Research Articles

Acute and Chronic Toxicity of Chlorine Dioxide (ClO₂) and Chlorite (ClO₂⁻) to Rainbow Trout (Oncorhynchus mykiss)

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Abstract

Goal, Scope and Background. Chlorite (ClO₂⁻) is a primary decomposition product when chlorine dioxide (ClO₂) is added during water treatment; therefore the toxic effects of both compounds on aquatic organisms are possible. Limited data are available concerning their toxicity to fish. The aim of this study was to investigate sensitivity of rainbow trout to acute and chronic toxicity of chlorine dioxide and chlorite, and to estimate the Maximum-Acceptable-Toxicant-Concentration (MATC) of those compounds in fish.

Methods. The acute and chronic toxicity of chlorine dioxide and chlorite to larval and adult rainbow trout was investigated in 96-hour to 20-day laboratory exposures evaluating the wide range spectrum of biological indices under semi-static conditions.

Results and Discussion. Median lethal concentration (96-hour LC50) values derived from the tests were: 2.2 mg/l for larvae; 8.3 mg/l for adult fish and 20-day LC50 for larvae was 1.6 mg/l of chlorine dioxide, respectively. Chlorite was found to be from 48 to 18 times less acutely toxic to larvae and adult fish, correspondingly. Both chemical compounds induced similar toxic effects in rainbow trout larvae during chronic tests (they affected cardio-respiratory and growth parameters), but chlorine dioxide had a higher toxic potency than chlorite. A significant decrease in the heart rate and respiration frequency of larvae was established. However, within an increase in exposure duration recovery of cardio-respiratory responses was seen to have occurred in larvae exposed to chlorite. Meanwhile, in larvae exposed to chlorine dioxide, a significant decrease in cardio-respiratory responses remained during all 20-day chronic bioassays. Chlorine dioxide also more strongly affected growth parameters of rainbow trout larvae at much lower test concentrations. Decreased rate of yolk-sack resorption occurred only in the tests with chlorine dioxide.

Conclusions. Maximum-Acceptable-Toxicant-Concentration (MATC) of 0.21 mg/l for chlorine dioxide and of 3.3 mg/l for chlorite to fish was derived from chronic tests based on the most sensitive parameter of rainbow trout larvae (growth rate). According to substance toxicity classification accepted for Lithuanian inland waters, chlorine dioxide and chlorite can be referred to substances of 'moderate' toxicity to fish.

Recommendations and Outlook. Due to its very reactive nature, chlorine dioxide is rapidly (in a few hours) reduced to chlorite, which is persistent also as a biocide but 16 times less toxic to fish, according to MATC. Therefore, it is much more likely that fish will be exposed to chlorite than to chlorine dioxide in natural waters. Presently accepted, the Maximum-Permitted-Concentration of total residual chlorine (TRC) in wastewater discharging into receiving waters is 0.6 mg/l. If this requirement will not be exceeded, it is unlikely that fish would be exposed to lethal or even to sublethal concentrations of chlorine dioxide or chlorite. Furthermore, chlorine dioxide does not generate toxic nitrogenous (chloramines) or carcinogenic organic residuals (trihalomethanes). All these properties make chlorine dioxide a more promising biocide than chlorite.

Keywords: Acute toxicity; chlorine dioxide; chlorite; chronic toxicity; fish; rainbow trout (Oncorhynchus mykiss)

Introduction

Chlorine dioxide (ClO₂) as a primary disinfectant and pre-oxidant in drinking water treatment is under consideration as an alternative to chlorine, because it is a much more powerful biocide, has a long-lasting effect and seems to be safe for humans (Berg et al. 1980). Commonly, chlorine dioxide is rapidly reduced to chlorite (ClO₂⁻), its primary decomposition product when applied to natural waters (Harrington et al. 1989). Since chlorite residual is persistent, the toxic effects of both compounds on aquatic organisms are possible.

The effect of chlorine dioxide on virus, bacteria, algae, and zooplankton has been studied intensively during last decades (see Junli et al. 1997a, 1997b), however comparatively few studies have been conducted on the effects of these compounds to fish. Some of them are contradictory, difficult to compare, and mostly deal with acute toxic effects. No data are available on long-term effects of chlorine dioxide and chlorite to fish.

Meanwhile, every new chemical substance that is accepted for industrial purpose use must be investigated ecotoxicologically for protection of aquatic life. Experimental data must be obtained under controlled laboratory conditions in order to predict the effects that may occur in natural conditions (Brungs et al. 1976).

