

Deriving freshwater quality criteria of sulphocyanic sodium for the protection of aquatic life in China

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Abstract—The freshwater quality criteria of sulphocyanic sodium (NaSCN) were studied on the basis of the features of the aquatic biota in China, and with reference to U. S. EPA's guidelines. Acute tests were performed on twelve different domestic species to determine 48h- EC_{50} /96h- EC_{50} (or 96h- LC_{50}) values for NaSCN. 21d survival-reproduction test with *Daphnia magna*, 60d fry-juvenile part life stage test with *Carassius auratus gibelio* and 96h growth inhibition test with *Lemna minor* were also conducted to estimate lower chronic limit/upper chronic limit values. In the acute tests, *D. magna* was the most sensitive species to NaSCN followed by *Tilapia mossambica*, *Cyprinus carpio* and *C. auratus gibelio* in turn. The final acute value of NaSCN was 2.699 mg/L. In the chronic tests, reproduction of daphnids were significantly reduced by NaSCN at 1.0 mg/L. Acute-to-chronic ratios ranged from 5.96 to 19.1. A final chronic value of 0.2530 mg/L was obtained and a final plant value was 1346 mg/L. A criterion maximum concentration (1.349 mg/L) and a criterion continuous concentration (0.2530 mg/L) were derived respectively. The results of this study may provide useful data to derive national WQC for NaSCN as well as the procedures of deriving WQC of other chemicals for the protection of aquatic biota in China.

Keywords: freshwater quality criteria; sulphocyanic sodium; aquatic life.

1 Introduction

The impacts of toxic and hazardous chemicals in industrial effluent to aquatic ecosystem have been getting much more serious with the development of industries in China. The WQSS (China NEPA, 1988) were established mainly by means of consulting or quoting relevant foreign criteria or standards (Xia, 1990). However, the toxicity of a pollutants to aquatic organisms might be affected by many physical, chemical and biological factors. These factors, especially specific aquatic biota in China, could result in that foreign water quality criteria or standards are overprotective or

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underprotective for aquatic ecosystems in China. In addition, the current water quality standards, which cover only general physico-chemical parameters and heavy metals, included few toxic organic chemicals among thousands of pollutants in use (China NEPA, 1988). In order to reasonably and adequately protect aquatic ecosystem in China, it is very necessary to develop appropriate national water quality criteria for priority pollutants based on domestic aquatic biota.

Sulphocyanic sodium (NaSCN) is one of the pollutants in the wastewater of petroleum chemical industries. There is no water quality criteria or standards for it in China and no reports about its toxicity to domestic aquatic organisms of China and other countries has been published.

In this study, WQC for NaSCN were developed based on its acute/chronic toxicity data of aquatic animals and plant toxicity data using domestic aquatic organisms selected by referring to the technical guideline of U. S. EPA (U. S. EPA, 1985). The toxicity data of NaSCN were generated by conducting acute toxicity tests with twelve animals, chronic toxicity tests with *Daphnia magna* and *Carassius auratus gibelio*, and plant toxicity test with *Lemna minor*. The objective of this study was to provide useful data to derive national WQC for NaSCN as well as the procedures of deriving WQC for other chemicals based on aquatic biota in China.

2 Material and methods

2.1 Test Chemical

Analytical grade sulphocyanic sodium (NaSCN) was purchased from Chengdu Chemical Reagent Factory.

2.2 Dilution water

Tap water, dechlorinated with activated carbon, was used as dilution water for all tests. The quality parameters of dilution tap water are as follows: pH 7.0 ± 0.5 , DO 8.0 ± 0.34 mg/L, COD_{Mn} 1.423 ± 0.321 mg/L, Hardness 1.86 ± 0.08 mg/L as CaCO₃.

