Fact Sheet Date: SEP 1 1991

- AQUATIC LIFE FACT SHEET -
- Ambient Water Quality Value -

SUBSTANCE(S): *CHLORINE,* Total Residual

CAS REGISTRY NUMBER(S): NA

BASIS	**VALUE (ug/L)** FRESHWATER	SALTWATER
Fish Propagation, Survival and Tainting	5	7.5
Fish Survival and Tainting	19	13

SUMMARY OF INFORMATION:

The U.S. Environmental Protection Agency (EPA, 1976) recommended criteria of 2 ug/l for salmonid fish and 10 ug/l for other freshwater and marine organisms in order to protect sensitive aquatic life from the chronic effects of chlorine. The criterion of 2 ug/l was chosen in consideration of data that showed that 6 ug/l was lethal to salmonid fry. In 1978, the NYS Department of Environmental Conservation (DEC) proposed a water quality standard for chlorine of 2 ug/l, but concluded that different criteria to protect cold water species and all other aquatic life was not warranted (DEC, 1978). The International Joint Commission (IJC, 1978) has also recommended a single objective of 2 ug/l for all boundary waters of the USA and Canada. Both DEC (1978) AND IJC (1978) point out that data from the middle and latter 70's demonstrate the equal sensitivity of cold and warm water species to chlorine.

The Water Quality Section of the American Fisheries Society criticized the EPA (1976) recommendation for two criteria in freshwater (DeGraeve et al. 1979). However, these reviewers recommended that the single criterion should be between 3 to 5 ug/l; 3 ug/l to protect aquatic life and 5 ug/l in recognition of the difficulty of measuring chlorine at low levels. Teppen et al. (1976, cited in DeGraeve et al. 1979) were reported as measuring chlorine at 1.0 ug/l via modified amperometric titration. Regarding marine waters, a study was cited that suggested that a criterion of 10 ug/l would not protect some economically important species and the criterion should be expressed as "oxidant species" to account for the formation of toxic hypobromous acid upon the addition of chlorine to sea waters.

In 1985, EPA published revised water quality criteria for total residual chlorine (TRC) (EPA, 1985). EPA noted that numerous toxicity tests studied short-term exposures, intermittent exposures and increasing/decreasing concentration exposures, but that criteria derived by EPA were only applicable to continuous exposures of fluctuating or constant TRC concentrations. EPA criteria may not be applicable to short-term or intermittent exposures. However, EPA also stated that "the effects of short exposures will probably be under-estimated if the observation period is not extended to take into account delayed effects ...". EPA also introduced the term "chlorine produced oxidants" (CPO) in the 1985 criteria document. Chlorine added to sea water reacts to form several reaction products: hypochlorous acid, hypochlorite ion, hypobromous acid, hypobromite ion, and, if ammonia is present, chloramines and bromamines, all of which are measured as CPO at pH = 4. Data discussed and criteria derived by EPA were expressed as total residual chlorine in freshwater and CPO in salt water.

In EPA (1985), freshwater 48 or 96 hours LC50s for TRC are reported to range from 17 ug/l for Daphnia (zooplankters) to 710 ug/l for stickleback. Salmonids are the most sensitive fish family with a mean LC50 of 77 ug/l, but two minnow species were actually the most sensitive fish with LC50s of 40 and 45 ug/l. In saltwater, LC50s for CPO range from 25 ug/l for eastern oyster to 1,418 ug/l for a mixture of two shore crab species. Mortality from chlorine is rapid, nearly half occurring in the first 12 hours of acute tests.

Several factors may affect TRC or CPO toxicity, but EPA determined that changes were slight and the pattern inconsistent. These factors were not considered in determination of criteria. For example, chloramines may have a different rate of toxicity than free chlorine, but within 48 or 96 hours, both have about the same toxicity in terms of the LC50. Aquatic life appears to be more sensitive to chlorine in warmer water, but the difference is slight.

In freshwater, life cycle chronic tests were conducted with two invertebrate species, Daphnia magna and the scud (both crustaceans), and a fish, the fathead minnow, with results ranging from 5.3 to 17 ug/l (EPA, 1985). The invertebrates were most sensitive. Only one chronic test was reported for saltwater species, an early life stage test for the fish, the tidewater silverside, with a result of 46.48 ug/l.

Chlorine is often used to control nuisance algae in ponds and reservoirs. Available data indicate that aquatic plants are less sensitive to chlorine than aquatic animals.

As was expected, no data was found on the bioaccumulation of TRC or CPO. They are unlikely to bioaccumulate.

