

VALUE(S) ADDED 7-24-85

FACT SHEET REVISED -----

VALUE(S) REMOVED -----

Date: April 3, 1984

Surface Water Quality
Standard Documentation

Chemical: Fluoride

C.A.S. No.(s):

Basis (Human/Aquatic): Aquatic

Standard by Water Classification:

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

Remarks: * = $(0.02) \exp(0.907[\ln(\text{hardness ppm})] + 7.394)$
** = $(0.1) \exp(0.907[\ln(\text{hardness ppm})] + 7.394)$

Summary of Information

1. Stephan, et al. (1983).

-found that a natural log-log relationship best fit the data between hardness and metal toxicity; therefore regression of the natural log of fluoride toxicity on the natural log of hardness was used below.

2. A number of studies have been conducted which found a relationship between fluoride toxicity and hardness. Data on fluoride toxicity to rainbow trout from these studies is tabulated below and a regression, as described above, was calculated.

| <u>Hardness mg/l</u> | <u>ln Hardness</u> | <u>LC₅₀, ug/l</u> | <u>ln LC₅₀</u> |
|----------------------|--------------------|------------------------------|---------------------------|
| 7.5 ^a | 2.01 | 3,700 | 8.22 |
| 12 ^a | 2.48 | 10,000 | 9.21 |
| 12 ^b | 2.48 | 18,000 | 9.80 |
| 17 ^c | 2.83 | 51,000 | 10.84 |
| 36 ^a | 3.58 | 30,000 | 10.31 |
| 49 ^c | 3.89 | 128,000 | 11.76 |
| 62 ^a | 4.13 | 58,700 | 10.98 |
| 62 ^d | 4.13 | 175,000 | 12.07 |
| 182 ^c | 5.20 | 140,000 | 11.85 |
| 385 ^c | 5.95 | 193,000 | 12.17 |

$$r = .86, r^2 = .74$$

$$\ln LC_{50} = .907 \ln \text{Hardness} + 7.394$$

- a - Neuhold and Sigler (1960): LC₅₀ used in the regression calculation were calculated using the relationship provided in the paper and selected hardness values within the range tested.
- b - Herbert, D.W.M. and D.S. Shurben. 1964. The toxicity of fluoride to rainbow trout. Water and Waste Treatment J. 10:141-142.
- c - Pimentel and Bulkley (1983)
- d - Kennedy/Jenks Engineers (1984)
- Angelovic et al. (1961) tested fluoride toxicity to rainbow trout in soft water and found an LC₅₀ of about 4.3 mg/l at 55° F; water was softened with a commercial softener but a final hardness concentration was not given.
- 3. Kennedy/Jenks Engineers (1984) tested the effects of hardness on fluoride toxicity to fathead minnow, but using their data to calculate a regression of fluoride toxicity on hardness resulted in a negative correlation.
- 4. IJC (1977)
 - "Fluoride is considered to be of the main ligands responsible for keeping beryllium, aluminum, scandium, niobium, tantalum, iron, and tin in solution in natural waters (33)." P95
 - "All vegetation contains some fluoride due to uptake from soil and water ranging normally from 2 to 20 ug/g (dry weight)." P96.
 - Data presented indicates that freshwater invertebrates appear to be less sensitive to fluoride than vertebrates.

5. Neuhold and Sigler (1960) studied effects on the egg and embryo larval stage of rainbow trout at fluoride concentrations higher than used for adults. No long-term chronic studies have been done to determine concentrations at which fluoride could have sublethal effects on bone structure, growth, and ultimately population viability. Ellis et al. (1946) found hatching of fish eggs delayed at 1.5 ppm fluoride. Herbert and Shurben (1964) concluded that fluoride up to 1 ppm would have a negligible effect on trout populations.
6. Angelovic et al. (1961), Neuhold and Sigler (1960) and Pimental and Bulkley (1983) discuss the increase of fluoride toxicity with an increase in temperature; it appears that for rainbow trout fluoride toxicity levels off between 55° and 65° F (about 13-19° C).
7. NRC (1974) recommended a maximum fluoride level in forage for young dairy breeding stock of 30 ppm, dry weight.
8. NAS/NAE (1972) recommended a criterion of 2 mg/l fluoride in livestock drinking waters.
9. Crissman et al. (1980) found dental fluorosis, elevated fluoride in bone ash and other evidence of fluoride poisoning in dairy cattle feeding on forage with 13 to 25 ppm fluoride, resulting from air emissions from an aluminum plant.
10. Shupe (1980) provides fluoride tolerance for cattle: 30 mg/Kg in feed and 2.5-4 mg/l in water for dairy and beef heifers; the low values for water should be used for active animals in a warm climate.
11. Newman and Murphy (1979) found symptoms of fluorosis in black-tail deer feeding on forage ranging from 44 to 333 ppm fluoride, symptoms similar to those found in cattle and other wild deer species.

Standard Derivation

In order to protect freshwater aquatic life the following fluoride standards derived from the relationships in 2) above, are recommended:

$$\begin{aligned} \text{Standard for all freshwater} & & & (.907 [\ln (\text{hardness ppm})] + 7.394) \\ \text{classes except D, ug/l} & = & (0.02)^e & \\ \text{Standard for class D, ug/l} & = & (0.1)^e & (.907 [\ln (\text{hardness ppm})] + 7.394) \end{aligned}$$

For waters exceeding a hardness of 200 mg/l, standards should be calculated using hardness equal to 200 mg/l. LC_{50} calculated at 200 mg/l are at the highest level actually measured in studies and criteria calculated from these effect levels should be considered maxima for safety.

The value of 0.1 in the Class D formula is the recommended application factor (AF) for assuring no acute toxicity. For all other classes an AF of 0.02 is used because the potential for fluoride accumulation and long-term chronic effects in fish warrants use of an AF more conservative than 0.05. With an AF=0.02 criteria in soft water are similar to the maximum suggested by Herbert and Shurben (1964) and at or below the low level effect found by Ellis et al. (1946). Since the long-term effect of concern is likely to result from fluoride accumulation use of the stream MA30 CD10 is appropriate for calculating water quality based effluent limits.

Although temperature affects fluoride toxicity, all of the data used in the regression were from studies conducted at 12° C or greater (see #6 above) so the recommended criteria should be sufficient at all receiving water temperatures. Similarly rainbow trout appears to be a sensitive species so the criteria should protect all aquatic life.

Examples of standards at various levels of hardness are provided in the following table.

Fluoride Standards, ug/l

| <u>Hardness, mg/l</u> | <u>Class D</u> | <u>All Other FW Classes</u> |
|-----------------------|----------------|-----------------------------|
| 25 | 3,014 | 603 |
| 50 | 5,652 | 1,130 |
| 100 | 10,599 | 2,120 |
| 150 | 15,310 | 3,062 |
| 200 | 19,875 | 3,975 |

Notwithstanding the above standards to protect aquatic life, it is recommended that where fluoride will be discharged to surface waters consideration be made for terrestrial animals. Where fluoride will exceed 3 mg/l (a value based on information in numbers 8 and 10 above) deleterious effects on livestock or wildlife that use the water for drinking could occur. Where waters receiving a fluoride discharge serve as the water source for terrestrial vegetation there is potential for the vegetation to exceed recommended fluoride levels for forage. In these situations a more thorough environmental assessment of environmental impacts should be conducted. Finally, where fluoride is discharged with other metals noted in 4) fluoride may complex with these metals and impair their removal from the water.

REFERENCES

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