2.3 Test organisms

A total of twelve aquatic animals and one aquatic plant were tested representing eight families. The following organisms were field collected from water in Nanjing where these organism were abundant: *Bufo bufo gargarizans* and *Rana nigromaculata* from Xuanwu Lake, *L. minor* from an unpolluted outdoor pond, *Chironomus sp.* from an unimpacted outdoor stream, and *Limnodilus hoffmeisteri* from Shancha River. Great care was taken in collection and transportation back to laboratory. *D. magna* was obtained from in-house culture which has been cultured for several years. *Cyprinus carpio*, *Ctenophayngodon idellus*, *C. auratus gibelio*, *Aristichthys nobilis*, *Parabramis pekinensis*, *Hypophthalmichthys molitrix* and *Tilapia mossambica* were purchased from the Freshwater Fisheries Institute of Jiangsu Province of China. Upon arrival at the laboratory, all test organisms were allowed to gradually acclimate to dilution water for 48h or more.

2.4 Toxicity test

The test procedures followed the methods recommended by the relevant agencies (APHA-AWWA-WPCF, 1985; China NEPA, 1986; U. S. EPA, 1989).

2.4.1 Acute toxicity test

Except for flow-through tests for *C. auratus gibelio* and *Bufo bufo gargarizans*, all test were static ones. There were five concentrations and a control for each tests. Tests for *D. magna*, and *Chironomus sp.* were under 16:8 light:dark period, and *L. hoffmeisteri* test was conducted in darkness while other tests were under uncontrolled photoperiod. Endpoints were 48h- EC_{50} for *D. magna* and *Chironomus sp.*, 48h- EC_{50} /96h- EC_{50} for *L. hoffmeisteri*, and 48h- LC_{50} /96h- LC_{50} for other species. In this study median effective concentration (EC_{50}) means the concentration that causes 50% organism unmobility and death. All the animals were not fed during the tests. Each test was performed in duplicate, except that test of *C. magna* was in triplicate.

Healthy individuals of *L. hoffmeisteri* with length of 1–2 cm were chosen for the test at $27 \pm 2^\circ\text{C}$, each individual was put in 10 ml glass test-tubes containing 10 ml test solution in order to avoid their coiling together. Each treatment group has 10 tubes.

The test methods for fishes (Zhang, 1997), amphibian (Zhang, 1996a), daphnia (Zhang, 1996b) and larvae of *Chironomidae* (Zhang, 1996c) might be found in the corresponding references.

2.4.2 Chronic toxicity tests

D. magna 21d survival-reproduction test: 21d survival-reproduction test using young individual of *D. magna* aged no more than 24h were conducted in 150 ml beakers containing 100 ml test solution each at a water temperature of $24 \pm 1^\circ\text{C}$ in the static-renewal status under 16:8 light:dark period (Zhang, 1996b). The reproduction and survival data were recorded each day. Lower chronic limit (LCL), upper chronic limit (UCL) and chronic value (ChV) were derived by analyzing survival and reproduction data of the organisms exposed till the 21st day. LCL is the highest tested concentration in a chronic test, which did not cause an unacceptable amount of adverse effect, and below which no tested concentrations caused an unacceptable effect (U. S. EPA, 1985). UCL is the lowest tested concentration in a chronic test, which did cause an unacceptable amount of adverse effect on one specified biological measurements, and above which all tested concentrations also caused an unacceptable effect (U. S. EPA, 1985). ChV is the geometric mean of LCL and UCL (U.S.EPA, 1985).

C. auratus gibelio 60d fry-juvenile part life stages test: The *C. auratus gibelio* (1.53 ± 0.04 cm, 46.7 ± 0.4 mg) flow-through chronic test was conducted in partly-recycle river model with five concentration groups and one control group at 18–28°C under uncontrolled photoperiod. Each group hold 10 fish and was fed with 0.5g feedstuff every day. The test solution flow rate of 300 ml/min insured that solution in the rivers was renewed five times per day. The river model was cleaned and the solution concentration was determined once every five days (Luo, 1988). The $LCLs$, $UCLs$ and $ChVs$ were calculated from the data about survival and weight of fish after 60d exposure.

