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THE TOXICITY EVALUATION OF WASTEWATER FROM THE CHEMICAL INDUSTRY

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ABSTRACT

The purpose of our investigation was the acute and chronic toxicity evaluation of the wastewater from the chemical industry, while the previous study had indicated high toxicity of the receiving streams far away from the point of wastewater inflow. The luminescent bacteria *Photobacterium phosphoreum* and invertebrate *Daphnia magna* were used for toxicity tests. The results of the toxicity tests showed that the investigated wastewater contained toxic substances, which caused acute and chronic toxicity to test organisms. *Daphnia magna* were more sensitive than *Photobacterium phosphoreum*. The acute toxicity of the wastewater on *daphnids* disappeared after dilution to 1:420, but the chronic toxicity did not disappear earlier than 1:1350.

KEYWORDS

Acute and chronic toxicity; *Daphnia magna*; *Photobacterium phosphoreum*; toxicity test; wastewater.

INTRODUCTION

The release of wastewaters into streams causes a lot of ecological problems in aquatic ecosystems, among them the harmful effects of the toxic substances in the wastewaters and receiving streams are very important. In Slovenia we also have problems with the frequently toxic outflows of wastewaters.

In previous research, the toxicity of surface stream waters was examined, and the acute and chronic toxicity on *Daphnia magna* were determined in several investigated rivers (Tišler and Zagorc-Koncan, 1992). The main cause for high toxicity in the rivers was toxic substances in the wastewater from the chemical industry. The aim of our investigation was to find out the wastewater acute and chronic toxicity on two kinds of aquatic organisms. It was our purpose to determine whether the investigated wastewater from a chemical industry was the cause of high toxicity in the receiving rivers far away from the point of the wastewater inflow.

MATERIALS AND METHODS

pH, COD, BOD_5, suspended and dissolved zinc, barium, cadmium and copper were determined in the chemical industry wastewater (APHA-AWWA-WPCF, 1989). The acute toxicity of the investigated

wastewater was determined with the marine bacteria *Photobacterium phosphoreum* (Cohn 1878) Beijerinck 1889 and daphnids *Daphnia magna* Straus 1820; the chronic toxicity was evaluated with daphnids *Daphnia magna* Straus 1820. As dilution water, an unpolluted stream having pH 8.3, total hardness 135 mg/l CaO and alkalinity 132 mg/l CaO was used. Daphnids were also cultured in the above mentioned water.

In the acute toxicity test with marine freeze-dried bacteria *Photobacterium phosphoreum* the luminescence of bacteria was determined on the Lumistox apparatus at a test temperature of 15°C. Testing was performed according to instructions described in the operation manual (Lumistox dr. Lange, 1989), obtained results were statistically analysed using the computer program Lumissoft (Bruno Lange, 1990).

Daphnids were cultured in small aquariums and fed with yeast and green alga *Scenedesmus subspicatus* Chodat. The test temperature in acute and chronic toxicity tests with daphnids was 21 ± 2°C. The illumination in both kinds of daphnids tests was 1800 lx with 9:15 hours photoperiod. The acute toxicity test with daphnids was performed according to the ISO standard (International Organisation for Standardisation, 1989). Daphnid mortality was determined after 24 and 48 hours.

The chronic toxicity test with daphnids was performed in a static renewal system (Organisation for Economic Cooperation and Development, 1982; European Economic Community, 1982). On Monday, Wednesday and Friday survived daphnids (and also young daphnids when they appeared) were counted, transferred to newly prepared samples and fed with vitamin enriched alga *Scenedesmus subspicatus* at the rate 2.50 mg dry weight alga per litre. For each counting the percentage of daphnids mortality was calculated and after three weeks the number of young daphnids per adult for the control and each sample was summed. Data derived from the chronic toxicity tests were evaluated using Dunnett's test including analysis of variance (ANOVA) (Statistical Support Staff Computer Sciences Cooperation, 1988).

RESULTS AND DISCUSSION

In the chemical industry white pigment is produced. White pigment is a mixture of zinc sulphide and barium sulphate and so the wastewater is mainly polluted with metals. The results of chemical analysis of the investigated wastewater are given in Table 1.

TABLE 1. The Chemical Analysis of Investigated Wastewater

pH	7.8
COD_d (mg/l)	36.2
BOD_5 (mg/)	2.0
Zn diss. (mg/l)	39.5
Zn susp. (mg/l)	0.02
Ba diss. (mg/l)	165
Ba susp. (mg/l)	7
Cu diss. (μg/l)	<0.5
Cu susp. (μg/l)	<0.5
Cd diss. (μg/l)	0.3
Cd susp. (μg/l)	0.4

The wastewater was not highly polluted with organics, but it contained high concentrations of dissolved and suspended zinc and barium.

First, the acute toxicity chemical industry wastewater was investigated. The results of acute toxicity tests with daphnids *Daphnia magna* and luminescent bacteria *Photobacterium phosphoreum* are presented in table 2.

TABLE 2. The Results of the Acute Toxicity Tests with *Photobacterium Phosphoreum* and *Daphnia Magna* with Chemical Industry Wastewater

	Photobacterium phosphoreum	*Daphnia magna*	
Wastewater conc.(vol.%)	Luminescence inhibition (%)	Mortality (%) 24h	48h
100.0	83	-	-
50.0	82	-	-
33.3	72	-	-
25.0	62	-	-
16.6	48	-	-
12.5	35	-	-
10.0	-	90	100
8.3	23	-	-
6.3	14	-	-
4.2	12	-	-
4.0	-	57	60
3.1	5	-	-
2.0	-	43	50
1.0	-	30	43
0.5	-	0	15
0.3	-	0	0

The values for LC_{10}, LC_{50} and LC_{90} for daphnids (EC values for bacteria) were calculated from Table 2.