The objectives of this study were to determine acute and chronic toxicity of chlorine dioxide and its primary decomposition product chlorite to larval and adult rainbow trout, and to determine Maximum-Acceptable-Toxicant-Concentration (MATC) of these compounds to fish.
1 Materials and Methods

Rainbow trout larvae and adults (one-year-old) were obtained from the Želmėnų fish hatchery (Svenionys District, Lithuania). The test fish were acclimated to laboratory conditions at least for one week before starting the tests. Deep-well water was used for dilution. Average hardness of the water was approximately 284 mg/l as CaCO₃, alkalinity was 244 mg/l as HCO₃⁻, mean pH was 8.0, temperature was maintained at 10 ± 0.5°C (for larvae), 12 ± 0.5°C (for adult fish) and oxygen concentration was maintained at a range of from 8 to 10 mg/l.

All acute (96-hour) and long-term (20-day) toxicity tests were conducted under semi-static conditions and fish mortality observations were made at 24-hour intervals.

Rainbow trout larvae (7-day old) tests were conducted in a special incubator of system battery and were terminated before the active feeding of alevis. Each system included seven 1-litre volume boxes filled with aerated dilution water. Fifty larvae were placed into each box for 24-hour acclimation. Test larvae were exposed to a series of concentrations ranging from 0.15 to 4.8 mg/l of chlorine dioxide and from 2.3 to 74.6 mg/l of chlorite with six treatments and one control (dilution factor was 50%). Test solutions were renewed every day with a stock solution prepared at the start of the test; dead larvae were removed, weighed and measured. Live larvae were transferred into freshly prepared test solutions. Every test continued 20 days and was replicated twice. Morphological (total body mass in mg and total body length in mm) as well as physiological parameters (cardio-respiratory), such as heart rate (counts/min) and respiration frequency (counts/min), were also recorded daily.

Adult fish were tested by use of the system including seven, 40-litre volume, continuously aerated, test tanks. Mean total weight of test fish was 25.7 ± 1.6 g and mean total length was 133 ± 2.7 mm (mean ± SEM, respectively). Ten fish were placed into each tank for 24-hour acclimation. Test fish were exposed to a series of concentrations ranging from 4.2 to 17.9 mg/l of chlorine dioxide and from 89 to 373 mg/l of chlorite with six treatments and one control (dilution factor was 75%). Test solutions were renewed every day with a stock solution prepared at the start of the test; dead fish were removed, live fish were transferred into freshly prepared test solutions. Every test continued 96 hours and was replicated twice.

Sodium chlorite (NaClO₂) was used as the toxicant. Stock solution of chlorite was prepared by dissolving the necessary amount of sodium chlorite in distilled water. This chemical was of 80% purity (‘Fluca’ production, Switzerland) and chlorine dioxide (ClO₂) was prepared by adding in a certain proportion of chemically pure hydrochloric acid to a solution of sodium chlorite as it was described by Deininger et al. (1998). Chlorine dioxide and chlorite concentrations were measured at the start of the tests by use of amperometric titration method with phenylarsine oxide (APHA 1995). Samples were analysed immediately upon collection to avoid loss of chemicals due to holding.

All the data obtained were treated with standard statistical procedures used in Toxicology (Gad 2001). The median acutely lethal concentration (LC50) values and their 95% confidence intervals (CI) were calculated using the Trimmed Spearman-Karber Method (Hamilton et al. 1977). Threshold-Effect-Concentration (TEC) was estimated for every parameter studied by defining geometric mean between the Lowest-Observed-Effect-Concentration (LOEC) and the No-Observed-Effect-Concentration (NOEC). The Maximum-Acceptable-Toxicant-Concentration (MATC) was defined as the lowest TEC for the most sensitive parameter studied obtained in long-term tests (Van Leeuwen and Hermens 1995).

2 Results

Data on acute toxicity of chlorine dioxide and chlorite to rainbow trout larvae and adults are presented in Table 1. Exposure duration to chlorine dioxide evidently increased test larvae mortality, but no significant difference was found between 96-hour and 10-day LC50 values. Twenty-day exposure significantly decreased LC50 value and it was found to be 1.4 times lower than 96-hour LC50 values. In general, rainbow trout larvae were 3.8 times more sensitive to the acute toxic effect of chlorine dioxide than adult fish, according to 96-hour values.

Rainbow trout larvae were also found to be more sensitive to chlorite than adult fish, but a sharp boundary between toxic and non-toxic concentrations of chlorite was established. The maximum test concentration of chlorite (149 mg/l) was absolutely lethal to test larvae in 24 hours, while the next lower chlorite concentration (75 mg/l) was found to be non-toxic to test larvae independent of the exposure duration. Derived LC50 value of chlorite to rainbow trout larvae amounted to 106 mg/l, 95% confidence interval not being reliable. Exposure duration to both chemicals also significantly increased mortality in adult fish, but chlorine dioxide was found to be 18 times more toxic than chlorite according to 96-hour LC50 values.

Both chemical compounds tested (chlorine dioxide and chlorite) induced evident changes in cardio-respiratory responses of rainbow trout larvae. Chlorite in test concentr-