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Cyanatryn: Degradation and Effectiveness in Controlling Aquatic Plants

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Many ponds and small lakes in Ontario that were free of aquatic vegetation two decades ago are now covered with dense mats of algal blooms, and associated submersed and emerged aquatic plants. These plant growths have been promoted by increased nutrient levels and especially those nutrients that were limiting in the past. While programs are underway to stem the influx of nutrients into water bodies, these actions will take effect only in the long term. Under a provincial approved aquatic nuisance control permit herbicides have been field tested to provide short term measures for controlling excessive plant growth. One herbicide tested under this program was cyanatryn, 2-(1-cyano-1-methylethylamino)-4-ethylamino-6-methylthio-1,3,5-triazine. This paper reports on the efficacy of this herbicide in aquatic plant control and on the degradation in samll ponds in Southern Ontario.

MATERIALS AND METHODS

Three small, shallow ponds were selected for testing the efficacy of cyanatryn in controlling aquatic plants. The ponds were chosen because none had an appreciable outflow, all had constant water volume through the season, from underground springs and/or normal precipitation, none contained fish, and all were infested with aquatic macrophytes and algae. The details of the three ponds appear in Table 1 and all were treated with an attaclay granular formulation containing 10% cyanatryn. Application was done manually from a boat by scattering an amount over the surface to give a potential concentration of 200 ug/L. The rate of application was in keeping with that recommended by the British

Agrochemicals Association (Anon. 1976). At the time of application water temperatures and dissolved oxygen levels were recorded, the latter was determined using a portable Hach kit. Aquatic plant densities were determined by making quadrant counts of stems per m^2. Algal control was evaluated by changes in the percent surface coverage in pre and post treatment assessments.

Table 1. Details on three ponds treated with cyanatryn

Items	Pond #1 York County	Pond #2 Muskoka District	Pond #3 York County
Location (nearest city)	King City	Huntsville	King City
Surface Area (m^2)	422	657	805
Mean Depth (m)	2.00	1.75	2.05
Water Volume (m^3)	844	1150	1743
Cyanatryn (g a.i. per pond)	170	230	350
Date of Treatment	June 14	June 11	June 22

Pond 1, the smallest of the three bodies of water, was located near King City, York County on a loam belonging to the gray-brown podzolic group of soils. The surface of the pond was 60% covered by mats of filamentous algae (Cladophora spp.) and 35% Drepanocladus spp. (aquatic moss). Chara spp. (270 plants per m^2) occupied 9 m^2 of water surface in the deeper water. Some cattails (Typha spp.) were present around the periphery. Initial temperatures in the pond were 23C for surface and 21C for bottom waters while dissolved oxygen was 15 ppm at the surface and 10.5 ppm at the bottom. In order to give a potential concentration of 200 ug cyanatryn/L 170 g of active ingredient were applied to the surface on June 14, 1976 (Table 1).

Pond 2, located near Huntsville in the District Municipality of Muskoka was sited in the Canadian Shield. The Shield is a huge area of Precambrian granite rock covering Northern Canada where a thin layer of soil supports conifer forests and where the land is interspersed with a large number of lakes generally classed as oligotrophic to slight mesotrophic. Pond 2 contained exclusively stonewart (Nitella spp.) which covered 50% of the pond surface with a density of 380 plants/m^2 . Based on the calculated water volume, 230 g of cyanatryn (a.i.) was scattered over the pond surface on June 11 (Table 1).

Pond 3 was the largest of the ponds (Table 1). Vegetation included narrowleaf pondweed (Potamogeton strictifolius penn.) present at densities of 100 plants /m^2 and growing over 50% of the surface area, together with filamentous algae (Cladophora spp.) and muskgrass (Chara vulgaris L.) occupying 5% and 3.5% of the surface respectively. Initial water clarity was excellent (secci disc reading was 2.05). Initial temperatures in surface and bottom waters were 22C and 21.5C respectively while dissolved oxygen levels were 10.5 and 9.3 ppm. On June 22 350 g of cyanatryn (a.i.) were applied to the surface of Pond 3 to give the potentially desired 200 ug/L concentration.

For analysis of cyanatryn, composite water and sediment samples were collected at spaced intervals between 0 and 70 days after treatment. For water samples, a composite (1L) representing the entire water column was obtained by lowering an empty narrow-necked jar to the bottom and then raising it at a measured rate to entirely fill just as it reached the surface. Sediment samples were collected using a standard 15 cm square brass Eckman dredge which collected the top 5 cm. Samples were transported to the laboratory within 24 hours of collection.

The method followed was only a slight modification of that described by Ramsteiner et al. (1974) and Sirons et al. (1973). Dried sediments and plant tissues were prepared and extracted as described for soils by Sirons et al. (1973). Water (1.0 L) was extracted with two successive 100 mL portions of chloroform after adjusting the pH to 9 with dilute ammonia to improve extraction. The chloroform extract was dried by passage through dry absorbent cotton and the combined extracts were evaporated to about 2 mL; 10 mL of iso-octane was added and further evaporated to dryness. The dried extract was taken up in methanol.

Cyanatryn was measured by gas-liquid chromatography (GLC) using a column packed with 5% Carbowax 20M on 80/100 mesh Varaport 30. The column temperature was 210C. The carrier gas was helium flowing at 50 mL/min. The gas-liquid chromatograph was equipped with a Coulson conductivity cell operated in nitrogen mode. The detection limit was 0.04 u/L.

Cyanatryn was recovered from spiked samples with an 80 to 90% efficiency. Analytical results were presented uncorrected for recoveries.

