Toxicity of Metal Mining Wastes

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INTRODUCTION

Whereas many laboratory bioassays have been conducted with heavy metals (MCKEE and WOLF, 1963) few have been conducted in the field. The study using Whitewood Creek water was a field bioassay. Whitewood Creek is located in the Black Hills region of South Dakota and receives drainage and process water from gold and silver mines. Its waters contain salmoid fishes and a number of heavy metals, prior to receiving the discharge from a major mining company. The test water used in this study was collected upstream from this mining company's discharge; thus, the limiting amount of each heavy metal tested could be determined and safe limits for rainbow trout be recommended for Whitewood Creek. This study demonstrates the need for on-site bioassays.

METHODS

All 96-hour bioassays were conducted in a mobile bioassay laboratory and conducted according to STANDARD METHODS (1971) using a continuous flow proportional diluter; this facility provided a series of six dilutions of toxicant and a dilution water control.

Dilution water (receiving water) for all bioassays was obtained from Whitewood Creek 0.5 km (0.3 mi) upstream from the confluence of a major mining company's effluent. At this location, Whitewood Creek water contained the following heavy metals: Zn(<4.0-48.0 μg/l); Cr(<10.0-30.0 μg/l); Ni(<10.0-20.0 μg/l); Cd(<2.0-5.0 μg/l); Hg(0.63-1.8 μg/l); Pb(<50.0 μg/l); Cu(<30.0 μg/l); As(<10.0-20.0 μg/l) and Ag(<10.0 μg/l)(TABLE 1). During the investigation period (May 1 - June 7, 1975), the pH ranged from 6.4 to 8.3; total alkalinity from 82 to 132 mg/l and dissolved oxygen from 4.8 to 9.0 mg/l (TABLE 1) as measured in test chambers.

Test water for each bioassay was prepared by adding a stock concentration of reagent grade chemical to Whitewood Creek water. The chemicals used were sodium arsenate ($NaAsO_2$), cadmium nitrate

Bulletin of Environmental Contamination & Toxicology,
Vol. 17, No. 1

TABLE 1

Chemical Characteristics of Whitewood Creek (Test) Water[1]

Characteristic	Number of Analyses	Mean	Range
pH (units)	90	---	6.4-8.3
Dissolved Oxygen	90	6.8	4.8-9.0
Total Alkalinity	90	105	82-132
Total Arsenic	42	<0.01	<0.01-0.02
Total Cadmium	42	<0.002	<0.002-0.005
Total Chromium	42	<0.01	<0.01-0.03
Total Copper	42	<0.03	---
Total Lead	42	<0.05	---
Total Mercury (μg/l)	42	1.10	0.63-1.8
Total Nickel	42	<0.01	<0.01-0.02
Total Silver	42	<0.01	---
Total Zinc	42	0.018	<0.004-0.048

[1] Concentration in mg/l

[$Cd(NO_3)_2.4H_2O$], chromium nitrate [$Cr(NO_3)_3.9H_2O$], cupric nitrate [$Cu(NO_3)_2$], mercurous nitrate ($HgNO_3.H_2O$), lead nitrate [$Pb(NO_3)_2$], nickel nitrate [$Ni(NO_3)_2.6H_2O$], silver nitrate ($AgNO_3$) and zinc acetate [$Zn(C_2H_3O_2)_2.2H_2O$]. All stock solutions were made-up on the basis of active ingredient (e.g. 50 μg Cd, not 50 μg [$Cd(NO_3)_2.4H_2O$].

The test organisms used in all bioassays were young-of-the year (2-month-old) rainbow trout (Salmo gairdneri Richardson). The total length of these fish ranged from 51 to 76 mm (2 to 3 in).

Test chambers were made of glass and had an 8-liter capacity. Bioassay exposures were in duplicate at each test concentration with ten fish in each chamber. The minimum volumetric turnover for any chamber was 6 1/2 times in 24 hours.

Test water was monitored daily for pH, temperature, dissolved oxygen, total alkalinity, and heavy metals. One test chamber in each series was continuously monitored for temperature with a recording thermocouple.

Fish mortalities were recorded at 24-hour intervals. TL 50 values were estimated using a straight-line graphic interpolation (STANDARD METHODS, 1971).