Daphnia magna

24h LC_{10} = 0.44 vol.%
24h LC_{50} = 2.48 (1.56-3.64) vol.%
24h LC_{90} = 12.26 vol.%

Daphnia magna

48h LC_{10} = 0.24 vol.%
48h LC_{50} = 2.08 (1.27-4.91) vol.%
48h LC_{90} = 18.96 vol.%

Photobacterium phosphoreum

30min EC_{10} = 4.67 vol.%
30min EC_{50} = 18.26 vol.%
30min EC_{90} = 71.35 vol.%

The acute toxicity test results with bacteria and daphnids showed that *Daphnia magna* were more sensitive than *Photobacterium phosphoreum* to toxic metals in wastewater from the chemical industry. The 24h LC_{50} value from acute toxicity tests with daphnids was a starting-point for the first experiment in the chronic toxicity evaluation of the investigated wastewater: the results are given in Table 3. In the second experiment of chronic toxicity tests with *Daphnia magna* lower concentrations of chemical industry wastewater were tested; results are represented in Table 4.

The toxic substances in the wastewater had greater influence on the survival of daphnids than on reproduction (Table 4). In all investigated samples the first young daphnids appeared six days after the chronic toxicity test had been started. The sample with 0.052 vol.% of wastewater had no more influence on the survival and reproduction of daphnids. The chronic value for daphnids is 0.074 vol.%.

TABLE 3. The Results of the Chronic Toxicity Test – First Experiment with *Daphnia Magna* Chemical Industry Wastewater

Time (d)	1	2	4	7	9
Wastewater conc.(vol.%)	Daphnids mortality (%)				
0.000	0	0	0	3	3+
0.313	0	17	67	77	100*
0.625	10	47	93	100	100*
1.250	57x	77x	100	100	100*
2.500	43x	57x	97x	100	100*

\+ young daphnids appeared in the water
x movement of daphnids was not normal
* the value for this group is significantly different from the control

TABLE 4. The Results of the Chronic Toxicity Test – Second Experiment with *Daphnia Magna* with Chemical Industry Wastewater

Time (d)	1	4	6	8	11	13	15	18	20	21	21
Wastewater conc.(vol.%)	Daphnids mortality (%)										Total young per female
0.000	0	0	3+	3	3	3	3	3	3	3	95
0.026	0	0	0+	0	0	0	0	16	16	16	98
0.052	0	0	0+	0	0	3	3	12	12	12	99
0.104	0	0	0+	3	3	3	13	70	70	77*	83
0.208	0	0	0+	3	3	20	57	93	93	93*	64*
0.417	10	57	57+	57	60	67	90	100	100	100*	44*

\+ young daphnids appeared in the water
* the value for this group is significantly different from the control

From the obtained results (Table 4) NOEC, LOEC, NOLC, LOLC and ChV values were calculated:

NOLC = 0.052 vol.% NOEC = 0.104 vol.% ChV = 0.074 vol.%
LOLC = 0.104 vol.% LOEC = 0.208 vol.%

The probable reason for toxicity of chemical industry wastewater on daphnids was zinc. In general zinc is not to be found among the most toxic metals. The reported LC_{50} values are between 0.5 and 5.0 mg/l for invertebrates, but for crustacea the toxicity of zinc begins at lower concentrations (LC_{50} values are between 0.04 and 5.5 mg/l). For Daphnia hyalina the 48h LC_{50} value 0.055 mg/l was found (Connell and Miller, 1984; Moore and Ramammorthy, 1984). Biesinger and Christensen (1972) established that the 16% inhibition of daphnids reproduction appeared at 0.070 mg/l of zinc. Some kinds of organisms may be adapted to higher concentrations of zinc in the water and for there organisms zinc is not very toxic. As with in other metals the toxicity of zinc is dependent upon physical and chemical properties of water (pH, water hardness).

The wastewater also contained a high concentration of barium (Table 1). The toxicity of barium is low, therefore little literature data about its toxicity is available. The 48h LC_{50} value for daphnids was 14.5 mg/l, 21d LC_{50} 13.5 mg/l and 16% inhibition of daphnids reproduction was at 5.8 mg/l of barium (Biesinger and Christensen, 1972). Literature data showed that concentrations of dissolved barium higher than 50 mg/l were

also nontoxic to aquatic organisms (Office of Water, 1987). In the streams sulphate and carbonate precipitate barium into insoluble, nontoxic matter was present.

The toxicity study with daphnids and bacteria *Photobacterium phosphoreum* showed that the investigated wastewater from the chemical industry was toxic, especially for *Daphnia magna*. The acute toxicity of the wastewater on daphnids disappeared after dilution to 1:420. The chronic value for investigated wastewater obtained from the chronic toxicity test with daphnids was 0.074 vol.% (dilution 1:1350). The results obtained in the toxicity tests with chemical industry wastewater were in agreement with the previous toxicity measurements in the receiving streams (Tišler and Zagorc-Koncan, 1992). At the time when the measurements of the river toxicity had been done, the flow rates of the receiving rivers were low and therefore the required dilution (1:1350) of the wastewater from the chemical industry was not achieved.

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