Water quality criteria for Swamp Creek and water quality related effluent limitations for the Exxon Minerals Company. 1983

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WATER QUALITY CRITERIA FOR SWAMP CREEK AND WATER QUALITY RELATED EFFLUENT LIMITATIONS FOR THE EXXON MINERALS COMPANY

By

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PURPOSE/INTRODUCTION

The purpose of this document is:

1. To establish site-specific water quality criteria to provide for the protection and propagation of fish and aquatic life and recreational uses in Swamp Creek for toxic, conventional, and nonconventional pollutants present in a proposed discharge of treated wastewater from the Crandon Mine, and

2. To provide a summary of the water quality-related effluent limitations which will be proposed in a Wisconsin Pollutant Discharge Elimination System (WPDES) permit for the Exxon Minerals Company's proposed wastewater discharge.

The water quality criteria developed through the procedures outlined in this document are based upon the toxicity of each pollutant to aquatic species indigenous to Wisconsin surface waters. In some cases, the data base used to derive a criterion include test results from species not indigenous to Wisconsin. These selected test results are used as surrogates for the populations of organisms which do exist in Swamp Creek. For the conventional and nonconventional pollutants, specific criteria are either taken from the existing standards or are derived through a specified methodology other than the toxicity derivation procedures.

The effluent limits established in this document will be proposed in the WPDES permit when it is publicly noticed. In addition, the information provided in this document should be of assistance to Exxon Minerals in assessing their wastewater treatment alternatives and to the public in understanding and evaluating the impacts on the aquatic resources.

The criteria and limits which are recommended are based upon a given set of background stream chemistry, stream low flow and discharge volume characteristics. Different criteria and/or effluent limitations may be applicable if any one or all of these conditions change. If such changes are made, addenda to this report will be prepared.

DISCHARGE LOCATION AND PARAMETERS CONSIDERED

The proposed discharge site (Figure 1) is located in the NW quarter of Section 32, T35N, R12E. The discharge location corresponds to sampling site 3 of the 1981-83 Aquatic Monitoring Program conducted on Swamp Creek by Exxon consultants. Four other sampling locations are also shown in Figure 1. Along with station 3, sampling site 1, located at County "M", provides data on background conditions, while sites 4, 5, and 6 provide an indication of conditions downstream from the outfall location.

The complete list of pollutants projected to be present in the proposed wastewater discharge was obtained from Phase III of the Water Management Study (CH_2M Hill, 1982). Many of the substances listed in the Phase III study are metals, but other parameters will also be present. Water quality criteria and effluent limits were determined for the following pollutants: arsenic, barium, cadmium, fluoride, lead, mercury, selenium, silver, copper, iron, zinc, chromium (+3), chromium (+6), cyanide, pH, total suspended solids, total dissolved solids, and BOD. Not all of the above-mentioned parameters are categorized as "toxic" pollutants. For example, pH, total suspended solids, and BOD are "conventional" pollutants while barium, fluoride, iron, and total dissolved solids are "nonconventional" pollutants. However, the criteria for these parameters were developed to protect the uses in the receiving stream from the respective impacts of these pollutants. (A more detailed discussion follows later in this document). Two elements, manganese and aluminum, were lacking information on aquatic toxicity, so criteria and effluent limits were not calculated for those pollutants.

WATER QUALITY STANDARDS

Criteria and Application

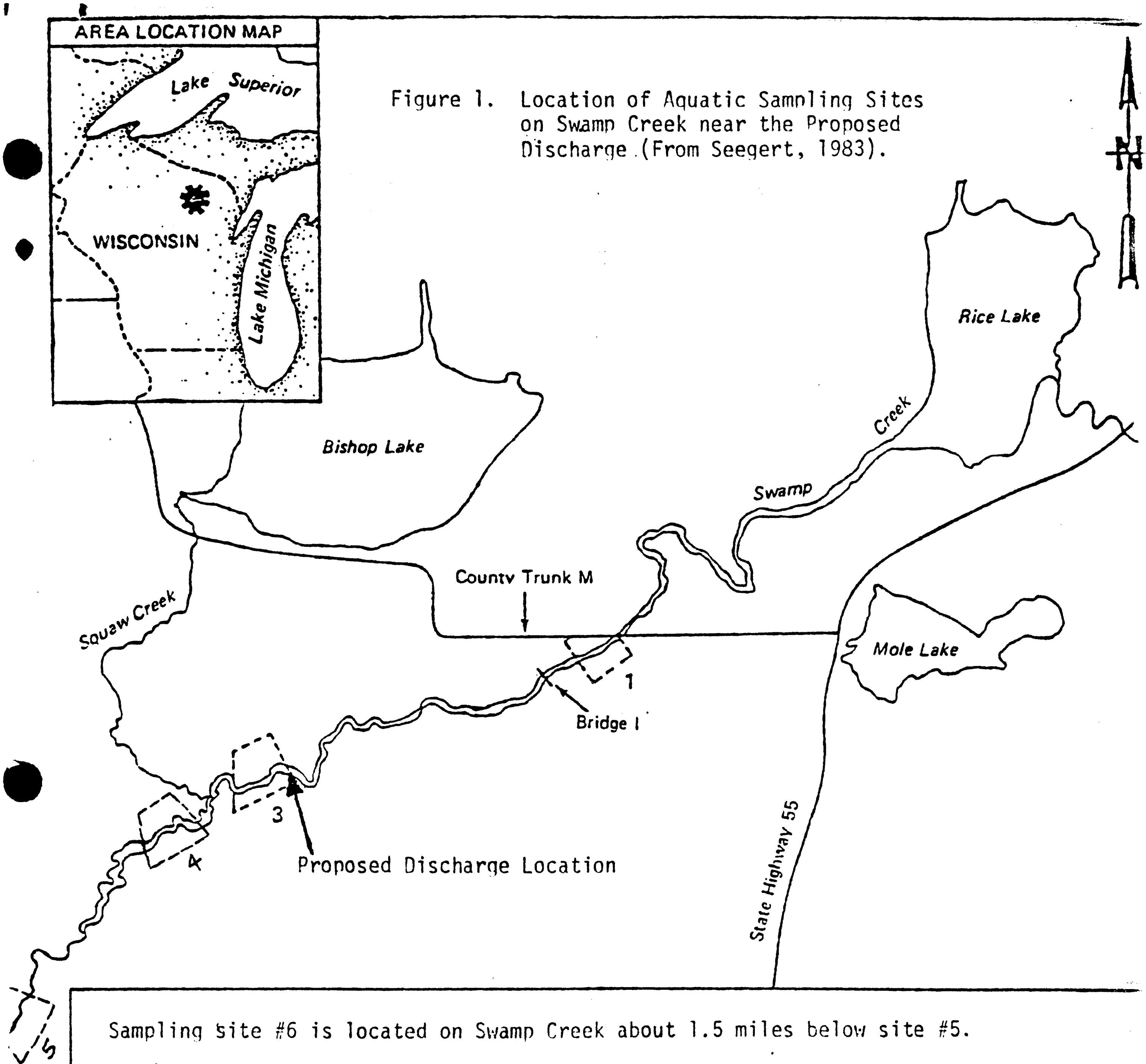
The Wisconsin Administrative Code (Wis. Adm. Code) contains the state water quality standards and specific requirements governing the presence of toxic pollutants in state waters. All of the provisions in NR 102 were considered in developing water quality criteria for Swamp Creek. Some of the specific sections of NR 102 which are most applicable are listed below:

- Substances in concentrations or combinations which are toxic or harmful to humans shall not be present in amounts found to be of public health significance, nor shall substances be present in amounts which are acutely harmful to animal, plant or aquatic life. (NR 102.02(1)(d), Wis. Adm. Code)

- STANDARDS FOR FISH AND AQUATIC LIFE. Except for natural conditions, all waters classified for fish and aquatic life shall meet the following criteria:

    (a) Dissolved oxygen: Except for waters classified as trout streams in Wisconsin Trout Streams, Publication 213-72, the dissolved oxygen content in surface waters shall not be lowered to less than 5 mg/l at any time.

Figure 1. Location of Aquatic Sampling Sites on Swamp Creek near the Proposed Discharge (From Seegert, 1983).



Sampling site #6 is located on Swamp Creek about 1.5 miles below site #5.

MILES 0 0.5 1.0

KILOMETERS 0 0.5 1.0

LEGEND:

1-3 = SAMPLING STATIONS

EXXON MINERALS COMPANY
CRANDON PROJECT

SAMPLING STATIONS FOR THE 1982-1983 AQUATIC MONITORING PROGRAM ON SWAMP CREEK

ECOLOGICAL ANALYSTS

(b) Temperature: 1. There shall be no temperature changes that may adversely affect aquatic life.

2. Natural daily and seasonal temperature fluctuations shall be maintained.

3. The maximum temperature rise at the edge of the mixing zone above the existing natural temperature shall not exceed 5°F for streams and 3°F for lakes.

4. The temperature shall not exceed 89°F for warm water fish.

(c) pH: The pH shall be within the range of 6.0 to 9.0, with no change greater than 0.5 units outside the estimated natural seasonal maximum and minimum.

(d) Unauthorized concentrations of substances are not permitted that alone or in combination with other materials present are toxic to fish or other aquatic life. The determination of the toxicity of a substance shall be based upon the available scientific data base. (NR 102.02(3), Wis. Adm. Code)

- ANTIDEGRADATION. No waters of the state shall be lowered in quality unless it has been affirmatively demonstrated to the department that such a change is justified as a result of necessary economic and social development, provided that no new or increased effluent interferes with or becomes injurious to any assigned uses made of or presently possible in such waters (NR 102.03(2), Wis. Adm. Code).

- As a guide to the delineation of a mixing zone, the following shall be taken into consideration:

(a) Limiting mixing zones to as small an area as practicable, and conforming to the time exposure responses of aquatic life.

(b) Providing passageways in rivers for fish and other mobile aquatic organisms.

(c) Where possible, mixing zones being no larger than 25% of the cross-sectional area or volume of flow of the stream and not extending more than 50% of the width.

(d) For contaminants other than heat, the 96-hour TLM to indigenous fish and fish food organisms not being exceeded at any point in the mixing zone.

(f) Mixing zones not interfering with spawning or nursery areas, migratory routes, nor mouths of tributary streams. (NR 102.03(4), Wis. Adm. Code).

To satisfy the above-mentioned provisions in the code, site-specific water quality criteria were developed based on the aquatic life and recreational uses of the receiving water.

Designated Use

Swamp Creek below Rice Lake supports a diversity of aquatic organisms. In addition to sustaining a warmwater fishery, Swamp Creek has a variety of benthic macroinvertebrates, phytoplankton and zooplankton species, periphytic algae, and aquatic macrophytes. The current water quality standards (NR 104.08, Wis. Adm. Code) require that all streams in Forest County (including Swamp Creek and downstream waters) must meet the standards and criteria for fish and aquatic life and recreational use.

The Department of Natural Resources has conducted a stream classification of Swamp Creek based on its habitat characteristics (Appendix A). As a result of the stream classification and the variety of aquatic organisms present, Swamp Creek below Rice Lake has been confirmed as a stream which shall meet the criteria for fish and aquatic life and recreational uses. This means that all the aquatic organisms present in the stream, including the entire food chain, is to be protected. In addition, fish spawning sites in Swamp Creek must also be preserved. Consequently, the site specific water quality criteria developed for Swamp Creek are designed to protect all aquatic organisms in that stream including their reproduction, growth and well-being.