2.4.3 Plant toxicity test

96h growth inhibition test was conducted with *L. minor* (Zhang, 1995). At the end of test, the fronds in each dish were collected to analysis the concentration of chlorophyll A. LCL , UCL and ChV were obtained by analyzing data on inhibition of NaSCN to duckweed growth and

reduction of chlorophyll A.

2.5 Statistic analysis and data integration

Trimmed Spearman-Katver (TSK) method was employed to calculate EC_{50} and LC_{50} (Hamiton, 1977; Rand, 1985). If there was no partly mortality in one test, Binomial Confidence Internals was used to calculate EC_{50} and LC_{50} values (Rand, 1985). Data on survival of daphnids and fish were analyzed using Fisher's Exact method (U. S. EPA, 1989). Original data on reproduction of daphnids were not normal distribution and should be tested using Steel's Many One Rank procedure according to U. S. EPA (U. S. EPA, 1989). The data of fish weight and data in plant toxicity test were analyzed using Dunnett's method (U. S. EPA, 1989). The LCL and UCL for the most sensitive biological parameter in each test were derived as the LCL and UCL NaSCN to the corresponding species.

Integration of toxicity data was conducted according to the methods mentioned in U. S. EPA's guideline (U. S. EPA, 1985). Final acute value (FAV) was derived using FAV equation. Acute-to-chronic ratios (ACR) for *D. magna* and *C. auratus gibelio* were obtained by dividing their 48h- EC_{50} or 96h- LC_{50} with corresponding $ChVs$. Final acute-to-chronic ratio (FACR) was the geometric mean of all ACRs. To obtain final chronic value (FCV), FAV was divided by FACR. Final plant value (FPV) was a ChV obtained in 96h growth inhibition test with duckweed. In this study, criterion maximum concentration (CMC) was FAV divided by two and the minimum value between FCV and FPV was considered as criterion continuous concentration (CCC).

3 Result and discussion

The results of acute toxicity tests using 12 species shown in Table 1 indicated that *D. magna*

Table 1 Acute toxicity of NaSCN to 12 aquatic species

Species	48h- EC_{50} , mg/L				96h- LC_{50} or EC_{50} , mg/L		
	1	2	3	Average	1	2	Average
<i>D. magna</i>	3.11	4.29	5.63	4.22			
<i>T. mossambica</i>	157	171	—	164	124	87.2	104
<i>C. auratus gibelio</i>	434	408	—	421	205	187	194
<i>C. carpio</i>	742	742	—	742	321	291	306
<i>R. nigromaculata</i>	—	—	—	—	318	324	321
<i>Chironomus sp.</i>	317	383	—	349			
<i>P. pekinensis</i>	697	522	—	603	441	313	372
<i>Bufo bufo gargarizans</i>	1230	1131	—	1179	389	390	390
<i>C. idellus</i>	782	877	—	828	440	406	423
<i>A. nobilis</i>	1107	1047	—	1077	621	493	553
<i>H. molitrix</i>	1165	1866	—	1474	494	931	678
<i>L. hoffmeisteri</i>	2847	2023	—	2400	2267	1262	1691

was the most sensitive species to NaSCN followed by *T. mossambica*, *C. auratus gibelio* and *C. carpio* in turn. The LC_{50} s of NaSCN to *Chironomus sp.* and two species of amphibian in this study were among the LC_{50} s of NaSCN to several fish and *L. hoffmeisteri* was the most tolerant species to NaSCN. According to toxicity of this chemical to fish, NaSCN was considered as a chemical with medium toxicity (Joint, 1969). Using FAV equation, a FAV and 2.698 mg/L NaSCN was obtained.

