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Acute Toxicity of Cyanate to *Daphnia magna*

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The regulation of cyanides discharged into streams and waterways is complicated by the controversy over what to regulate. The major question is whether to measure total cyanide (free plus complex forms) or some specific cyanide form. DOUDOROFF (1977) argued after the publication of the EPA quality criteria for water (1976) that water quality standards for cyanide should be based on free cyanide (HCN plus CN^-). This approach places major emphasis on the most toxic form of cyanide (HCN) but does not account for less toxic forms in waterways, which may convert under environmental conditions to free cyanides. The recommended criterion for cyanide published in EPA's Water Quality Criteria (1976) was for total cyanide. This conservative approach to cyanide regulation provides the greatest degree of protection but is also the most expensive. Recently the EPA has apparently changed their position as the proposed water quality criteria for cyanide as published in the July, 1979 Federal Register, is based on free cyanide. The debate that exists over the cyanide regulations is not likely to be settled until the behavior of the variety of cyanide compounds discharged to the environment is fully understood.

The determination of the toxicity of specific cyanide compounds is integrally tied to the analytical methods used to identify those compounds. When toxic forms can be isolated then the problems associated with cyanides can be investigated in a more direct manner. In this study two analytical procedures are interfaced to verify the presence of a single toxicant (cyanate) and its toxicity to Daphnia magna.

A major environmental concern about cyanides is the photochemical conversion of relatively non-toxic metallocyanide complexes, such as ferrocyanide ion, into more toxic forms, such as HCN. Work in this laboratory has provided evidence that cyanate, CNO^-, is a product of the photochemical decomposition of some metal cyanide complexes. The toxicity of CNO^- to the aquatic population may be small compared to that of HCN, but if CNO^- is a major product of metal cyanide breakdown it becomes important to know its toxicity.

Cyanate toxicity has been studied by WASHBURN (1948) and BUCKSTEEG AND THIELE (1957). WASHBURN (1948) reported that 75 mg/l as NaCNO was the tolerance limit for creek chub (48.5 mg/l as CNO^-; or 30 mg/l as CN^-). BUCKSTEEG AND THIELE (1957) claimed 75 mg/l as CN^- to be the lower limit of KCNO concentra-

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tion harmful to fish (species not reported), 35 mg/l for Daphnia (species not reported) and 300 mg/l to Escherichia coli. In both studies analytical procedures measured only free cyanide; CNO^- concentrations were estimated by calculation.

METHODS

The toxicity test with cyanate was conducted using less than 24-hour old Daphnia magna in reconstituted hard water. Methods used were those recommended by the COMMITTEE FOR TOXICITY TESTING (1975). LC50 values and confidence limits were determined by probit analysis (FINNEY 1977).

Cyanate was analyzed using a Princeton Applied Research Model 174A polarographic analyzer. To each 10 ml sample 10 mg of KNO was added to make the samples 10^{-2}M in electrolyte. The samples were transferred to the polarographic cell and dearated for 10 minutes by purging with zero grade nitrogen. A cathodic differential pulse polarogram was then made from +0.25 to 0.0v vs. SCE at a scan rate of 10mV/sec. using a current range of 10uA and a drop time of 0.5 seconds. The cyanate in the sample was reduced at +0.20v.

To examine the samples for free cyanide, a gas chromatographic analytical method developed by NOTA et al. (1976) was used. This method uses an electron capture detector to measure the amount of BrCN produced after the addition of bromine water to the cyanide sample. This method measured only free cyanide in the test solutions and thereby provided a means of quantifying the background cyanide interference which could complicate the interpretation of the cyanate toxicity test results.

RESULTS

Sample concentrations were checked before and after the test for both cyanate and cyanide. Polarographic analysis for cyanate revealed that within the precision of the method the same concentration of cyanate added at the beginning of the test was recovered after the test (See Table 1). The gas chromatographic analysis confirmed the absence of free cyanide in the solutions (less than 10µg/l) both before and after the test.

The 48-hour LC50 for Daphnia magna for cyanate was 18 mg/l as CNO^-. The LC50 was based on 30 organisms per concentration run as 3 replicate groups of 10 organisms. The 95% confidence limits were 15.2 and 24.2 mg/l CNO^-.

DISCUSSION

The significance of this test lies in the specific toxicity index derived for the cyanate ion. Using two analytical procedures, it was possible to quantify the cyanate ion and examine its toxicity independent of free cyanide.

TABLE 1

Cyanate Concentrations Before and After the Toxicity Tests

(mg/l*)

Before the test	After the test
3.25(0.09)	3.20(0.16)
5.49(0.08)	5.24(0.28)
9.10(0.26)	9.03(0.15)
14.87(0.23)	14.98(0.10)
24.95(0.43)	24.89(0.11)

*mean and one standard deviation, N = 3

The LC50 value determined for cyanate is about one third of the value previously reported for daphnids. But the toxicity of CNO^- is much less than that reported for free cyanide. Therefore, CNO^- will become important in the evaluation of total cyanide toxicity only if it is the predominant component of the system and occurs at relatively high concentrations.

REFERENCES

BUCKSTEEG, W. & H. THIELE: Gas Wasserfach. 98, 909 (1957).

COMMITTEE ON METHODS FOR TOXICITY TESTS WITH AQUATIC ORGANISMS: Methods for acute toxicity tests with fish, macroinvertebrates and amphibians. USEPA Report No. EPA-660/3-75-009 (1975).

DOUDOROFF, P. in Recent advances in Fish toxicology. R.A. TUBB (ed.) USEPA Report No. EPA-600/3-77-085, pp. 191-203 (1977).

FINNEY, D.J.: Probit analysis. 3 ed. Cambridge: Cambridge University Press, 1977.

NOTA, G., R. PALOMBARI & C. IMPROTA: J. Chromatogr. 123, 411 (1976).

U.S. ENVIRONMENTAL PROTECTION AGENCY: Quality criteria for water. EPA-440/9-76-023 (1976).

U.S. ENVIRONMENTAL PROTECTION AGENCY: Fed. Regist. 44, 43660 (1979).

WASHBURN, G.N.: Sewage Works J. 20, 1074 (1948).