Information Sources for the Criteria Data Base

An extensive data base exists on the effect of toxic substances on fish and fish food organisms. The Department utilized the available data in calculating water quality-based effluent limits for toxic substances. Examples of the general data sources used to determine the criteria values for toxic and other pollutants include:

- Ambient water quality criteria documents which have been published by EPA. The availability of these documents and the criteria determination procedures used are detailed by EPA in the November 28, 1980 or subsequent editions of the Code of Federal Regulations.

- <u>Water Quality Based Effluent Limits for Heavy Metals and Cyanide</u>, Michigan DNR (October, 1981).

- The National Research Council of Canada (1976-1982) has published a number of documents on the effects of contaminants on the Canadian (Aquatic) Environment. Documents for ten substances were utilized as information sources and include the following:

    - Effects of Arsenic in the Canadian Environment
    - Effects of Cadmium in the Canadian Environment
    - Effects of Chromium in the Canadian Environment
    - Copper in the Aquatic Environment: Chemistry, Distribution, and Toxicology

- The Effects of Cyanides on Aquatic Organisms with Emphasis upon Freshwater Fish
- Environmental Fluoride 1977
- Effects of Lead in the Environment - 1978
- Effects of Mercury in the Canadian Environment
- Interactions of Selenium
- Zinc in the Aquatic Environment: Chemistry, Distribution, and Toxicology

- Journal Water Pollution Control Federation Literature Review Issues (June, 1980, 1981, 1982, 1983). Information found here is essentially an update of that found in the EPA (1980) criteria documents. June JWPCF issues from 1979 and earlier contain information which is redundant to that in the EPA (1980) documents.

- Water Quality Criteria, Federal Water Pollution Control Administration, 1968.

- Water Quality Criteria 1972, National Academy of Sciences and National Academy of Engineering, 1973.

- Quality Criteria for Water, U.S. Environmental Protection Agency, 1976.

- Water Quality Criteria, Resources Agency of California, State Water Resources Control Board, 1971.

- A Review of the EPA Red Book: Quality Criteria for Water, American Fisheries Society, 1979.

Other peer-reviewed literature may also have been used in determining the criteria. Specific literature citations are provided in the individual criteria reports.

The sources listed above may also provide guidelines for development of criteria levels or specific recommendations for protection of aquatic resources for a wide variety of pollutants. In general, the criteria derived below were based upon the methodology described in the following section. However, in some cases the approach to criteria development used here may be similar to that employed by others.

WATER QUALITY CRITERIA AND LIMITATIONS FOR THE TOXIC POLLUTANTS

A general explanation of acute and chronic criteria development for toxic substances is included in the discussion in this section. Specific determinations of the criteria (acute and chronic) are incorporated as separate appendices to this report; one appendix is listed for each of the pollutants in Exxon's proposed wastewater discharge.

Initial screening of the data base involves restricting that toxicity data base to only those species found in Wisconsin surface waters. Further screening is then performed for factors such as exposure time and life stages studied. The final criteria protects the most sensitive species for which data is available. The approach used in Wisconsin for toxic pollutant criteria development uses only species indigenous to Wisconsin or species which represent organisms which may be present.* In addition, Wisconsin's approach is site-specific to provide the necessary level of protection for uses in the receiving water.

It should be noted that the criteria derivation process employs a methodology which uses mean values from tests are also reported (in many cases) as mean (50%) survival. Therefore, even though the criteria are derived to protect the most sensitive species, there will be test results which show an effect in excess of the noted protection level (acute or chronic toxicity).

Procedures for Developing Acute Toxicity Criteria

Acute or short-term toxicity data are usually expressed as 96-hour LC50 values. LC50 concentrations have a lethal effect on half of a test group of the particular aquatic organism in the noted time period. Acute toxicity values are based on exposure times appropriate to the life stage of the species tested. For most aquatic species, the generally accepted duration for acute toxicity testing is 96 hours. However, acute toxicity data should be limited to 48-hour LC50 values for daphnids and other cladocerans, as well as midge larvae, because of the short life cycle of these organisms.

The "nontoxic" chemical characteristics of water do, in many cases, affect the toxicity of some pollutants. In the Exxon situation, and based upon the results of criteria development by the U.S. Environmental Protection Agency, water hardness (expressed as calcium carbonate) is related to toxicity of most of the metals which may be present. An average hardness value of 94 mg/l $CaCO_3$ was calculated from background stream concentration levels in Swamp Creek (Table 1). The hardness value of 94 mg/l $CaCO_3$ was utilized to determine water quality criteria for those parameters in the proposed discharge where hardness is a factor affecting toxicity. Because there is an inverse relationship between streamflow and hardness in Swamp Creek, use of the average value provides a conservative approach to water quality protection.

Acute criteria are expressed either 1) as an equation when related to another characteristic such as hardness, or 2) as a single value applicable in all waters. The testing of the relationship between hardness and toxicity is the initial step in determining how a criterion is expressed. If there are two or more LC50 data values for a particular substance, and if each LC50 value has a

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*Daphnia magna data are used in the determination of the criteria in the absence of useful toxicity data for other dapnids, even though this species is not indigenous to Wisconsin. Other daphnids do exist in Wisconsin waters and an inspection of the overall data base reveals that the various species of daphnia exhibit similar sensitivites to toxic contaminants. These organisms provide a useful indicator of impacts on the lower levels of the food chain.

corresponding and related value for water hardness, a species acute equation (SAE) can be developed. This is accomplished by performing several linear and curvilinear regression analyses on the data. Various assumed relationships between hardness and LC50 values for each species are tested to determine the "best fit" relationship. Four basic relationships are tested:

- LINEAR: A straight line of hardness (H) versus LC50 in the form: $LC50 = a + bH$
- LOG NORMAL - An exponential curve of hardness versus the logarithm of LC50 in the form: $LC50 = a(b)^H$
- DOUBLE LOG (POWER FUNCTION): An exponential curve of the logarithm of hardness versus the logarithm of LC50 in the form: $LC50 = a(H)^b$
- PARABOLA: An exponential curve of the square of hardness versus LC50 in the form: $LC50 = a + bH^2$

For each species, the best fit relationship from the above equations is determined through use of a correlation coefficient (r-factor) which provides an indication of how well the two parameters (LC50 and hardness) are related to each other. To arrive at a Final Acute Equation (FAE) for a toxic substance, a geometric mean of the r-factors for the individual SAEs is calculated to determine which of the curve types provide the best "overall" description of the data. This particular curve form is then utilized to develop the FAE for the range of hardness values typically found in Wisconsin waters (20-400 mg/l). This procedure ensures adequate protection of the most sensitive species and, thus, the designated uses of the stream.

If the above analysis does not reveal a toxicity-hardness relationship, then a single value for toxicity is determined. For each species which has 2 or more LC50 data values for a particular toxic substance, a species mean acute value (SMAV) is calculated. The SMAV is the geometric mean of the available and reliable LC50 test results. Single LC50 test values are assumed to be mean values if the species and/or the toxic substance is important in a given situation. After the acute values are calculated for the individual species, the Final Acute Value (FAV) is determined from the lowest SMAV or single value.

Procedures for Developing Chronic Toxicity Criteria

Chronic toxicity refers to long-term exposure effects from a toxic pollutant. Data on chronic toxicity to aquatic life is found in results from whole or partial life-cycle tests. If these data are unavailable for a particular species, early life stage toxicity tests consisting of 28 to 32 day exposures from shortly after fertilization through early development may be utilized. For any of the above-mentioned exposures, chronic criteria are geometric means of the highest tested no-effect concentrations and the lowest tested LC50 concentrations, or other similar adverse effects.

If the amount of chronic data is about the same as the acute data, the procedure for developing chronic water quality criteria is identical to the acute procedure described above. However, for the majority of toxic substances, the chronic toxicity data base is considerably smaller than the acute data base; in many cases, it may be a single reported value for a species. Therefore, chronic criteria can be developed through utilization of the acute toxicity data base by using "acute-chronic ratios" (A/C ratios). Whenever test conditions are such that chronic data can be compared to acute data, an A/C ratio is calculated by dividing the acute values by the chronic whole or partial life-cycle test results. The assumption in using this method is that chronic toxicity effects are related to other water quality characteristics in a manner similar to the acute toxicity relationships.

Where data are available, species mean chronic values (SMCVs) and species chronic equations (SCEs) are calculated in a manner similar to SMAVs and SAEs for acute criteria. The only parameter that had enough data to calculate chronic criteria in this manner was silver.

When the data base is insufficient to conduct the above analysis, other methods for determining chronic criteria are employed. If the most acutely sensitive species has only one corresponding chronic test result, an A/C ratio can be calculated for that species. Chronic values or equations for other species are then calculated by dividing the acute value or equation for these species by the above A/C ratio. For comparison, A/C ratios are calculated in a similar manner for all other species with available chronic data and applied to the acute data to determine which species have the most sensitive SMCV or SCE. The following parameters had values determined from A/C ratios: arsenic, lead, selenium, mercury, chromium (+3), and chromium (+6).

If the most acutely sensitive species has no chronic toxicity data, but other species have A/C ratios, chronic criteria were calculated by dividing the Final Acute Value by an arithmetic mean of all available A/C ratios. An arithmetic mean A/C ratio is used instead of a geometric mean in this case because a geometric mean was already used to calculate the acute value to which the ratio is applied. A mean A/C ratio was only used in developing chronic criteria for cyanide.

A combination of methods, which includes use of A/C ratios where appropriate (only one chronic test) and SMCVs or SCEs when multiple chronic tests for the same toxic substance are available with different species, is usually the most practical way to derive the FCV or FCE. Such a collection of data was utilized to generate chronic numbers for the following toxic pollutants present in Exxon's discharge: cadmium, copper and zinc.

If a substance contains no species with chronic toxicity information, no chronic criterion can be developed. For Exxon's situation, there was sufficient information to determine chronic criteria values for all the parameters in the proposed discharge.

Additional Criteria Considerations

In addition to developing acute and chronic toxicity criteria to protect fish and aquatic life, other guidelines for protection of aquatic life are necessary. Plants are protected by selecting the lowest toxicity value for plant species found in Wisconsin. These values are measured toxic substance concentrations which have been shown to reduce the amount of growth in a 96-hour or longer test on algae or in a chronic test on aquatic vascular plants. None of the parameters in Exxon's proposed discharge had chronic plant values available.

The Final Residue Value (FRV) is intended to prevent aquatic organisms from accumulating material to amounts in excess of Food and Drug Administration (FDA) action levels or other similar criteria. In addition, the FRV is designed to protect wildlife which consume these aquatic organisms from demonstrated adverse effects. Two kinds of data are necessary to calculate the FRV: a bioconcentration factor (BCF) and a maximum permissible tissue concentration. The latter value is either the FDA action level for fish oil or the edible portion of fish or shellfish, or the maximum acceptable dietary intake based on observations of survival, growth, or reproduction in a chronic wildlife feeding study. If a permissible tissue concentration is not available, a Final Residue Value cannot be calculated. The BCF is equivalent to the concentration of a toxic substance in an aquatic organism divided by the concentration of the substance in the water. The Environmental Protection Agency methodology for calculating FRV's is used for criteria calculation (refer to the November 28, 1980 issue of the Code of Federal Regulations). Mercury is the only pollutant in Exxon's proposed discharge which exhibits this characteristic and for which an FRV is calculated.

Toxic Criteria Summary

Two criteria concentration levels are developed from the existing toxicity data base--a maximum value and a monthly average (Table 3). The methods for determining each of the parameter criteria values are presented in the appendices for each parameter. The two criteria levels established are designed to protect fish and aquatic life from acute (maximum value) and chronic (monthly average) effects of both cumulative and noncumulative substances.