EPA concluded that an important generality that could be drawn from study data not used in the criteria document, was that a variety of lethal and sublethal effects can occur at concentrations just above the calculated National Criteria. EPA also cited several field and laboratory studies in which fresh and saltwater fish avoided various chlorine concentrations. Tsai (1973) found none of 45 fish species collected at upstream sites present at downstream sites of 149 chlorinated sewage effluents where TRC was above about 400 ug/l. Ten species, mostly salmonids and cyprinids, were not found above 40 ug/l. Seegert (1979, cited in EPA, 1985) found fish below 11 wastewater effluents in New Jersey only where TRC was less than or equal to 100 ug/l. Middaugh et al. (1977, cited in EPA, 1985) found that juvenile spot (a saltwater fish) avoided 180 ug/l CPO at 10 °C and 50 ug/l CPO at 15 °C. Hose and Stoffel (1980, cited in EPA, 1985) found that blacksmith (a saltwater fish) avoided 162 ug/l CPO in the absence of food, but 203 ug/l CPO was required to elicit avoidance when food was present. Aside from one questionable result where no survival of daphnids was found at 2 ug/l after 7 days (Arthur et al. 1975, cited in EPA, 1985) sand dollar sperm was most sensitive to CPO among all organisms tested for sublethal effects. Dinnel et al. (1981, cited in EPA, 1985) found that exposure of sand dollar sperm to 2 ug/l for five minutes resulted in a 50 percent reduction in egg fertilization.

The National Guidelines (Stephan et al. 1985) require that a minimum data base be available to derive criteria to protect aquatic life from the toxic effects of a substance and to prevent accumulation of the substance in aquatic life to levels that are unsafe for consumption by humans or fish and wildlife. The minimum data base requirement was met for toxic effects to aquatic life and the following criteria were derived by EPA (1985). To protect freshwater aquatic life, TRC should not exceed 11 ug/l as a four-day average and 19 ug/l as a one-hour average. To protect saltwater aquatic life, CPO should not exceed 7.5 ug/l as a four-day average and 13 ug/l as a one-hour average. USEPA (1985) recommended that criteria should not be exceeded more than once in any three year period in order to allow stressed systems to recover.

The EPA (1985) criteria to protect aquatic life were derived from laboratory studies. Results of field studies are available which indicate that the criteria are appropriate to apply in natural surface waters. Spodaryk et al. (1986) conducted an acute, in situ chlorine toxicity test with caged, fingerling brown trout in the West Branch Reservoir, NY, to evaluate the impact of chlorinated Hudson River water on the fishery resource in the reservoir. Brown trout were held at various sites in the reservoir with mean TRC concentrations ranging from0.05 - 0.6 mg/l. The stability of the TRC concentration over time enabled the calculation of 48-hour LC50 of 0.10 mg TRC/1. This value is within the trout species mean acute values of 0.06 - 0.117 mg/l reported in EPA (1985). Neuderfer (1984) reported on the effects of chlorination of a municipal treatment plant effluent on Gooseberry Creek, Tannersville, NY. There was a 29-fold decrease in trout biomass below the discharge compared to upstream. Four years after installation of dechlorination facilities there was only a four-fold reduction in trout biomass below the discharge. TRC concentrations were not given in Neuderfer (1984). Information in the Tannersville POTW SPDES permit and compliance monitoring file, indicate that prior to dechlorination TRC in Gooseberry Creek at the MA7CD10 (minimum average, seven consecutive day flow in ten year period) flow of 1 cfs was 0.3 mg/l.

Neuderfer (1984) also summarized the records of the NYSDEC Bureau of Environmental Protection fishkill investigation unit. Of the 469 fish mortality events investigated from 1970-1983, 19 were caused by chlorine, all resulting from malfunctions of chlorination equipment or changes in operation resulting in unusually high chlorine concentrations in the receiving water. Neuderfer (1984) concluded that "slug" discharges of chlorine apparently overwhelmed the fishes' avoidance mechanisms.

Other studies also demonstrate effects of TRC at low levels in the field. The 96-hour LC50 for rainbow trout held in cages downstream from chlorinated sewage treatment plant effluents were 0.023 mg/l TRC (Basch et al. 1973). In another study, mortality of rainbow trout caged below chlorinated sewage treatment plant effluent was observed at 0.02 mg/l TRC (Servizi and Martens 1974, in Brungs, 1976). A study of intermittent chlorine discharges from a power plant found rainbow trout avoidance beginning at 0.05 to 0.01 mg/l TRC (Schumacher and Ney 1980).