RESULTS AND DISCUSSION

By day 8 Cladophora and Drepanocladus spp. in Pond 1 had turned brown and settled on the pond floor while Chara spp. were not visibly affected. By day 16, Chara spp. had turned brown and fragmented. No live aquatic vegetation was present on day 28 through day 70. Pond temperatures throughout the study period ranged from 22-26°C at the surface and 21-23°C at the bottom. Dissolved oxygen levels declined rapidly throughout the water column to lows of 2.4 ppm (top) and 0.2 (bottom) at day 22. Recovery by day 70 was only marginal (Table 2).

In Pond 2, all the Nitella spp. (except approximately 10% in the deeper pond area) had turned brown or black and decomposed. No live vegetation was observed at 29 through 57 days after treatment.

In Pond 3, P. strictifolius exhibited signs of chlorosis by day 8. By day 14, all the pondweeds lay lateral on the pond floor brown and decomposing. The first onset of necrosis in Chara was observed on day 14. By day 28 no live stems could be found. Cladophora spp. were reduced to approximately 30% of their critical growth by day 8 and by day 14 post treatment all filaments appeared to have settled on the bottom of the pond and had decomposed (Table 2).

In Pond 1, cyanatryn residues in water were found to peak on day 22 with 153 ug/L and decline to 92 ug/L by day 70. Cyanatryn levels in sediment were found to be highest at day 3, 5.8 mg/L and decline to 3.5 mg/L by day 70. The high SD values were deemed attributed to the inclusion or exclusion of one or two undissolved granules in the replicated sediment samples (Table 2).

In Pond 2, cyanatryn residue levels in water peaked by day 29 (26.2 ug/L) and declined to 15.5 ug/L by day 57 (Table 3). Sediment sampling in this pond proved impossible due to the thin soil layers over the granite substrate; therefore the extremely low value found on day 29 can be possibly explained by the difficulty in trapping undissolved granules (in sediment with the Eckman sampler).

In Pond 3, the highest cyanatryn level was found on the last sampling day i.e. 117 ug/L on day 62.

Table 2. Balance sheet in water and sediment of cyanatryn

Day After Application	Dissolved Oxygen (ppm)		Cyanatryn In Water (ug/L)		(g)	Cyanatryn in Sediment (Dried) (ug/kg)		(g)	Cyanatryn Total Amount Present (g)
	Surface	Bottom	Mean	SD		Mean	SD		
Pond 1 - King City									
0	14.7	10.5	ND	-	0	ND	-	0	0
1	12.5	10.3	3.6	2.1	3	220	130	2	5
3	7.5	6.7	34	2.8	29	5880	6400	61	90
8	3.0	0.4	95	28	81	3700	4700	51	132
16	2.5	1.5	151	18	127	3500	4600	49	176
22	2.4	0.2	153	17	129	2500	1400	35	164
70	2.8	1.8	92	32	78	3500	3000	49	127
Pond 3 - King City									
0	10.5	9.3	ND	-	0	ND	-	0	0
2	8.3	5.2	8.9	9.4	16	62	85	6	22
8	4.0	0.4	50	20	87	3330	2088	240	327
14	4.5	0.0	93	35	162	590	820	43	205
28	6.8	1.0	94	15	164	210	197	15	179
62	7.4	2.4	117	25	204	502	309	37	241

Table 3. Pond 2 located at Huntsville and treated with cyanatryn June 11, 1976

Days After Application	Cyanatryn in Water ug/L		g	Days After Application	Cyanatryn in Water ug/L		g
0	0.2[1]	d	0.2	29	26.2[1]	a	30
3	13.0	b	15	35	9.5	c	11
7	18.6	a,b	21	39	10.0	c	11
10	18.6	a,b	21	57	15.5	b,c	18

[1]Cyanatryn levels in sediment on day 0 were not detected and 20 ug/kg on day 29

The highest sediment residue value was found on day 8 post treatment at 3330 ug/kg and this declined to 502 ug/kg by day 62.

In all three ponds the cyanatryn concentrations in water were considerably lower than the intended 200 ug/L, nevertheless the concentrations produced were strongly herbicidal. According to Scorgie (1980) it took approximately three months to obtain the intended concentration of 200 ug/L in a treated drainage channel. In two of our three ponds cyanatryn concentrations in water did increase over the study period - 62 and 70 days but only attained maximum levels of 117 and 153 ug/L respectively.

The efficacy of cyanatryn in controlling vascular macrophytes, especially Potamogeton strictifolius in a closed pond system was excellent at actual concentrations ranging from 50 to 150 ug/L. In fact these concentrations were non selective being equally effective on all species of Cladophora, Nitella and Chara and within 14 to 28 days of treatment. This created a difficulty in pond management in that adequate dissolved oxygen levels could not be sustained and recovery to levels of 2.5 ppm dissolved oxygen took at least 60 days.

Cyanatryn residues in water appeared to increase over the test period and the fluctuations were not taken as an indication of a decline in residues. In sediment residues in Ponds 1 and 3 appeared to peak on days 3 and 8 respectively. Unfortunately half-life disappearance of cyanatryn in sediment was not possible from the limited data collected and because

of the slowness for the herbicide to become dissolved in the water column. In the sediments the mean concentrations of cyanatryn appeared to change little once the dissolved oxygen concentrations in bottom waters declined to less than 1 ppm. This implied that aerobic microbiological degradation, which may play a role in cyanatryn degradation, was halted.

Before cyanatryn is considered for aquatic plant control more research is needed on its persistence and impact on the total aquatic ecosystem.

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