RESULTS AND DISCUSSION

The toxicity of arsenic, cadmium, chromium, copper, lead mercury, nickel, silver and zinc to 2-month-old rainbow trout in Whitewood Creek water was tested in continuous flow, 96-hour bioassays. The results obtained are discussed in the sections that follow.

Arsenic

Less than 10 μg/l of arsenic was found in Whitewood Creek during the study period (May 1-June 7,1975). Arsenic concentrations, in samples from 130 stations in the United States, ranged from 5.0 to 336.0 μg/l with a mean level of 64.0 μg/l (KOPP, 1969). Arsenic is a cumulative toxicant. A succession of small doses may add up to a final lethal dose (BUCHANAN, 1962).

Test concentrations of arsenic ranged from 2.31 to 37.0 mg As/l. The 96-hour TL 50 for 2-month-old rainbow trout was calculated to be 10.8 mg As/l (TABLE 2).

Cadmium

Cadmium occurs in nature chiefly as a sulfide salt, frequently in association with zinc and lead ores. Accumulation of cadmium in soils in the vicinity of mines and smelters may result in high local concentrations in nearby waters.

In Whitewood Creek, cadmium concentrations were below detectable limits (<2.0 μg/l). Cadmium concentrations in the bioassay ranged from 1.8 to 28.0 μg Cd/l. The TL 50 was determined to be 6.6 μg Cd/l (TABLE 2).

Cadmium was found to be more toxic in Whitewood Creek water than has been reported from laboratory studies by other investigators using salmonids (BENOIT et al., 1975; EATON and MCKIM, 1975). Lethal concentrations of cadmium for fish vary depending on the test animal, the type of water, temperature, and time of exposure (MCKEE and WOLF, 1963).

TABLE 2

Test Range and Toxicity of Nine Heavy Metals in Whitewood Creek Water[1]

Heavy Metal	Range Tested	TL 50
Arsenic	2.31-37.0	10.8
Cadmium	0.0018-0.0280	0.0066
Chromium	4.02-64.25	24.09
Copper	0.078-1.250	0.253
Lead	0.875-14.000	8.00
Mercury (μg/l)	22.9-366.6	33.0
Nickel	6.11-97.75	35.50
Silver	0.005-0.080	0.0288
Zinc	0.066-1.053	0.550

[1] Concentrations in mg/l

Chromium

Chromium is the seventeenth most abundant nongaseous element ranking ahead of copper, zinc, nickel, and cadmium (SCHROEDER, 1970). Only the trivalent and hexavalent forms are found in nature. It is rarely found in natural waters. Whitewood Creek, upstream from the confluence of the mining company's effluent, contained concentrations ranging from below detectable limits, <10.0 μg/l to 30.0 μg Cr/l (TABLE 1).

Bioassay tests to determine the toxicity of chromium to 2-month-old rainbow trout were conducted using 4.02 to 64.25 mg/l (as Cr) solutions of chromium nitrate [$Cr(NO_3)_3.9H_2O$] in Whitewood Creek water. The 96-hour TL 50 was determined to be 24.09 mg Cr/l (TABLE 2). With the addition of Cr there was a drop in pH from 8.1-8.3 in the control to 4.6-5.0 in the 100% concentration.

Copper

Copper is relatively insoluble in natural waters. KOPP and KRONER (1967) examined over 1500 surface water samples in the United States and found soluble copper in 74% of the samples with an average concentration of 15.0 µg/l. Whitewood Creek water contined 44 µg Cu/l in January, 1975.

During the May-June 1975 investigation, Whitewood Creek water contained less than 30.0 µg Cu/l. The 96-hour TL 50 value for copper, using 2-month-old rainbow trout, was 253.0 µg/l (TABLE 2).

The toxicity of copper varies with the physical and chemical characteristics of water, such as temperature, hardness, turbidity and carbon dioxide content (TARZWELL, 1957; TRAMA, 1954). The toxicity may not be related to difference in hardness per se, but to the difference in alkalinity of the water that accompanies changes in hardness (STIFF, 1971).

Lead

Lead and its compounds occur naturally and may enter and contaminate the environment at any stage during mining, smelting, processing, and use. It exists in nature as lead sulfide (galena). Most lead salts are low in solubility. The aqueous solubility of lead ranges from 500.0 µg/l in soft water to 3.0 µg/l in hard water. The toxicity of lead in water, like other heavy metals, is affected by pH, hardness, organic materials and other metals. Lead is a cumulative systemic toxicant.