The maximum concentration, which is not to be exceeded at any time, is obtained from either the Final Acute Value (FAV) or the Final Acute Equation (FAE). The monthly average concentration is obtained by selecting the lowest available value from the Final Chronic Value (FCV), the Final Chronic Equation (FCE), the Final Plant Value (FPV), or Final Residue Value (FRV). The use of equations for both acute and chronic protection is dependent on the occurrence of significant relationships between toxicity and water hardness.

Determination of Effluent Limitations

The maximum criterion concentration level is applicable at the point of discharge to Swamp Creek. The monthly average concentration is applicable at the edge of the mixing zone of Swamp Creek and the wastewater discharge. The procedures and the data utilized to generate specific criteria to calculate the maximum and the edge of mixing zone values are addressed in individual appendices on each toxic substance. (Appendices B-L).

Background Water Quality of Swamp Creek

Water quality data has been collected on Swamp Creek at two locations (Stations 1 and 3, Figure 1) in the vicinity of the proposed discharge for one year (from April 1982 through March 1983). Data for each parameter from both Station 1 (at County "M") and Station 3 (near the proposed discharge) were arithmetically averaged to determine background stream concentration levels in Swamp Creek which are then used in the calculation of the effluent limitations (Table 1).

For many parameters, especially the metals, concentration levels were frequently recorded as less than the detection limit. Statistically, a number of approaches can be used to calculate averages or other statistics for values reported as such. However, to afford the maximum level of protection for fish and aquatic life in Swamp Creek, and to be consistent with Department goals to provide for the protection and propagation of fish and aquatic life in Wisconsin surface waters, parameter values reported as less than a value are assumed to be equal to that value.

Calculation of Effluent Limitations Based on Chronic Toxicity

Using the chronic criteria, water quality standards are established which are applicable at every point outside of an established mixing zone. NR 102.03(4)(c), Wis. Adm. Code, defines, in part, the size of the mixing zone as follows:

> The size of the mixing zone cannot be uniformly prescribed, but shall be based on such factors as effluent quality and quantity, available dilution, temperature, current, type of outfall, channel configuration and restrictions to fish movement. As a guide to the delineation of a mixing zone, the following shall be taken into consideration:
>
> (c) Where possible, mixing zones being no larger than 25% of the cross-sectional area or volume of flow of the stream and not extending more than 50% of the width.

Thus, in the case of the proposed Exxon discharge, the mixing zone is limited to one-quarter of the stream flow of Swamp Creek. Wisconsin water quality standards are to be met at all flows greater than or equal to the minimum 7-day flow which occurs once in 10 years ($Q_{7,10}$). The amount of upstream flow allowed for dilution then, incorporating the 25 percent mixing zone concept, is one-quarter of the $Q_{7,10}$. For Swamp Creek at County "M", the U.S. Geological Survey has determined that this value is 15 cubic feet per second (cfs).

Assuming that the effluent will instantaneously mix with one-quarter of the stream flow in Swamp Creek, the following formula, developed from a mass balance equation, applies:

$$C_E = \frac{Q_M C_M - Q_S C_S}{Q_E} \qquad (1)$$

where:
C_E = effluent concentration
C_M = chronic criterion concentration
C_S = background stream concentration levels in Swamp Creek
Q_E = effluent flow
Q_S = upstream flow in Swamp Creek (1/4 $Q_{7,10}$)
Q_M = mixing zone flow (Q_E + Q_S)

Q_E values of 2000 gpm, an average effluent flow rate, and 3000 gpm, a maximum flow rate, were used in the above calculations (treatment plant flows are from the WPDES permit application). The background stream concentration levels in Swamp Creek (C_S) were determined from data collected by Ecological Analysts from April 1982 - March 1983 at stations 1 and 3. The effluent concentration (C_E) is the end of pipe effluent limitation that would appear in the WPDES as a monthly average concentration. C_M, the chronic criterion concentration, is applicable at every point outside the mixing zone and is determined as described earlier. For some parameters, the ambient or background stream levels are at or near the recommended criteria concentrations. In these cases, it is recommended that either 1) discharge above the background stream levels in Swamp Creek not be allowed, or 2) the calculated effluent limit be very stringent. For those parameters where the above equation was utilized to determine C_E values, the various values used (C_M, C_S, Q_E, Q_S, and Q_M) in the calculations are summarized in Table 2. The calculated effluent limits (both maximum and monthly average values) are listed in Table 3.

WATER QUALITY CRITERIA AND LIMITATIONS FOR THE CONVENTIONAL POLLUTANTS

Biochemical oxygen demand, total suspended solids, and pH are the conventional pollutants in the Exxon discharge for which effluent limits are established. The water quality standards (NR 102, Wis. Adm. Code) contain specific criteria for or related to the pH and BOD (dissolved oxygen) parameters. The portion of this document titled "WATER QUALITY STANDARDS" contains the applicable pH and dissolved oxygen criteria for fish and aquatic life protection.

The standard for pH that has to be met for the protection of fish and aquatic life is specified in NR 102.02(3)(c), Wis. Adm. Code. The daily minimum and maximum pH values that apply are 6 and 9 with no change greater than 0.5 units outside the estimated natural seasonal maximum and minimum.

The "General" section of the standards categories addresses the suspended solids parameter (NR 102.02(1), Wis. Adm. Code):

(a) Substances that will cause objectionable deposits on the shore or in the bed of a body of water, shall not be present in such amounts as to interfere with public rights in waters of the state.

(b) Materials producing color, odor, taste or unsightliness shall not be present in such amounts as to interfere with public sights in waters of the state.

No specific numerical standards for suspended solids for the protection of fish and aquatic life are contained in the Wisconsin Administrative Code or in the literature. However, the Code of Federal Regulations (December 3, 1982) stipulates categorical effluent guidelines for New Source Performance Standards (NSPS) for ore mining activities which are applicable for the proposed Exxon discharge. The categorical limits that apply for suspended solids are 30 mg/l for a daily maximum and 20 mg/l for a monthly average. These limits are sufficient to protect surface waters from exceeding the conditions noted above.

Water quality based limits for BOD were determined using an empirical model. The specific criteria for dissolved oxygen contained in NR 102, Wis. Adm. Code, was utilized in determining the BOD effluent limit. The procedures and data utilized to generate the particular criteria as well as the calculations to determine the effluent limits for BOD are contained in Appendix M.

Weekly average effluent limits for BOD_5 are 20 mg/l in the summer months (May 1 through October 31) and 40 mg/l in the winter months (November 1 through April 30) based on an average treatment plant flow of 2000 gpm, and 15 mg/l and 30 mg/l in the summer and winter months respectively, based on a treatment plant flow of between 2000-3000 gpm.

WATER QUALITY CRITERIA AND LIMITATIONS FOR THE NONCONVENTIONAL POLLUTANTS

Barium, fluoride, iron, total dissolved solids and sulfate are nonconventional pollutants that will be present in the proposed discharge to Swamp Creek. As is the case with the conventional pollutants, there is no uniform procedure utilized for developing water quality criteria for these pollutants. The specific approach used to generate the criteria for each parameter is based upon the potential impacts that the particular pollutant has on aquatic life in the ecosystem. The criteria are designed to protect aquatic life from impairment to reproduction, growth or survival. The individual criteria developed for each of the nonconventional pollutants are contained in Appendices N-Q. Table 3 contains the calculated effluent limitations for these prarameters.

SUMMARY

This report contains a description of the procedures used in determining the site-specific water quality criteria and effluent limitations for a wastewater discharge from the proposed Exxon Minerals Company Crandon Mine to Swamp Creek. The designated uses of this receiving water require the attainment of standards and criteria necessary to support fish and aquatic life and recreational uses. The criteria and effluent limits derived in this document are established to protect the stream environment from the impacts of acute and chronic toxicity as well as preventing other adverse effects. The recommended values are based upon a given set of known conditions regarding stream and effluent flow and ambient water chemistry. Modifications to these recommendations may be appropriate under other wastewater discharge conditions.

Criteria and limitations are developed for those parameters which are currently projected to be present in this discharge. As new information becomes available regarding the presence of other contaminants, criteria and limitations will be determined. Similarly, as the data base used in the derivation of the criteria changes, modifications of the criteria and the limitations may also be necessary.

In accordance with the state's water quality nondradation policy, there will be no interference with the uses in Swamp Creek and other waters if the recommended criteria and limitations are attained. The Environmental Impact Statement will assess the social and economic necessity of the project as required by this policy.

References Cited

CH_2M Hill, for Exxon Minerals Company Crandon Project. 1982. Phase III Water Management Study.

Seegert, Greg and Lewis, Randall. 1983. Final Report on the aquatic biology of Swamp Creek for the Crandon project. Ecological Analysts, Inc., Northbrook, Illinois. 67 pp.

Table 1. Background Stream Concentration Levels (C_S Values) in Swamp Creek (Data Collected by Ecological Analysts from 4/82 - 3/83).

Parameter	Station 1	Station 3	Average C_S Values Between Stations 1 & 3
Fluoride (mg/l)	6@<0.1, .11, .08, .09, .02, .02, .05	6@<0.1, .09, .06, .08, 0.1, .02, .04	.08
Arsenic (ug/l)	3@<2, <.2, 1, <.5, <1, .3, 1	3@<2, <.2, <1, <.5, <1, <.3, 1.1	1.2
Barium (ug/l)	7, 15, 11, 14, 9, 15, 9, 15, <5, 11, 9, 15	8, 15, 5, 11, 12, 13, 9, 19, 5, 17, 7, 9	11
Cadmium (ug/l)	4@<.1, 1.4, .2, .5, <.2, .2, .4, .3, .3	6@<.1, 0.2, <0.2, .4, .2, .3, .4	0.26
Chromium^{+3} (ug/l)	4@<1, <4, 3, <2, <3, <4	3@<2, <4, 3, <1.5, <3, <1, <1	2.2
Chromium^{+6} (ug/l)	4@<1, <4, <3, <4, <2, <4	4@<1, <4, <3, 3@<2	2.1
Copper (ug/l)	22.8, <1, 6.4, 8, <1, 1.7, 1.2, 7, 6, 4.5, 6.3, 6.7	6.3, 4.5, 4.7, 1.4, 7.1, 3, <1, 1.6, 1.1, 2, 9, 5.5	5.0
Iron (ug/l)	300, 220, 200, 210, 210, 140, 175, 260, 610, 140, 440, 90	<30, 490, 220, 200, 270, 270, 175, 230, 350, 680, 80, 400	267
Lead (ug/l)	5@<1, 1, 3.6, 3, 1, 2, 3.4, 5	7@<1, 1, 2, 1, 1, 3	1.6
Manganese (ug/l)	38, 37, 40, 26, 23, 19, 35, 37, 35	45, 15, 10, 23, 27, 23, 40, 37, 39	30
Mercury (ug/l)	8@<0.2, <0.05, <0.03, <0.1, 0.2	8@<0.2, <.05, <.03, <.1, .2	0.17
Selenium (ug/l)	5@<1, 1.4, <4, <2, 2@<.5, <2, 1.1	5@<1, 1.2, <4, <2, 2@<0.5, <2, 1.1	1.4
Silver (ug/l)	7@<.2, <.3, <.1, 0.5, <1, 0.1	7@<.2, 0.3, <0.1, <.5, <1, <.1	0.3
Zinc (ug/l)	2.5, 3.1, 6.1, 20, 30, 1.2, 1.7, 1.1, 7.1, 2.3, 31, 42	4.9, 3.7, 9.6, 43, 40, 1.0, 3.7, 0.9, 1.9, 2.7, 14, 11	11.8
Aluminum (ug/l)	43, 73, 37, 9, 51, 6, 33, 26	47, 116, 44, 8, 45, 10, 31, 22	37.6
Cobalt (ug/l)	5@<1, <2, 2, 2.1	5@<1, <2, <2, 2.1	1.4
Molybdenum (ug/l)	3, <1, <2, <2, 1, <1, 3, 2.4	3, <1, <2, <2, 1, 1.2, 3.1, 2.9	2.0
Nickel (ug/l)	<5, 5, 9, 8, <1, 1, <2, <1	<5, 5.5, 7, 7, <1, 1, <2, <1	3.8
COD (mg/l)	52, 40, 13, 35	85, 14, 12, 39	36
Total Cyanide (mg/l)	12@<.01	12@<.01	.01
Sulfate (mg/l)	6.6, 6.1, 4.0, 5.1, 4.5, 5.5, 4, 4.1, 6, 5, <5, 7	6.5, 5.9, 4.4, 4.7, 3@ 4, 3.8, 6, 6, 5, 7	5.2
Chloride (mg/l)	1.7, 2.3, 2.5, 3.7, 3.0, 2.8, 2.8, 2.9, 3.5, 3.1, 3.1, 3.2	1.7, 2.3, 2.4, 2.9, 3.0, 2.9, 2.9, 2.9, 3.2, 3.2, 3.3, 3.3	2.9
Total Dissolved Solids (mg/l)	158, 141, 109, 150	91, 126, 119, 177	134
Total Hardness (mg/l)	72, 116, 93, 85, 85, 85, 105, 116, 87	76, 113, 92, 83, 85, 82, 106, 116, 87	94
BOD_5 (mg/l)	2.9, 2.1, 1.0, 1.0	2.3, 2.3, <1, 1.1	1.7

