.4
8	ND	0.037	0.42	8.2
15	ND		1.2	1.4
29	0.037	0.029	0.085	2.0
45	0.005	0.012	0.087	0.42
91	0.003	0.007	0.042	0.25
114	0.013	0.010	0.17	0.69
134	0.007	0.053	0.13	1.0
155	0.003	0.020	0.066	0.18
176	0.002	0.023	0.13	0.26
197	0.003	0.022	0.12	0.23
220	0.005	0.026	0.085	0.26
246	ND	0.017	0.048	0.25
326	0.005	0.025	0.14	0.29
346	0.002	0.045	0.066	0.32
April 2, 1971----Simazine applied----				
5	0.037	0.13	0.26	8.2
15	0.015	0.12	0.64	11.
28			1.9	6.4
40	0.045	0.061	0.53	3.2
55	0.032	0.017	0.21	2.9
81	0.034	0.061	0.18	0.48
99	0.042	0.11	0.69	1.3
110	0.013	0.079	0.56	1.2
123	0.029	0.093	0.48	0.95
138			0.058	
164	0.004			0.22
193	0.009			0.015
456	<0.001	0.010	0.012	0.16

Concentrations of simazine residues in water, like those in mud, were directly proportional to the rates of application (Table 2). In general, the residues were somewhat lower in water than in mud, and seldom exceeded one-third to one-half the total calculated amount applied. Simazine was still present in water 1 year after the first application and 456 days after the second application. The rates of dissipation of residual simazine in water and in the substrate were parallel. However, more simazine was present in the water on windy than on calm days; we believe this difference was due primarily to the mixing of water and mud.

The invertebrates available for sampling consisted primarily of dragonfly nymphs and midge larvae in the control pond and the ponds treated with 0.1 and 0.3 µg/ml, and mayflies (Hexagenia sp.) in the ponds treated with 1.0 and 3.0 µg/ml. Simazine residues in these benthic invertebrates were also directly proportional to the amounts applied, but usually far exceeded those in water for at least 86 days after the 1970 application (Table 3). Between 86 and 114 days after this application, residues in invertebrates declined sharply -- expecially in the pond treated at the rate of 3.0 µg/ml. This decline was not apparent until 193 days following the 1971 treatment. Simazine residues in invertebrates sampled in 1971 were comparable to or less than residues in invertebrates taken at similar intervals after the 1970 treatment, and gave little evidence of bioaccumulation. For example, simazine residues in invertebrates taken from the most heavily treated pond were 1.3 µg/g in October 1970 and 1.5 µg/g in October 1971. Simazine residues had declined to almost undetectable limits 456 days after the final application. Simazine treatments or residues appeared to have no adverse effects on survival of invertebrates.

Simazine was present in fish from all the treated ponds up to 1 year after the initial application (Table 4), but rapidly declined between 142 and 176 days after treatment. In both 1970 and 1971, this decrease was evident in the 1- and 3- µg/ml treatments. Residue concentrations were highest immediately after simazine application in both years. Very little simazine accumulated in fish tissue after 2 consecutive years of application, although it was detectable in fish throughout the post-treatment period of observation. Residues in bluegills did not cause any observable adverse effect.

Discussion

Bioaccumulation of simazine was evident only in invertebrates for the first 86 days although some simazine was present in fish and invertebrates for at least 1 year. In general, simazine residues in water, invertebrates, and fish were similar to or less than treatment concentrations. Residual simazine in fish generally did not exceed that in water from which the fish were taken. RODGERS (1970) stated that simazine residues in bluegills disappeared 7 days after the fish were transferred to fresh water.

The persistence of simazine in mud, water, benthic inverte-

Table 2. Concentration of simazine residues (µg/ml) in water from four ponds at successive intervals after treatment with simazine at 0.1, 0.3, 1.0, or 3.0 µg/ml on March 29, 1970 and April 2, 1971. (ND = not detectable. Simazine was not detectable in any samples taken from an untreated control pond during the 27-month period.)