The occurrence of lead in Whitewood Creek, during the study period was less than the detectable limit (50.0 µg Pb/l). Concentrations of test solutions ranged from 0.875 to 14.0 mg Pb/l. For 2-month-old rainbow trout the 96-hour TL 50 for lead was 8.0 mg/l (TABLE 2).

Mercury

Mercury is a biologically non-essential, non-beneficial element, historically recognized as an element of high toxic potential. In water under naturally occurring conditions of pH and temperature, metallic mercury can be readily converted to methyl mercury (BISOGNI and LAWRENCE, 1973), i.e., in anaerobic sediments, bacteria can convert inorganic metallic mercury into methyl mercury compounds. JENNE (1972) found that the majority of the U. S. water contained less than 0.1 µg/l of mercury. Mercury is a cumulative systemic toxicant.

Mercury in Whitewood Creek water ranged from 0.24 to 1.8 µg/l with a mean of 1.04 µg/l. Mercurous salts are less soluble than mercuric salts. Toxicity of mercury was determined through bioassay using mercurous nitrate in Whitewood Creek water.

Mercury concentrations tested ranged from 22.9 μg/l to 366.66 μg/l. The 96-hour TL 50 was 33.0 μg Hg/l (TABLE 2).

Nickel

Nickel, as a pure metal, is insoluble in water; however, many salts of nickel are highly soluble and can occur in leachate from nickel-bearing ores. It occurs normally in surface waters at low concentrations. Toxicity of nickel to aquatic life varies widely with species, pH, synergistic effects and other factors (MCKEE and WOLF, 1963).

In Whitewood Creek, nickel was found to be present in concentrations ranging from <10.0 μg/l to 20.0 μg/l. Test fish were exposed to nickel concentrations ranging from 6.11 to 97.75 mg/l. The 96-hour TL 50 was found to be 35.5 mg Ni/l (TABLE 2).

Silver

Silver is found in nature as elemental silver or as silver compounds in ores. It has a solubility of 0.1 to 10.0 mg/l depending on pH and chloride concentration. At 130 sampling points in the United States, 104 samples contained more than 0.1 μg/l.

In Whitewood Creek, the presence of silver was found to be <10.0 μg/l. Biologically silver is a non-essential, non-beneficial element recognized as being systemically toxic to aquatic life.

In the silver bioassay, test concentrations ranged from 5.0 to 80.0 μg/l. The 96-hour TL 50 was observed to be 28.8 μg Ag/l (TABLE 2).

Zinc

Zinc occurs to the extent of about 120 grams per ton of the earth's crust. It is usually found in nature as a sulfide, and is often associated with sulfides of other metals especially lead, copper cadmium and iron. KOPP and KRONER (1967) reported soluble zinc in more than 76% (1,207 tests) of all water samples tested in U. S. waterways. Zinc was found in Whitewood Creek in concentrations ranging from <0.004 to 0.048 mg/l. The toxicity of zinc compounds to aquatic animals is modified by several environmental factors, especially hardness, dissolved oxygen and temperature. MCKEE and WOLF (1963) report that the sensitivity of fish to zinc varies with species, age and condition of the fish, as well as the physical and chemical characteristics of the water.

In the bioassay using Whitewood Creek water, zinc concentrations ranged from 0.066 to 1.053 mg/l (TABLE 2). The resulting 96-hour TL 50 for the test was 0.55 mg Zn/l; or somewhat less than reported in the literature. EATON (1973) determined that it took less copper, cadmium and zinc in combination to reach a lethal threshold concentration than would be expected (i.e., the results indicate that their summations were enhanced). These three metals and other heavy metals are present in Whitewood Creek; thus some or all of the metals tested may be more toxic than if heavy metals were absent from Whitewood Creek water. The Whitewood Creek study cannot be compared with laboratory studies in which the chemical nature of the water is controlled. It is a site specific study. No two streams have exactly the same chemical composition; thus, each effluent requires bioassay testing using the receiving stream as dilution water.

The most toxic metals tested were cadmium, silver and mercury in that order.

Acknowledgment: The author is grateful to the U. S. Fish and Wildlife Service personnel at McNenny National Fish Hatchery, Spearfish, South Dakota, for providing the rainbow trout for the bioassay. Members of the EPA National Enforcement Investigation Staff for their help in the field investigation as well as editorial suggestions, especially Robert Schneider, Chief of the Biology Branch.

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