Table 2. Criteria Summary and List of Values Used in Calculating the Effluent Limitations (C_E)

Parameter	Acute Criteria (Daily max in mg/l)	Chronic Criteria (C_M values in mg/l)	C_S (mg/l)	Q_S (cfs)	Q_E (cfs) Ave(1) flow	Q_E (cfs) Max(2) flow	Q_M (cfs) Ave(1) Q_E	Q_M (cfs) Max(2) Q_E
Arsenic	1.48	0.29	0.0012	3.75	4.46	6.68	8.21	10.43
Cadmium	0.074	0.00025	0.00026	3.75	4.46	6.68	8.21	10.43
Chromium^{+6}	0.059	0.0096	0.0021	3.75	4.46	6.68	8.21	10.43
Chromium^{+3}	11.1	0.105	0.0022	3.75	4.46	6.68	8.21	10.43
Copper	0.025	0.013	0.005	3.75	4.46	6.68	8.21	10.43
Cyanide	0.096	0.011	0.01	3.75	4.46	6.68	8.21	10.43
Lead	1.0	0.042	0.0016	3.75	4.46	6.68	8.21	10.43
Mercury	0.002	0.0002	0.00017	3.75	4.46	6.68	8.21	10.43
Selenium	1.0	0.077	0.0014	3.75	4.46	6.68	8.21	10.43
Silver	0.007	no rec'd value	0.0003	3.75	4.46	6.68	8.21	10.43
Zinc	0.44	0.071	0.0118	3.75	4.46	6.68	8.21	10.43
Barium		5.0	0.011	3.75	4.46	6.68	8.21	10.43
Fluoride		6.8	0.08	3.75	4.46	6.68	8.21	10.43
Iron		1.0	0.267	3.75	4.46	6.68	8.21	10.43

(1) Based on an average flow from the treatment plant of 2000 gpm (from the WPDES permit application).

(2) Based on a maximum flow from the treatment plant of 3000 gpm (from the WPDES permit application).

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Table 3. Calculated Effluent Limits. All Values are in mg/l Unless Stated Differently.

	Parameter	Daily max[1]	Monthly Average @ Q_E Values $\leq$2000 gpm	Monthly Average @ Q_E Values 2000-3000 gpm
Toxic Pollutants	Arsenic	1.48	0.55	0.45
	Cadmium	0.074	0.00026	0.00026
	Chromium^{+6}	0.059	0.016	0.014
	Chromium^{+3}	11.1	0.2	0.17
	Copper	0.025	0.02	0.017
	Cyanide	0.096	0.012	0.012
	Lead	1.0	0.076	0.065
	Mercury	0.002	0.0002	0.0002
	Selenium	1.0	0.14	0.12
	Silver	0.007	no rec'd value	no rec'd value
	Zinc	0.44	0.12	0.10
Conventional Pollutants	BOD		20 (summer)[2] 40 (winter)[2]	15 (summer)[2] 30 (winter)[2]
	Total Suspended Solids	30[3]	20[3]	20[3]
	pH	6-9[4]		
Conventional Pollutants	Barium		9.2	7.8
	Fluoride		12.5	10.6
	Iron		1.6	1.4
	Total Dissolved Solids[5]	1055[6]		

(1) Developed from acute toxicity data (except for total suspended solids).

(2) BOD limits are applied as weekly rather than monthly averages.

(3) Categorical limits based on New Source Performance Standards.

(4) pH is in standard units.

(5) Chlorides and sulfates are regulated as part of the TDS limit.

(6) 1055 mg/l is the daily maximum value for TDS when $Q_E \leq 2000$ gpm, and 915 mg/l is the daily maximum value when Q_E is between 2000 and 3000 gpm.

APPENDIX A

SWAMP CREEK-FOREST COUNTY STREAM CLASSIFICATION

October, 1983
by Bill Jaeger - North Central District-Rhinelander

Introduction

The Exxon Minerals Company proposes to discharge wastewater from a zinc-copper mine and ore processing facility to Swamp Creek at a site in the SW 1/4 of the NW 1/4 of Section 32, T35N, R12E, in Forest County. This appendix documents an investigation of the aquatic habitat of Swamp Creek immediately below CTH "M" in Forest County and recommends a classification for that portion of Swamp Creek.

Habitat Characteristics

The watershed of Swamp Creek is mostly forest covered. There is little evidence or likelihood of erosion in the watershed. A small area near CTH "M" is used for irrigation,but since this area is quite flat, it presents little erosion potential. There is also little influence from nonpoint source pollution. A small urban area at Crandon, and the shores of Lakes Metonga and Lucerne are developed for recreational dwellings, but these areas probably have little effect on this section of Swamp Creek. Most of the watershed is minimally disturbed, so nonpoint sources are relatively unimportant. Wetlands are a natural compromising factor in the watershed. Swamp Creek passes through Rice Lake which may be best characterized as a large wetland. The wetlands have an effect of depressing dissolved oxygen concentrations in Swamp Creek.

The streambank along this section of Swamp Creek can be characterized as two types. The greatest length is low bank with overhanging vegetation. These banks are easily overflowed because of their low elevation. High flows probably do little to erode them because of the vegetative cover. The other common type of bank is found where Swamp Creek flows along uplands. The upland soils seem to be loose sand and quite erodible. These banks are steep and quite high. Where the stream makes a bend along these high, sandy banks, it undercuts them and erodes the soil. The upper bank then sloughs, adding more sediment to the stream and exposing more unvegetated soil to erosion.

Stream bottom characteristics of two general categories were found. The reach surveyed about 1,000 feet below CTH "M" has a fairly stable bottom. Sand is the predominant substrate, but fine gravel also covers much of the bottom. Aquatic vegetation is common in this area. The other two reaches had comparatively unstable bottom substrate. The bottom is a mixture of soft sand and silt and the stream is broad and shallow. The sand-silt combination is easily disturbed, resulting in scouring and deposition. Heavy growths of aquatic macrophytes help stabilize the bottom and, probably, provides the majority of benthic habitat.

The $Q_{7,10}$ of Swamp Creek at CTH "M" is 15 cfs. There are few riffles, but deep pools have formed at the sharp bends. The pools, along with the good base flow provides adequate habitat for most fish species, except the larger predators. Flow monitoring has shown flat hydrographs, indicating stable flow conditions.

The aesthetic qualities of Swamp Creek are very good. There is some agricultural development for a short distance below CTH "M". Most of the upland is wooded and the extensive wetland area is shrubby marsh. The wetland provides wildlife habitat.

A survey of the aquatic habitat was conducted on October 24, 1983. Three reaches were evaluated using the Stream System Habitat Rating Form (Ball, 1982). The reaches are located 1,000 feet below CTH "M", at the proposed discharge location, and near the mouth of Squaw Creek. Copies of the forms are attached to this report. Reach scores were 102 for the upstream reach and 116 for the two lower reaches. These scores correspond to a rating of "Good" for aquatic habitat. As expected, there was little change in habitat over the approximately two miles encompassed by the survey.

Aquatic Biology

The biota of Swamp Creek has received much study in recent years for the Exxon Environmental Impact Report (Seegert, 1983). Fish were surveyed in 1966 by Dr. George Becker of the University of Wisconsin-Stevens Point (Becker. 1966, cited by Seegert, 1983) and in 1974 by Wisconsin Department of Natural Resources (1974, cited by Seegert, 1983). The Department of Natural Resources (DNR) has also done some verification surveys on the benthic macroinvertebrate community (Young, 1983).

DNR fisheries personnel have classified Swamp Creek as Class II trout waters above Highway 55 (WDNR, 1980). Below Highway 55, Swamp Creek supports a warmwater fishery.

Table 1 lists species and numbers of individuals collected in surveys by Seegert below CTH "M" during 1982. The fishery resource was more extensively surveyed during 1982 than in any previous collections. Twelve species were captured in the Seegert Survey that were not reported in the DNR survey. The DNR caught one individual of each of three species (largemouth bass, bluegill, longnose dace) that were not found by Seegert. Most of the species are normally found in warmwater habitats. One brown trout was collected but is considered an isolated incident. Six of the more common species[1] collected (northern pike, black bullhead, yellow bullhead, yellow perch, rock bass, pumpkinseed) are classified as sport fish in the Stream Classification Guidelines for Wisconsin (Ball, 1982). Two (mottled sculpin and hornyhead chub) are species considered intolerant of less than ideal water quality. Six species are considered tolerant of some degraded water quality, and one (central mudminnow) is very tolerant of low oxygen conditions. In general, the existing fishery of this part of Swamp Creek can be considered tolerant of some degradation of water quality. The sport fishery is not of high quality, probably because the stream is physically too small to provide habitat for the larger warmwater gamefish.

The benthic macroinvertebrate community of this section of Swamp Creek is fairly diverse and seems to maintain a sizeable population. The greatest limiting factors may be the lack of stable substrate and periodically depressed dissolved oxygen conditions. The majority of bottom material is sand and silt, but extensive macrophyte beds seasonally provide additional habitat. Table 2 summarizes a 1983 study of benthic arthropods of Swamp Creek (Young, 1983). The samples were collected, processed and analyzed following the Biotic Index procedure developed by Hilsenhoff (1982). The indices ranged from 2.74 to 3.31. This indicates "fair" water quality with some apparent degradation. The degradation is most likely due to naturally occurring low levels of dissolved oxygen.

Water Quality

Swamp Creek has had little impact from man-made pollution. There are no point source discharges. Residential, urban and agricultural nonpoint sources are believed to be of only minor importance. Dissolved oxygen falls to limiting concentrations at times. Winter seems to be a critical time with dissolved oxygen recorded as low as 1.0 ppm (Seegert, 1983). The large amount of wetlands in the watershed, including Rice Lake, are the likely source of degradation. Summer can also stress dissolved oxygen concentrations. Diurnal oxygen monitoring has shown early morning dissolved oxygen levels of 1-2 ppm coincident with afternoon peaks of 9-10 ppm (Lewis, 1983). This is almost certainly the result of dense macrophyte and algae populations and their primary production and respiration activities.

Instream temperatures of Swamp Creek are not conducive to a cold water fishery. Summer stream temperatures have often been recorded above 75°F and as high as 84.5°F.