In conducting the acute toxicity tests to derive WQC for a chemical, species selection is an important factor that affects the results (Dobbs, 1994). The test organisms should be good represents for the aquatic animals. The guideline of U.S. EPA gives out the demand for the test organisms. However, this requirement still be a wide range. In that range, different test animal sets would led to criteria with great difference (Dobbs, 1994). In addition to a broad range of taxes, availability, sensitivity, economic significance and distribution in China of test organisms are actually necessary to be taken into account.

It is necessary to include fish toxicity test data for deriving water quality criteria because fish is an important part in aquatic ecosystems. Thus guideline of U.S. EPA pay more attention to test fishes and requires that fishes from two different families should be tested. According to U.S. EPA guideline, fish from the family salmonoil must be selected as one of the test animals from eight different families due to that the family Salmonoil is the first important fish in the North America. In China more than 50% of fish species is in *Cyprinidae* family, thus fish from *Cyprinidae* family must be tested to derive water quality criteria in China. Among fish of *Cyprinidae* family, *C. carpio*, *C. idellus*, *C. auratus gibelio*, and *H. molitrix* were the frequently used species in aquatic bioassay in China (China NEPA, 1986; 1990) and important commercial species for food. They are always available from fish farms or in-house culture. Therefore they would be suitable organisms to be used in toxicity tests to derive WQC for priority pollutants in China. In this study the sensitivity of these *Cyprinidae* fish was similar and 96h- LC_{50} s of them were from 194 mg/L to 678 mg/L. *C. Carpio*, *C. idellus* and *C. auratus gibelio* were the more sensitive species among them. In this study *T. mossambica*, one fish species not belonging to *Cyprinidae* family, was chosen to be tested according to the principle of the guideline (U.S. EPA, 1985). This fish has been widely cultured in China now and would be a good representative for the fish in families other than *Cyprinidae* in deriving WQC. The result of this study indicated that *T. mossambica* was more sensitive to NaSCN than those *Cyprinidae* fish.

The results of this study indicate that *D. magna* is more sensitive than other test animals. Just because *D. magna* is a standard test species in aquatic bioassay all around the world (China NEPA, 1986; 1990; Gersich, 1990; Zhou, 1990) and it is more sensitive to most chemicals than other animals, it is the elementary test animal to derive water quality criteria. The researchers, who advice to reduce the kinds of test animals for WQC deriving, also include *D. magna* in their sets of test animals (Kimerir, 1985). Thus daphnids should be included while selecting toxicity test species for deriving WQC in China.

Amphibian, such as *B. bufo gargarizans* and *R. nigromaculata*, playing an important role in agriculture, are widely distributed in ecosystems in China and other countries. However some

researchers criticized that more attention should be paid to amphibian while deriving *WQC* (Boyer, 1995). Now in the U. S. EPA guideline, amphibian only is an alternative test animal not a necessary organism for *WQC* deriving. Underprotection and overprotection for amphibian might be resulted if *WQC* is derived only using data of other animals. Thus amphibian should be one of the primary test animals to derive *WQC*. *B. bufo gargarizans* and *R. nigromaculata* have similar sensitivity to chemicals as it showed in this study. Due to their similar sensitivity, either *R. nigromaculata* or *B. bufo gargarizans* can be used to represent amphibian in toxicity tests for *WQC* derivation in China.

U. S. EPA guideline requires that toxicity data of aquatic insects must be got for *WQC* deriving. Larvae of Chironomidae are the important benthic organisms with a biomass equal to 70%—80% of that for total benthic organisms. They act as food for fish and their activities can affect the properties of sediment. In the past, larvae of Chironomidae were scarcely used in acute toxicity test partly because their tolerance to pollutants. However in addition to sensitivity of species, a broad range of taxes is required in *WQC* deriving. Recent studies have demonstrated that not all species of Chironomidae are highly tolerant to pollutants and a species is not able to tolerate all pollutants, moreover, organisms at different life stages may have significantly different tolerance to one pollutant (Buhl, 1989). Thus U. S. EPA guideline suggest that larvae of Chironomidae might be a representative for aquatic insects. In this study, larvae of Chironomidae (*Chironomus sp.*) less than 24h was used to finish the test. The results demonstrated that *Chironomus sp.* be more sensitive to NaSCN than amphibian, *L. hoffmeisteri* and several kinds of fish. The authors of this paper hold that toxicity data of sensitive kinds and life stage for larvae of Chironomidae should be necessary for *WQC* deriving.