As noted above, EPA (1985) did not fully discuss nor consider in criteria derivation results of studies which assess toxicity of intermittent chlorine exposures. A number of studies have shown an increase in median lethal mortality concentration when subjected to intermittent or short chlorine exposures (Brooks and Seegart 1977; Seegart and Brooks 1978; Seegart et al. 1979; Brooks and Bartos 1984). However, typically these tests are short exposures of up to two hours or several short exposures in one day (e.g., four 30 minute exposures). Brooks and Seegart (1977) concluded that one exposure of trout or perch to 200 ug/l for 30 minutes might not cause mortality, but, in situations where fish would be exposed to chlorine for longer times or repeated doses over some time, non-lethal concentrations of chlorine would probably be lower than 200 ug/l. There is no information on long-term intermittent exposure of aquatic life to chlorine that would enable derivation of separate criteria for such exposures. Wang and Hanson (1985) suggest that for fish, a minimum exposure to intermittent chlorination of about four days might be necessary to assess effects. Murray et al. (1985) found that mayfly eggs pre-exposed intermittently to 200 ug/l free available chlorine (FAC) exhibited increased nymphal mortality when the nymphs were later exposed to only 50 ug/l FAC for intermittent periods. Heath (1978) tested four fish species, exposing fish to FAC intermittently, for about 40 min. and non-exposure periods of about 8 hrs. He found 96-hr. LC50s for rainbow trout and channel catfish that were similar to the LC50s for these species in EPA (1985). Heath determined 96-hr. LC50s for golden shiner and bluefish were somwhat higher than most LC50s for these species reported by EPA (1985), but the differences were less than a factor of 2.

DERIVATION OF VALUES:

The water quality criteria developed by EPA (1985) for total residual chlorine were derived in accordance with Stephan et al. (1985). The data evaluations and criteria development for freshwater acute, saltwater chronic and saltwater acute applications are appropriate for NYS waters and should be adopted as values. A more stringent value should be adopted for freshwater classes to protect against chronic effects. The calculation procedure in the

National Guidelines (Stephan et al. 1985) will generally result in criteria that will protect aquatic life. The EPA chronic criterion (referred to as a four-day average by EPA) for saltwater should be adopted as the values for all saltwater classes except SD. The EPA acute criteria (referred to as a one-hour average by EPA) for fresh and saltwater should be adopted as the standards for classes D and SD, respectively. The four-day average criterion for freshwater published by EPA (1985) may provide inadequate protection for aquatic life from chronic effects of chlorine. The value of 11 ug/l recommended by EPA is higher than the geometric mean of test results for the only two invertebrate species that received chronic testing (5.3 ug/l for Daphnia magna and 7.2 ug/l for Gammarus pseudolimnaeus). In order to protect aquatic life, the geometric mean of the results from chronic tests with Daphnia magna, 5.0 ug/l, should be adopted as the value for all freshwater classes except D.

It is recommended that reference to CPOs not be included in the definition of TRC. CPOs are a factor in the toxicity resulting from chlorination of seawater but the inclusion of the term in regulation is unnecessary and could create some confusion. CPOs were likely to be present in the marine toxicity tests that formed the basis for the values, but they would have been detected by the TRC analytical method which measures most or all CPOs. Although the term TRC is a misnomer for all the toxicity resulting from chlorination of seawater, operationally, it is the most appropriate term.

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DFW

Date: April 11, 1984

Surface Water Quality
Standard Documentation

Chemical: 1-Bromo-3-chloro-5,5-dimethyl hydantoin

C.A.S, No.(s): 16079-88-2

Basis (Human/Aquatic): Aquatic

Standard by Water Classification:

	ug/l	Notes
Classes AA,AA-s;A;A-s;B;C	*	
Class D	*	
Classes SA;SB;SC;I	*	
Class SD	*	

Remarks: * See chlorine

Summary of Information and Standard Derivation

Concern for this compound is the liberation of free chlorine and bromine. Standards are therefore equivalent to those for chlorine and standards documentation for chlorine applies to this compound as well.

Date: April 11, 1984

Surface Water Quality
Standard Documentation

Chemical: Trichloro-s-triazinetrione

C.A.S, No.(s): 87-90-1

Basis (Human/Aquatic): Aquatic

Standard by Water Classification:

	ug/1	Notes
Classes AA,AA-s;A;A-s;B;C	*	
Class D	*	
Classes SA;SB;SC;I	*	
Class SD	*	

Remarks: * See chlorine

Summary of Information and Standard Derivation

This compound liberates free chlorine in water. Standards are therefore equivalent to those for chlorine and standards documentation for chlorine applies to this compound as well.