Summary

Swamp Creek below CTH "M" supports a warmwater fishery of moderate quality and value. Dissolved oxygen is apparently limiting under certain conditions, probably as a result of the large amount of wetland drainage and stream morphology. The flow regime is quite stable with a $Q_{7,10}$ of 15 cfs and a $Q_{7,2}$ of 20 cfs. This flow is sufficient to maintain the existing fishery even under extreme drought conditions. Some sport species are present but this section of Swamp Creek is incapable of supporting trout. There are no point source discharges and only minimal to moderate nonpoint pollution sources; therefore, little improvement of water quality can be anticipated.

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[1]For this report, the "more common species" are those that had at least 10 individuals captured.

Recommendations

This stream classification was conducted for the portion of Swamp Creek from CTH "M" to a short distance below the proposed discharge, but is probably valid at least for the reach starting immediately below Rice Lake to CTH "K". The classification pursuant to NR 104, Wisconsin Administrative Code, should be "continuous stream" for the hydrologic category and the water quality classification should be "fish and aquatic life".

Using the proposed Stream Classification Guidelines for Wisconsin, Swamp Creek should be designated Class B, "capable of supporting warm water sport fish".

References Cited

Ball, Joe. 1982. Stream classification guidelines for Wisconsin. Wis. Dept. Nat. Resour. Tech. Bull. (unnumbered draft) 12 pp.

Becker, G. 1966. Fisheries data provided by Don Fago, Wisconsin DNR, Madison.

Hilsenhoff, W. L. 1982. Using a Biotic Index to evaluate water quality in streams. Wis. Dept. Nat. Resour. Tech. Bull. No. 132. 22 pp.

Lewis, Howard S. 1983. Water chemistry data forwarded by letter to Terrence C. McKnight, dated October 26, 1983. 5 pp.

Seegert, Greg and Lewis, Randall. 1983. Final report on the aquatic biology of Swamp Creek for the Crandon project. Ecological Analysts, Inc., Northbrook, IL. 67 pp. and appendix.

Wisconsin Department of Natural Resources. 1974. Trout inventory and classification of Swamp Creek. Intradepartmental memo, Woodruff, WI. 3 pp. and appendices.

Wisconsin Department of Natural Resources. 1980. Wisconsin Trout Streams. Information publication by WDNR.

Young, Robert D. 1983. Unpublished data, DNR district files, North Central District, Rhinelander.

Table A-1.

COMPARISON OF FISHES COLLECTED FROM SWAMP CREEK IN JUNE AND NOVEMBER 1982

COMMON NAME	STATION 1		STATION 2		STATION 3		ALL STATIONS	
	JUNE	NOV.	JUNE	NOV.	JUNE	NOV.	JUNE	NOV.
Brown trout	0	0	0	0	1	0	1	0
Largescale stoneroller	0	0	1	0	0	0	1	0
Blacknose dace	0	0	1	0	3	0	4	0
Creek chub	6	1	17	5	28	0	51	6
Pearl dace	0	1	0	0	0	1	0	2
Hornyhead chub	107	8	123	80	180	21	410	109
Bluntnose minnow	12	46	26	28	5	5	43	79
Golden shiner	3	32	0	0	1	4	4	36
Brassy minnow	5	0	5	0	0	0	10	0
Common shiner	171	553	904	168	141	185	1216	906
Blacknose shiner	0	34	0	6	0	1	0	41
Blackchin shiner	0	1	1	0	1	1	2	2
White sucker	10	6	2	6	26	1	38	13
Shorthead redhorse	1	0	0	0	0	0	1	0
Northern hog sucker	0	0	0	1	0	0	0	1
Central mudminnow	0	0	3	0	65	4	68	4
Northern pike	2	1	1	15	3	0	6	16
Black bullhead	21	16	19	4	22	1	62	21
Yellow bullhead	0	3	6	0	9	0	15	3
Tadpole madtom	0	0	0	0	10	0	10	0
Yellow perch	0	2	3	9	51	1	54	12
Iowa darter	0	0	0	0	4	0	4	0
Johnny darter	2	0	27	4	9	0	38	4
Rock bass	10	1	42	9	144	1	196	11
Pumpkinseed	5	1	6	5	14	3	25	9
Black crappie	0	0	0	0	1	0	1	0
Mottled sculpin	1	0	12	4	12	0	25	4
Total Number	356	706	1199	344	730	229	2285	1279
Both Months Combined	1062		1543		959		3564	
Total Species	14	15	18	14	21	13	24	19
Both Months Combined	19		20		23		27	

From Seegert, 1983.

*Station locations are shown in Figure 1.

Table A-2.

Swamp Creek Biotic Indices

Station*	Biotic Index Values Replicate 1	Replicate 2	Replicate 3	Mean
1	2.94	3.20	3.31	3.15
2	2.99	2.91	3.11	3.00
3	2.74	2.82	-	2.78
4	3.27	3.31	3.20	3.26
5	2.95	3.03	3.02	3.00

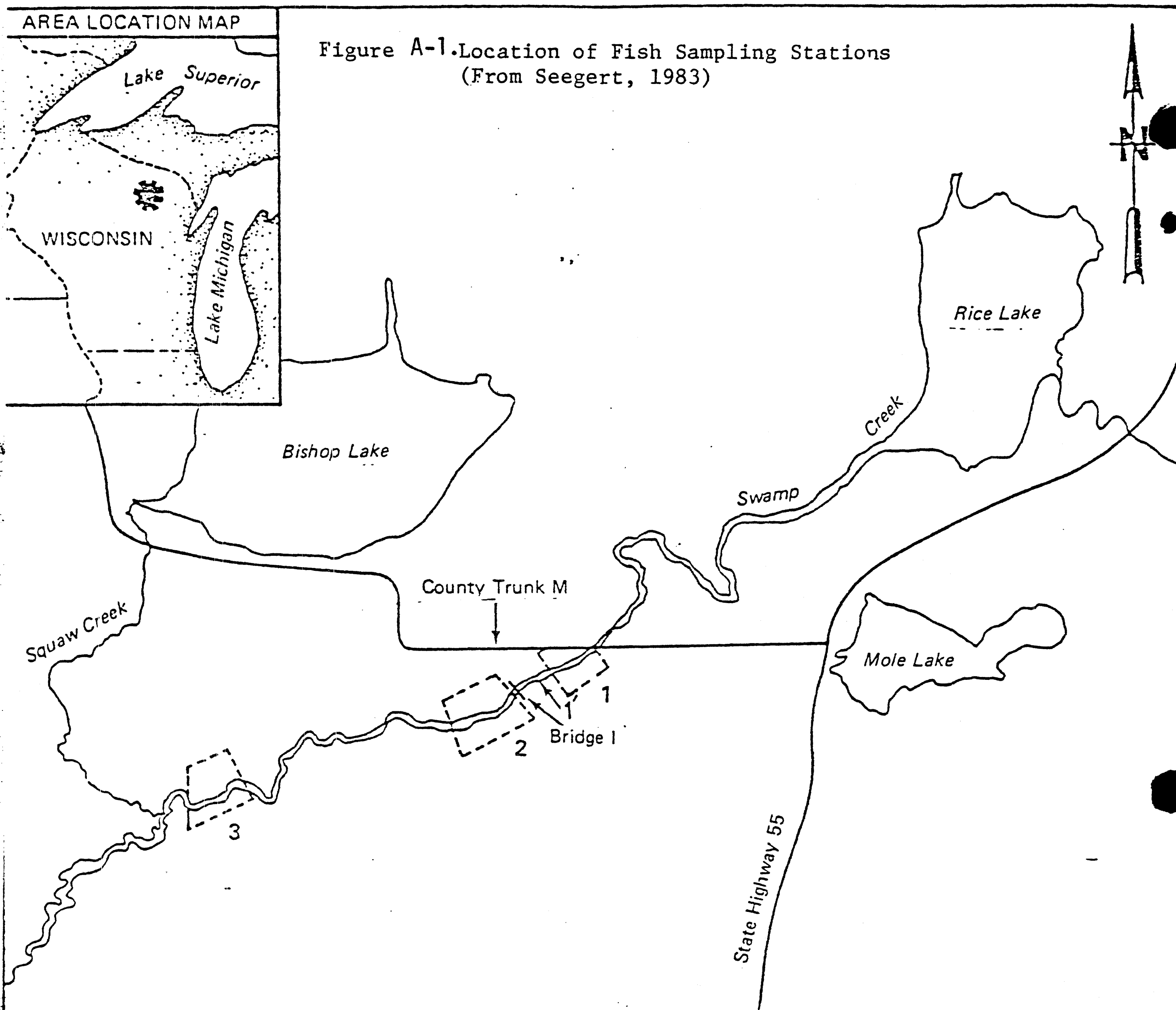
From Young, 1983.
*Station locations are shown in Figure 2.

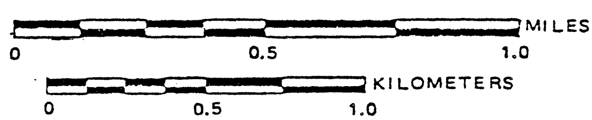
TABLE A-3 Evaluation of water quality using biotic index values of samples collected between October and May.

Biotic Index	Water Quality	Degree of Organic Pollution
0.00 - 1.75	Excellent	No organic pollution
1.76 - 2.25	Very good	Possible slight organic pollution
2.26 - 2.75	Good	Some organic pollution
2.76 - 3.50	Fair	Significant organic pollution
3.51 - 4.25	Poor	Very significant organic pollution
4.26 - 5.00	Very Poor	Severe organic pollution

From Hilsenhoff, 1982.

Figure A-1. Location of Fish Sampling Stations (From Seegert, 1983)





LEGEND:

1-3 = SAMPLING STATIONS

EXXON MINERALS COMPANY
CRANDON PROJECT

SAMPLING STATIONS FOR THE 1982-1983 AQUATIC MONITORING PROGRAM ON SWAMP CREEK BETWEEN COUNTY TRUNK HIGHWAY M AND SQUAW CREEK