3.1 Chronic toxicity

Results of 21d test with *D. magna* showed that lower reproduction rates were significantly observed at 1.0 mg/L NaSCN compared to control (Table 2). But survival rates were not remarkably reduced even at 2.0 mg/L NaSCN. *LCL* and *UCL* for reproduction was 0.5 mg/L and 1.0 mg/L NaSCN respectively. Using *ChV* and *ACR* equations, the *ChV* 0.707 mg/L and *ACR* 5.96 were derived (Table 3).

Table 2 Chronic toxicity of NaSCN to two species

Species	<i>LCL/UCL</i> , mg/L NaSCN		
	Survival	Reproduction	Weight
<i>D. magna</i>	2.0/—	0.5/1.0	—/—
<i>C. auratus gibelio</i>	13.5/26.5	—	7.11/13.5

Table 3 Acute/chronic toxicity values and acute-to-chronic ratios

Species	<i>LC</i> ₅₀ , mg/L	<i>LCL</i> , mg/L	<i>UCL</i> , mg/L	<i>ChV</i> , mg/L	<i>ACR</i>
<i>D. magna</i>	4.22	0.5	1.0	0.707	5.96
<i>C. auratus gibelio</i>	194	7.11	13.5	9.79	19.1

In order to derive *WQC*, it is permitted to use data on part life stage tests to estimate the chronic toxicity of chemicals (U. S. EPA, 1985). Therefore, in this study, it was practical and feasible to use fry-juvenile test with *C. auratus gibelio* to estimate the chronic toxicity of NaSCN to fish. In part life stage test with *C. auratus gibelio*, the lowest *LCL* (7.11 mg/L) indicated that fish weight as an indicator was more sensitive than survival. The *ACR* value derived in this test was 19.1 (Table 3). According to the guideline, a chronic test of NaSCN with one aquatic animal remain to be conducted in future in order to obtain *FACR* (Final acute-chronic ratio). In this study the *FACR* of 10.67 and *FCV* of 0.2530 mg/L were derived from the chronic toxicity data of two species.

Survival, development, reproduction (fertility, spawning and hatching), and growth (length and weight) are the main common indicators observed in chronic toxicity test with single species to derive *LCL* and *UCL* values. In this study, the finding that the reproduction of *D. magna* was a more sensitive indicator than survival was in agreement with that reported in literature (Gersich, 1986). Analyzing the data in Table 2, it was found that survival, in the two chronic tests, was less sensitive than reproduction or growth (fish weight). Therefore, in chronic toxicity test to derive *WQC*, other indicators besides survival, such as reproduction, growth and so on, should be included to avoid underprotection.

3.2 Plant toxicity

The results of 96h growth inhibition test with *L. minor* indicated that frond growth was more sensitivity to NaSCN than chlorophyll A. Based on the results, $FPV = ChV = 1346$ mg/L NaSCN were derived (Table 4).

Table 4 Plant toxicity of NaSCN to *L. minor*

	<i>LCL</i> , mg/L	<i>UCL</i> , mg/L	<i>ChV</i>
Chlorophyll A	2560	3920	3168
Growth of fronds	1080	1680	1346

3.3 NaSCN criteria calculation

According to the equation recommended in U. S. EPA's guidelines (U. S. EPA, 1985), *CMC* of 1.349 mg/L NaSCN was obtained by dividing *FAV* (2.698 mg/L) with 2. In this study, the lower value between *FCV* (0.2530 mg/L NaSCN) and *FPV* (1346 mg/L NaSCN) was chosen as $CCC = 0.2530$ mg/L NaSCN.

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