Time after treatment (days)	Treatment concentration (µg/ml) 0.1	0.3	1.0	3.0
-2	ND	ND	ND	ND
March 29, 1970----Simazine applied----				
1	0.02	0.10	0.45	0.87
3	0.05	0.23	0.42	0.58
8	0.07	0.18	0.37	0.65
29	0.05	0.17	0.48	0.86
45	0.02	0.04	0.22	0.66
50	0.02	0.12	0.29	0.52
72	0.02	0.05	0.25	0.59
91	0.02	0.05	0.32	0.62
114	0.02	0.11	0.30	0.50
134	0.01	0.04	0.32	1.0
155	0.01	0.05	0.22	0.74
176	0.01	0.08	0.30	1.2
197	0.01	0.04	0.19	0.45
220	<0.01	0.02	0.21	0.52
246	<0.01	0.02	0.11	0.16
346	<0.01	0.03	0.09	0.14
April 2, 1971----Simazine applied----				
5	0.11	0.66	0.90	1.2
18	0.12	0.28	1.4	2.1
28	0.11	0.36	1.4	2.5
40	0.13	0.34	1.5	2.2
54	0.15	0.35	1.5	3.3
81	0.08	0.20	0.94	1.2
99	0.07	0.25	1.0	2.0
110	0.07	0.21	1.0	2.6
123	0.03	0.13	0.65	1.7
138	0.06	0.20	0.82	2.2
165	0.07	0.22	0.90	2.4
193	0.06	0.20	1.2	2.5
456	0.01	0.07	0.42	0.50

Table 3. Concentration of simazine residues (µg/g) in benthic invertebrates from four ponds at successive intervals after treatment with simazine at 0.1, 0.3, 1.0, or 3.0 µg/ml on March 29, 1970 and April 2, 1971. (ND = not detectable. Simazine was not detectable in any samples taken from an untreated control pond during the 27-month period.)

Time after treatment (days)	Treatment concentration (µg/ml) 0.1	0.3	1.0	3.0
-2	ND	ND	ND	ND
March 29, 1970----Simazine applied----				
3	ND	1.2	2.7	27
8	ND	ND	1.8	60
15	ND			14
29	0.20	0.50	1.7	13
86	0.03	0.20	0.70	21
114	0.03	0.08		0.80
142		0.09	0.90	2.4
176		0.10	0.20	0.90
197		0.06	0.20	1.3
367		0.04	0.10	
April 2, 1971----Simazine applied----				
40	ND	ND	2.0	10
55	ND	ND	0.70	5.0
83	ND	0.50	2.1	2.5
110	0.07	0.07	0.90	6.5
123	ND	ND	0.20	2.2
138	ND	0.09	0.40	2.0
193	ND	ND	0.90	1.5
456	<0.01	<0.01	0.02	0.05

Table 4. Concentrations of simazine residues (µg/g) in bluegills (Lepomis macrochirus) from four ponds at successive intervals after treatment with simazine at 0.1, 0.3, 1.0, or 3.0 µg/ml on March 29, 1970 and April 2, 1971. (ND = not detectable. Simazine was not detectable in any samples taken from an untreated control pond during the 27-month period.)

Time after treatment (days)	Treatment concentrations (µg/ml)			
	0.1	0.3	1.0	3.0
-2	ND	ND	ND	ND
March 29, 1970----Simazine applied----				
1	0.86	0.49	0.95	2.0
3	0.05	0.29	0.17	0.52
8	0.08	0.11	0.69	0.89
15	0.04	0.09	0.27	0.67
29	0.05	0.11	0.20	0.61
86		0.03	0.06	0.80
114			0.18	0.47
142		0.03	0.55	0.72
176		0.01	0.01	0.13
197		<0.001	0.04	0.11
367	0.01	0.03	0.35	0.30
April 2, 1971----Simazine applied----				
31		0.33	1.4	1.6
110	ND	ND	0.42	0.61
143	ND	ND	0.004	0.041
456	ND	ND	0.006	0.049

brates, and fish could have been related to the lack of vegetative material present at treatment times. SUTTON (1965) stated that simazine residues in the water immediately after treatment seemed to decrease more rapidly in ponds that had a heavy growth of aquatic plants than in ponds with only a light growth. In the present study, ponds were treated with simazine early in spring before vegetation began to grow, and because of the lack of aquatic vegetation, simazine residues were probably greater and persisted longer than would occur if the herbicide had been applied according to recommended practices.

The use of simazine as a pre-emergent herbicide for aquatic vegetation control has excellent possibilities in fishery management for manipulation of vegetative cover. No harmful effects resulting from chemical persistence were observed during the 2 years of testing.

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