ECOLOGICAL ANALYSTS

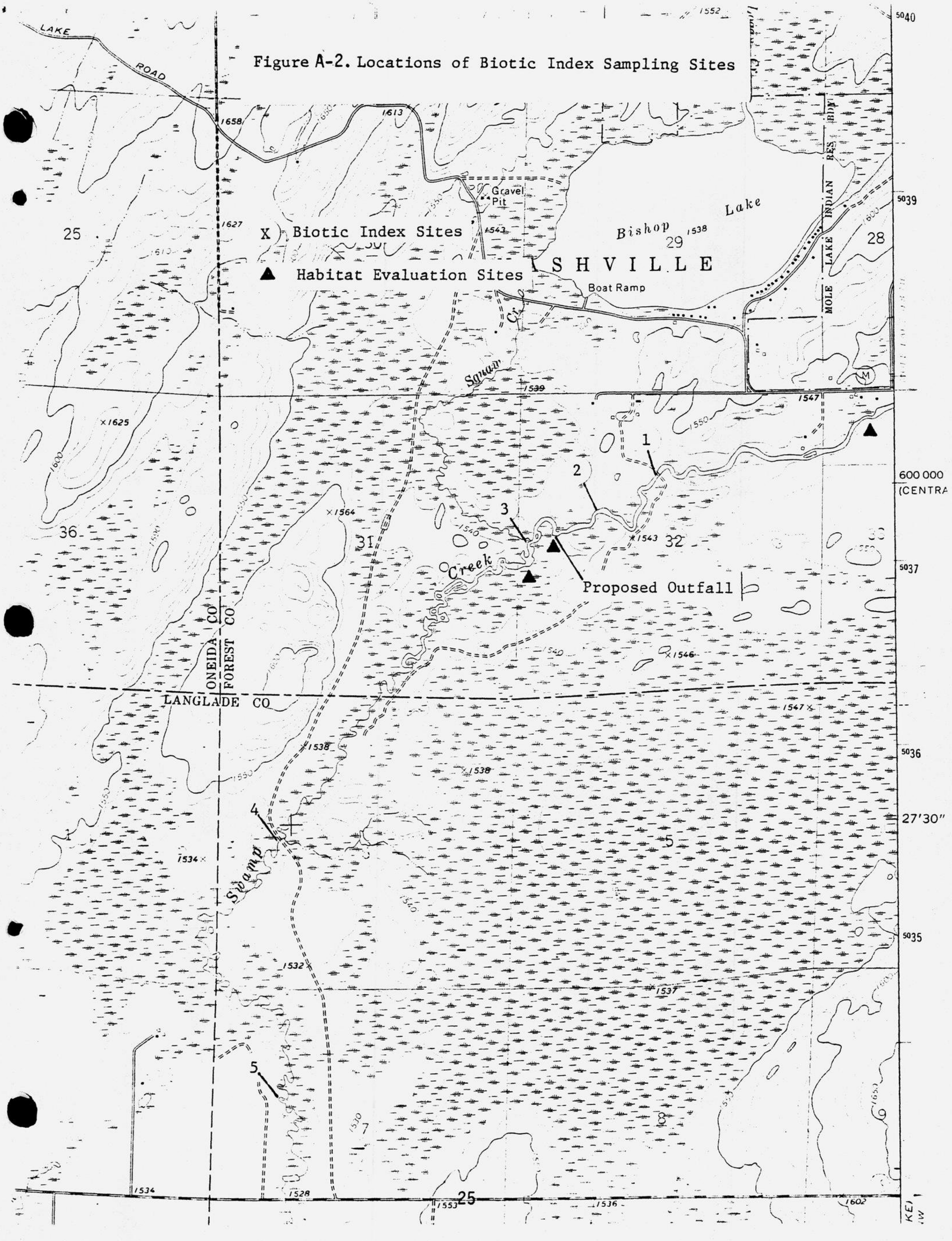


Figure A-2. Locations of Biotic Index Sampling Sites
X Biotic Index Sites
▲ Habitat Evaluation Sites
Proposed Outfall
1
2
3
4
5
LAKE ROAD
Gravel Pit
Bishop Lake
Boat Ramp
SHVILLE
MOLE LAKE INDIAN RES.
Squaw Cr.
Creek
Swamp
ONEIDA CO
FOREST CO
LANGLADE CO
25
28
29
31
32
36
5
7
8
9
1658
1613
1627
1625
1564
1543
1539
1538
1547
1550
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1532
1537
1528
1536
1602
1552
5040
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5037
5036
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(CENTRA
27'30"

Figure A-3.Swamp Creek 1,000 feet below CTH "M"

Figure A-4.Swamp Creek at Proposed Outfall Area.

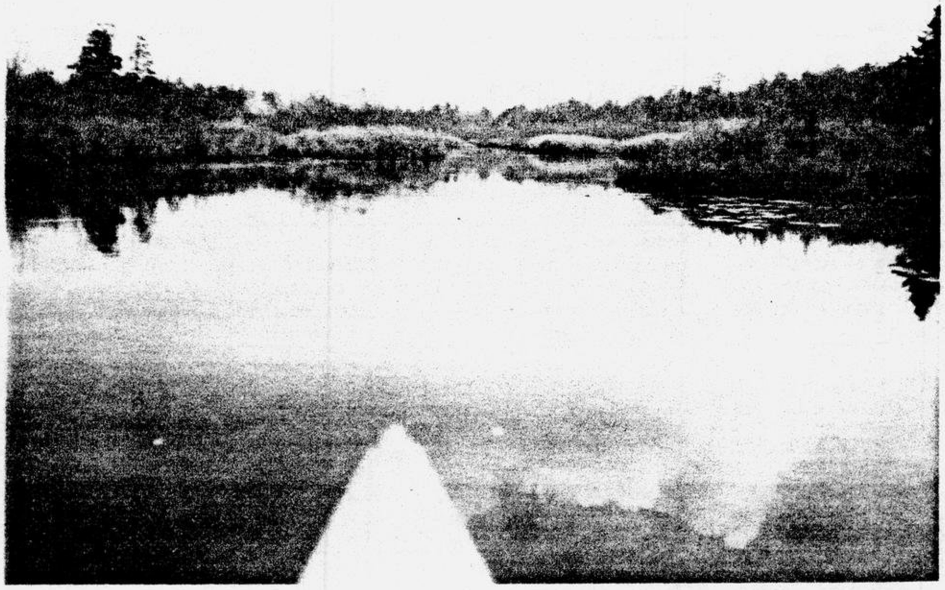

Figure A-5. Swamp Creek Below Confluence With Squaw Creek

APPENDIX: Stream System Habitat Rating Form

Stream: Swamp Creek Reach Location: 1000 feet below County "M" Reach Score/Rating: 102

County: Forest Date: 10/24/83 Evaluator: Bill Jaeger Classification: ______

Rating Item	Excellent		Good		Fair		Poor	
Watershed Erosion	No evidence of significant erosion. Stable forest or grass land. Little potential for future erosion.	**(8)**	Some erosion evident. No significant "raw" areas. Good land mgmt. practices in area. Low potential for significant erosion.	10	Moderate erosion evident. Erosion from heavy storm events obvious. Some "raw" areas. Potential for significant erosion.	14	Heavy erosion evident. Probable erosion from any runoff.	16
Watershed Nonpoint Source	No evidence of significant source. Little potential for future problem.	4	Some potential sources. (roads, urban area, farm fields).	8	Moderate sources. (Small wetlands, tile fields, urban area, intense agriculture).	16	Obvious sources. (Major wetland drainage, high use urban or industrial area, feed lots, impoundment).	**(20)**
Bank Erosion, Failure	No evidence of significant erosion or bank failure. Little potential for future problem.	**(6)**	Infrequent, small areas, mostly healed over. Some potential in extreme floods.	9	Moderate frequency and size. Some "raw" spots. Erosion potential during high flow.	15	Many eroded areas. "Raw" areas frequent along straight sections and bends.	18
Bank Vegetative Protection	90% plant density. Diverse trees, shrubs, grass. Plants healthy with apparently good root system.	**(6)**	70-90% density. Fewer plant species. A few barren or thin areas. Vegetation appears generally healthy.	9	50-70% density. Dominated by grass, sparse trees and shrubs. Plant types and conditions suggest poorer soil binding.	15	<50% density. Many raw areas. Thin grass, few if any trees and shrubs.	18
Lower Bank Channel Capacity	Ample for present peak flow plus some increase. Peak flows contained. W/D ratio <7.	8	Adequate. Overbank flows rare. W/D ratio 8-15.	**(10)**	Barely contains present peaks. Occasional overbank flow. W/D ratio 15-25.	14	Inadequate, overbank flow common. W/D ratio >25.	16
Lower Bank Deposition	Little or no enlargement of channel or point bars.	6	Some new increase in bar formation, mostly from coarse gravel.	**(9)**	Moderate deposition of new gravel and coarse sand on old and some new bars.	15	Heavy deposits of fine material, increased bar development.	18
Bottom Scouring and Deposition	Less than 5% of the bottom affected by scouring and deposition.	4	5-30% affected. Scour at constrictions and where grades steepen. Some deposition in pools.	**(8)**	30-50% affected. Deposits and scour at obstructions, constrictions and bends. Some filling of pools.	16	More than 50% of the bottom changing nearly year long. Pools almost absent due to deposition.	20
Bottom Substrate	Greater than 50% rubble, gravel or other stable habitat.	2	30-50% rubble, gravel or other stable habitat. Adequate habitat.	**(7)**	10-30% rubble, gravel or other stable habitat. Habitat availability less than desirable.	17	Less than 10% rubble, gravel or other stable habitat. Lack of habitat is obvious.	22
Average Depth at Rep. Low Flow	Greater than 24 inches.	0	12 inches to 24 inches.	**(6)**	6 inches to 12 inches.	18	Less than 6 inches.	24
Flow, at Rep. Low Flow	Warm water >5 cfs. Cold water >2 cfs.	**(0)**	Warm water 2-5 cfs. Cold water 1-2 cfs.	6	Warm water 0.5-2 cfs. Cold water 0.5-1 cfs. Continuous blow.	18	Less than 0.5 cfs. Stream may cease to flow in very dry years.	24
Pool/Riffle, Run/Bend Ratio	5-7. Variety of habitat. Deep riffles and pools.	4	7-15. Adequate depth in pools and riffles. Bends provide habitat.	**(8)**	15-25. Occassional riffle or bend. Bottom contours provide some habitat.	16	>25. Essentially a straight stream. Generally all flat water inches or shallow riffle. Poor habitat.	20
Aesthetics	Wilderness characteristics, outstanding natural beauty. Usually wooded or unpastured corridor.	8	High natural beauty. Trees, historic site. Some development may be visible.	10	Common setting, not offensive. Developed but uncluttered area.	**(14)**	Stream does not inhance aesthetics. Condition of stream is offensive.	16

Column Total Without Effluent —

Column Total With Effluent —

Add Column Scores Without Effluent, E 20 +G 48 +F 14 +P 20 = Reach Score 102

Add Column Scores With Effluent, E____ +G____ +F____ +P____ = Reach Score

<70 = Excellent, 71-129 = Good, 130-200 = Fair, >200 = Poor

Stream width: average= 50 feet, range = 40 to 70 feet

Stream depth: 12 to 24 inches

Bottom characteristics: 30% gravel, 15% silt, 55% sand

Water clarity ‡ good

Aquatic life: many fingnail clams, elodea abundant

Corresponds to Figure A.3.

APPENDIX: Stream System Habitat Rating Form

Stream Swamp Creek **Reach Location** Exxon's proposed outfall area (SW quarter of NW quarter of Sec. 32) **Reach Score/Rating** 116

County Forest **Date** 10/24/83 **Evaluator** Bill Jaeger **Classification** ______

Rating Item	Category: Excellent		Good		Fair		Poor	
Watershed Erosion	No evidence of significant erosion. Stable forest or grass land. Little potential for future erosion.	(8)	Some erosion evident. No significant "raw" areas. Good land mgmt. practices in area. Low potential for significant erosion.	10	Moderate erosion evident. Erosion from heavy storm events obvious. Some "raw" areas. Potential for significant erosion.	14	Heavy erosion evident. Probable erosion from any runoff.	16
Watershed Nonpoint Source	No evidence of significant source. Little potential for future problem.	4	Some potential sources. (roads, urban area, farm fields).	8	Moderate sources. (Small wetlands, tile fields, urban area, intense agriculture).	16	Obvious sources. (Major wetland drainage, high use urban or industrial area, feed lots, impoundment).	(20)
Bank Erosion, Failure	No evidence of significant erosion or bank failure. Little potential for future problem.	6	Infrequent, small areas, mostly healed over. Some potential in extreme floods.	(9)	Moderate frequency and size. Some "raw" spots. Erosion potential during high flow.	15	Many eroded areas. "Raw" areas frequent along straight sections and bends.	18
Bank Vegetative Protection	90% plant density. Diverse trees, shrubs, grass. Plants healthy with apparently good root system.	(6)	70-90% density. Fewer plant species. A few barren or thin areas. Vegetation appears generally healthy.	9	50-70% density. Dominated by grass, sparse trees and shrubs. Plant types and conditions suggest poorer soil binding.	15	<50% density. Many raw areas. Thin grass, few if any trees and shrubs.	18
Lower Bank Channel Capacity	Ample for present peak flow plus some increase. Peak flows contained. W/D ratio <7.	(8)	Adequate. Overbank flows rare. W/D ratio 8-15.	10	Barely contains present peaks. Occasional overbank flow. W/D ratio 15-25.	14	Inadequate, overbank flow common. W/D ratio >25.	16
Lower Bank Deposition	Little or no enlargement of channel or point bars.	6	Some new increase in bar formation, mostly from coarse gravel.	(9)	Moderate deposition of new gravel and coarse sand on old and some new bars.	15	Heavy deposits of fine material, increased bar development.	18
Bottom Scouring and Deposition	Less than 5% of the bottom affected by scouring and deposition.	4	5-30% affected. Scour at constrictions and where grades steepen. Some deposition in pools.	8	30-50% affected. Deposits and scour at obstructions, constrictions and bends. Some filling of pools.	(16)	More than 50% of the bottom changing nearly year long. Pools almost absent due to deposition.	20
Bottom Substrate	Greater than 50% rubble, gravel or other stable habitat.	2	30-50% rubble, gravel or other stable habitat. Adequate habitat.	7	10-30% rubble, gravel or other stable habitat. Habitat availability less than desirable.	17	Less than 10% rubble, gravel or other stable habitat. Lack of habitat is obvious.	(22)
Average Depth at Rep. Low Flow	Greater than 24 inches.	(0)	12 inches to 24 inches.	6	6 inches to 12 inches.	18	Less than 6 inches.	24
Flow, at Rep. Low Flow	Warm water >5 cfs. Cold water >2 cfs.	(0)	Warm water 2-5 cfs. Cold water 1-2 cfs.	6	Warm water 0.5-2 cfs. Cold water 0.5-1 cfs. Continuous blow.	18	Less than 0.5 cfs. Stream may cease to flow in very dry years.	24
Pool/Riffle, Run/Bend Ratio	5-7. Variety of habitat. Deep riffles and pools.	4	7-15. Adequate depth in pools and riffles. Bends provide habitat.	(8)	15-25. Occassional riffle or bend. Bottom contours provide some habitat.	16	>25. Essentially a straight stream. Generally all flat water inches or shallow riffle. Poor habitat.	20
Aesthetics	Wilderness characteristics, outstanding natural beauty. Usually wooded or unpastured corridor.	8	High natural beauty. Trees, historic site. Some development may be visible.	(10)	Common setting, not offensive. Developed but uncluttered area.	14	Stream does not inhance aesthetics. Condition of stream is offensive.	16

Column Total Without Effluent —
Column Total With Effluent —

Add Column Scores Without Effluent, E 22 +G 36 +F 16 +P 42 = Reach Score 116
Add Column Scores With Effluent, E____ +G____ +F____ +P____ = Reach Score

<70 = Excellent, 71-129 = Good, 130-200 = Fair, >200 = Poor

Stream width: average = 40 feet, range = 20 to 70 feet
Stream depth: 18 to 48 inches
Bottom characteristics: 50% sand, 50% silt
Vegetation: very heavy elodea and algae growth
Wetlands are present along much of the bank

Corresponds to Figure A.4.

APPENDIX: Stream System Habitat Rating Form

Stream Swamp Creek **Reach Location** Station 4 below Squaw Creek **Reach Score/Rating** 116

County Forest **Date** 10/24/83 **Evaluator** Bill Jaeger **Classification** ______

Rating Item	Category: Excellent		Good		Fair		Poor	
Watershed Erosion	No evidence of significant erosion. Stable forest or grass land. Little potential for future erosion.	(8)	Some erosion evident. No significant "raw" areas. Good land mgmt. practices in area. Low potential for significant erosion.	10	Moderate erosion evident. Erosion from heavy storm events obvious. Some "raw" areas. Potential for significant erosion.	14	Heavy erosion evident. Probable erosion from any runoff.	16
Watershed Nonpoint Source	No evidence of significant source. Little potential for future problem.	4	Some potential sources. (roads, urban area, farm fields).	8	Moderate sources. (Small wetlands, tile fields, urban area, intense agriculture).	16	Obvious sources. (Major wetland drainage, high use urban or industrial area, feed lots, impoundment).	(20)
Bank Erosion, Failure	No evidence of significant erosion or bank failure. Little potential for future problem.	6	Infrequent, small areas, mostly healed over. Some potential in extreme floods.	(9)	Moderate frequency and size. Some "raw" spots. Erosion potential during high flow.	15	Many eroded areas. "Raw" areas frequent along straight sections and bends.	18
Bank Vegetative Protection	90% plant density. Diverse trees, shrubs, grass. Plants healthy with apparently good root system.	(6)	70-90% density. Fewer plant species. A few barren or thin areas. Vegetation appears generally healthy.	9	50-70% density. Dominated by grass, sparse trees and shrubs. Plant types and conditions suggest poorer soil binding.	15	<50% density. Many raw areas. Thin grass, few if any trees and shrubs.	18
Lower Bank Channel Capacity	Ample for present peak flow plus some increase. Peak flows contained. W/D ratio <7.	(8)	Adequate. Overbank flows rare. W/D ratio 8-15.	10	Barely contains present peaks. Occasional overbank flow. W/D ratio 15-25.	14	Inadequate, overbank flow common. W/D ratio >25.	16
Lower Bank Deposition	Little or no enlargement of channel or point bars.	6	Some new increase in bar formation, mostly from coarse gravel.	(9)	Moderate deposition of new gravel and coarse sand on old and some new bars.	15	Heavy deposits of fine material, increased bar development.	18
Bottom Scouring and Deposition	Less than 5% of the bottom affected by scouring and deposition.	4	5-30% affected. Scour at constrictions and where grades steepen. Some deposition in pools.	8	30-50% affected. Deposits and scour at obstructions, constrictions and bends. Some filling of pools.	(16)	More than 50% of the bottom changing nearly year long. Pools almost absent due to deposition.	20
Bottom Substrate	Greater than 50% rubble, gravel or other stable habitat.	2	30-50% rubble, gravel or other stable habitat. Adequate habitat.	7	10-30% rubble, gravel or other stable habitat. Habitat availability less than desirable.	17	Less than 10% rubble, gravel or other stable habitat. Lack of habitat is obvious.	(22)
Average Depth at Rep. Low Flow	Greater than 24 inches.	(0)	12 inches to 24 inches.	6	6 inches to 12 inches.	18	Less than 6 inches.	24
Flow, at Rep. Low Flow	Warm water >5 cfs. Cold water >2 cfs.	(0)	Warm water 2-5 cfs. Cold water 1-2 cfs.	6	Warm water 0.5-2 cfs. Cold water 0.5-1 cfs. Continuous blow.	18	Less than 0.5 cfs. Stream may cease to flow in very dry years.	24
Pool/Riffle, Run/Bend Ratio	5-7. Variety of habitat. Deep riffles and pools.	4	7-15. Adequate depth in pools and riffles. Bends provide habitat.	(8)	15-25. Occassional riffle or bend. Bottom contours provide some habitat.	16	>25. Essentially a straight stream. Generally all flat water inches or shallow riffle. Poor habitat.	20
Aesthetics	Wilderness characteristics, outstanding natural beauty. Usually wooded or unpastured corridor.	8	High natural beauty. Trees, historic site. Some development may be visible.	(10)	Common setting, not offensive. Developed but uncluttered area.	14	Stream does not inhance aesthetics. Condition of stream is offensive.	16

Column Total Without Effluent —
Column Total With Effluent —

Add Column Scores Without Effluent, E 22 +G 36 +F 16 +P 42 = Reach Score 116
Add Column Scores With Effluent, E____ +G____ +F____ +P____ = Reach Score

≤70 = Excellent, 71-129 = Good, 130-200 = Fair, >200 = Poor

Bank Vegetation: Willow sedge, reeds, alder
Other characteristics similar to the outfall area
Corresponds to Figure A. 5.

APPENDIX B

WATER QUALITY BASED LIMITS FOR ARSENIC

Criteria

1.48 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.29 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects .

Introduction

Arsenic exists in oxidation states of +5, +3, 0, and -3. Arsenic as a free element (oxidation state of 0) is rarely encountered in natural waters. Soluble inorganic arsenate (+5) predominates under normal conditions since it is more stable than arsenite (+3). Both arsenate and arsenite can be removed from the water column by adsorption onto iron oxides. Oxidation of arsenite to arsenate occurs slowly at neutral pH and faster in strongly acid or alkaline solutions. The organic forms comprise the largest group of arsenic compounds. The majority of the toxicity tests have been conducted with arsenite (+3); some data are also available on arsenate (+5).

Acute Criterion

There is a difference in relative toxicity between arsenate (+5) and arsenite (+3). Since the pH of Swamp Creek is near neutral, arsenite is likely to predominate in the stream. Consequently, water quality criteria are established only for arsenic (+3). Analysis of the data for arsenite reveals that there is no relationship between hardness and LC 50 concentrations for this parameter. Four species (Daphnia pulex, goldfish, channel catfish, and bluegill) have data on acute arsenic toxicity. Geometric mean values were calculated for each of the above-mentioned species. The Final Acute Value for arsenic was based on the lowest species mean acute number. Three species (a scud, a cladoceran, and fathead minnow) have only one reported test result each. Since these species had only single test results, the data was not included in determination of a criterion value for arsenic.

Table B-1 provides a summary of the acute data utilized in generating the criterion for arsenic.

Table B-1. Acute Data Summary. References are taken from the EPA ambient water quality criteria document for arsenic unless they are footnoted.

Species	LC50 (mg/l)	Geometric Means (mg/l)	Reference
Daphnia pulex (cladoceran)	1.04	1.48	Sanders & Cope, 1966
"	1.74		Fish Pesticide Research Laboratory, 1980
Goldfish	26	29.7	Cardwell, et al. 1976
"	34		Gilderhus, 1966[1]
Channel catfish	18.1	16.5	Cardwell, et al. 1976
"	15.0		Clemens & Sneed, 1959
Bluegill	41.8	21.5	Cardwell, et al. 1976
"		15.4	Inglis & Davis, 1972
"	16.2		Inglis & Davis, 1972
"	15.5		Inglis & Davis, 1972
"	17.4		Fish Pesticide Research Laboratory, 1980
"	35		Luh, et al. 1973[2]

(1)Gilderhus, P.A. 1966. Some effects of sublethal concentrations of sodium arsenite on bluegills and the aquatic environment. Trans. Am. Fish Soc. 95:289.

(2)Luh, et al. 1973. Arsenic analysis and toxicity - a review. Sci. Total Environ. 2(1):1.

The lowest Species Mean Acute Value (SMAV) from Table B-1 was 1.48 mg/l based on the geometric mean for Daphnia pulex. The Final Acute Value (FAV) used for arsenic is the same as the lowest SMAV (1.48 mg/l).

Chronic Criterion

Only one chronic test result (for fathead minnow) is available for arsenite. Fathead minnow has also been tested for acute arsenic toxicity. However, the chronic and acute tests are documented by difference sources, and there is no assurance the tests were performed under similar conditions (hardness, temperature, and pH). Since this is the only data reported for an indigenous

Wisconsin species, the acute and chronic arsenite tests on fathead minnow were used to calculate an acute/chronic (A/C) ratio. The acute value for fathead minnow was 15.7 mg/l and the chronic value was 3.03 mg/l (A/C ratio = 15.7 3.03 = 5.18). The FAV for arsenite (1.48 mg/l) was then divided by the A/C ratio (5.18). This resulted in a Final Chronic Value for arsenic of 0.29 mg/l. Table B-2 provides a summary of the chronic data utilized in generating the criterion for arsenic.

Table B-2. Chronic Data Summary

Species	Chronic Value (mg/l)	Reference
Fathead Minnow	3.03	Lima, et. al. Manuscript[(1)]

[(1)]Lima, et al. Manuscript. Acute and chronic toxicities of arsenic to selected freshwater organisms. University of Wisconsin-Superior.

APPENDIX C

WATER QUALITY BASED LIMITS FOR CADMIUM

Criteria

0.074 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.00025 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Cadmium exists in a variety of possible chemical forms that display different levels of toxicity and bioaccumulation. The solubility of cadmium compounds in water depends on the nature of the compounds and on the water quality. Cadmium ions are precipitated from solution by carbonate, hydroxide and sulfide ions and forms soluble complexes with other anions. Cadmium strongly absorbs to soil and organic materials which tend to remove it from the water column by precipitation.

In the aquatic environment, cadmium is acutely and chronically toxic to aquatic organisms in very low concentrations. In addition, cadmium bioconcentrates in fish tissues (ie: the liver and kidney) to levels many times greater than in ambient waters. Consequently, the toxicity limits established for cadmium to protect fish and aquatic life are relatively stringent.

Acute Criterion

Twenty aquatic life species indigenous to Wisconsin surface waters have been tested for acute cadmium toxicity. Analysis of the data reveals that four species have demonstrated relationships between hardness and acute cadmium toxicity over a wide range of hardness values. Equations have been developed to predict acutely toxic cadmium concentrations for these species, namely goldfish, fathead minnow, green sunfish, and bluegill.

One other species, Daphnia pulex, has three acute toxicity test results but with only one recorded hardness value. Consequently, a geometric mean was calculated for this species to predict a single toxicity value to be applied over all hardness conditions.

Neither equations could be developed nor geometric mean values calculated for the rest of the species with available cadmium acute toxicity data. This was because there was only one acute test result reported for a given species or the toxicity data reported was over too narrow a range of hardness values to predict acute cadmium toxicity with any degree of confidence.

Table C-1 summarizes the data that was utilized in developing the acute toxicity criterion for cadmium.

Table C-1. Acute Data Summary. References are taken from the EPA ambient water quality criteria document for cadmium unless they are footnoted.

Species	Hardness (mg/l)	LC50 Concentrations (ug/l)	Reference
Daphnia pulex (cladoceran)	NA(1)	93.5	Canton & Adema, 1978
"	NA(1)	93.5	Canton & Adema, 1978[2]
"	57	47	Bertram & Hart, 1979[3]
Goldfish	20	2340	Pickering & Henderson, 1966
"	20	2130	McCarty, et al. 1978
"	140	46,800	McCarty, et al. 1978
"	99	12,600	Brusacker, 1980[4]
Fathead minnow	20	1050	Pickering & Henderson, 1966
"	20	630	Pickering & Henderson, 1966
"	360	72,600	Pickering & Henderson, 1966
"	360	73,500	Pickering & Henderson, 1966
"	201	11,000	Pickering & Gast, 1972
"	201	12,000	Pickering & Gast, 1972
"	201	6,400	Pickering & Gast, 1972
"	201	2,000	Pickering & Gast, 1972
"	201	4,500	Pickering & Gast, 1972
Green sunfish	20	2,840	Pickering & Henderson, 1966

"	360	66,000	Pickering & Henderson, 1966
"	335	20,500	Jude, 1973
Bluegill	20	1,940	Pickering & Henderson, 1966
"	207	21,100	Eaton, 1980

(1)data not available for hardness

(2)Canton, J.H. and D.M.M. Adema. 1978. Reproducibility of short-term and reproduction toxicity experiments with Daphnia magna and comparison of the sensitivity of Daphnia magna with Daphnia pulex and Daphnia cucullata in short-term experiment. Hydrobiol. 59:135.

(3)Bertram, P.E. and B.A. Hart. 1979. Longevity and reproduction of Daphnia pulex (deGeer) exposed to cadmium-contaminated food or water. Environ. Pollut. 19:295.

(4)Brusacker, G.P. 1980. Osmoregulatory effects of acute cadmium toxicity in a model teleost. Dissertation Abs. 41:1269.

For those species listed in Table C-1, Daphnia pulex is the only species with a single concentration value based on the geometric mean of the acute toxicity numbers; these values do not change with hardness. The other four species (goldfish, fathead minnow, sunfish and bluegill) had species acute equations (SAE's) developed for each species. Calculations were made to determine the best fit relationship between cadmium toxicity and hardness among the four basic forms of equations. The best-fit relationship of these four equations was found by calculating a geometric mean of the r-factors for all Wisconsin species that had SAE's developed. Table C-2 summarizes the r-factors for each type of equation.

Table C-2. Summary of Correlation Coefficients

Equation Type	Geometric Mean ("r" value)
Hardness vs C(1)	.867
ln hardness vs ln C	.933
Hardness vs ln C	.972
$Hardness^2$ vs C	.926

(1) where C = acute toxicity concentration (LC 50 values) for cadmium

From Table C-2, the best fit relationship (from the geometric mean) was hardness vs ln C. Thus, the equations were in the form $C = a (b)^H$. Utilizing this form of equation, acute cadmium toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. The calculated toxicity values at these endpoint hardnesses, along with the geometric mean values for Daphnia pulex at those hardnesses, are listed in Table C-3.

Table C-3. Calculated Toxicity Values at Endpoint Hardnesses

Species	Number of Data Points	Species Acute Equation (C in ug/l)	C(ug/l) @ 20 mg/l	Hardness = 400 mg/l
Goldfish	4	$C = 1333 (1.025)^H$	2160	(1)
Fathead minnow	9	$C = 508 (1.013)^H$	661	97,600
Green sunfish	3	$C = 2333 (1.008)^H$	2740	57,000
Bluegill	2	$C = 1503 (1.013)^H$	1940	248,000
Daphnia pulex (cladoceran)	3	$C = 74.3$	74.3	74.3

(1)This value is significantly high so that it does not affect the FAE.

Daphnia pulex has the lowest values at the endpoint hardnesses at 20 and 400 mg/l. Consequently, the acute criterion for cadmium, was based on the cladoceran value of 74.3 ug/l.

Chronic Criterion

The chronic data base for cadmium is somewhat more limited than the acute information that is available. Two species (Daphnia magna and channel catfish) have demonstrated relationships between hardness and chronic cadmium toxicity over a wide range of hardness values. Thus, equations were developed to predict chronically toxic concentrations for cadmium for these species.

Two species (fathead minnow and bluegill) have only one reported chronic test result each. Since these chronic tests were done at the same hardness as one or more acute tests for the same species, acute/chronic (A/C) ratios were calculated for these species. Dividing the species acute equation (SAE) by the A/C ratio resulted in an equation to predict chronically toxic concentrations at any hardness.

Four other species (northern pike, white sucker, walleye, and smallmouth bass) had only one chronic test result reported. Since acute tests were not performed for these species, no estimate of the chronic effects can be made. Consequently these data were not used in determining the Final Chronic Equation (FCE).

Species chronic equations (SCE's) were developed for the four species mentioned above using either regression analyses (*Daphnia magna* and channel catfish) or A/C ratios (fathead minnow and bluegill). Fathead minnow and bluegill SCE's have the form $C = a\,(b)^H$ because this was the curve form of the SAE's that had the best overall fit. The SCE's for *Daphnia magna* and channel catfish had the same basic form of equation ($C = a\,(b)^H$) in order to be consistent with the A/C ratio-based equations and the SAE's.

Table C-4 summarizes the data that was utilized in developing the chronic toxicity criterion for cadmium.

Table C-4. Chronic Data Summary. References are taken from the EPA ambient water quality criteria document for cadmium.

Species	Hardness (mg/l)	Chronic Value (ug/l)	Reference
Daphnia magna (cladoceran)	45	0.34	Biesinger & Christensen, 1972
"	53	0.15	Chapman, Manuscript
"	103	0.21	Chapman, Manuscript
"	209	0.44	Chapman, Manuscript
Fathead minnow	201	45.9	Pickering & Gast, 1972
Channel catfish	37	13.7	Sauter, et al. 1976
"	185	14.3	Sauter, et al. 1976
Bluegill	207	49.8	Eaton, 1974

For the species listed in Table C-4, A/C ratios were calculated for fathead minnow and bluegill at similar hardness conditions. For fathead minnow the A/C ratio was determined at a hardness of 201 mg/l (A/C = 5970/45.9 = 130). The acute toxicity value was calculated from a geometric mean of five data points at hardness 201 and the chronic value of 45.9 was taken from Table C-4. For bluegill, the A/C ratio was determined at a hardness of 207 (A/C = 21,100/49.8 = 424). The acute toxicity value (21,000 ug/l) was taken from Table C-1 and the chronic value (49.8 ug/l) was obtained from Table C-4.

Utilizing the species chronic equations in the form of the curve $C = a\,(b)^H$, chronic cadmium toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. Table C-5 lists the four species and their respective calculated toxicity values at the endpoint hardnesses.

Table C-5. Calculated Chronic Values at Endpoint Hardnesses

Species	Number of Data Points	Species Chronic Equation (C in ug/l)	C (ug/l) @ Hardness = 20 mg/l	400 mg/l
Bluegill	1	$C = \frac{1503\ (1.013)^H}{424}$	4.6	574
Fathead minnow	1	$C = \frac{508\ (1.013)^H}{130}$	5.1	750
Daphnia magna	4	$C = .1746\ (1.004)^H$	0.19	0.85
Channel catfish	2	$C = 13.55\ (1.00)^H$	13.6	15.2

The lowest values at the endpoint hardnesses of 20 and 400 mg/l were connected by the equation form of $C = a\ (b)^H$. *Daphnia magna* has the lowest values at both endpoints. Consequently, the chronic criterion value for cadmium can be calculated from the following cladoceran equation from Table C-5:

$C = 0.1746\ (1.004)^H$

where C = the chronic criterion concentration in ug/l for cadmium
and H = the average hardness value for Swamp Creek (94 mg/l).

APPENDIX D

WATER QUALITY BASED LIMITS FOR HEXAVALENT CHROMIUM

Criteria

0.059 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.0096 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Chromium is a chemically complex metal. Several oxidation states are possible and hexavalent chromium is one of the more biologically and environmentally significant forms of the element. Under aerobic conditions, chromium VI is stable, but in anaerobic conditions chromium VI is reduced to chromium III.

Hexavalent chromium is very soluble in natural waters, and it exists in solution as a component of an anion. The three important anions are: hydrochromate, chromate, and dichromate. The proportion of hexavalent chromium present in each of these forms depends on the pH. The anionic form of chromium can affect its toxicity.

Acute Criterion

Information on the toxic effects of chromium on freshwater organisms is rather extensive for hexavalent chromium. The data indicates that water hardness does not influence the toxicity of chromium VI for all species. However, five species have demonstrated relationships between hardness and chromium VI toxicity over the range of hardness values found in Wisconsin waters (20-400 mg/l). Data from five species, *Physa heterostropha* (a snail), *Daphnia magna* (a cladoceran), goldfish, fathead minnow, and bluegill, were used to derive acute water quality criteria for chromium VI (The data on acute chromium VI toxicity is summarized in Table D-1).

Species acute equations (SAE's) were developed for each of the five species. Calculations were made to determine the best fit relationship between acute chromium VI toxicity and hardness among the four basic forms of equations.

Table D-2 summarizes the correlation coefficients (r - values) for each species.

Table D-1. Acute Data Summary. References are taken from the EPA ambient water quality criteria document for chromium unless they are footnoted.

Species	Hardness (mg/l)	LC50 Concentrations (ug/l)	Reference
P. heterostropha (snail)	45	17,300	Academy of Sciences, 1960
"	45	17,300	Academy of Sciences, 1960
"	171	40,600	Academy of Sciences, 1960
"	171	31,600	Academy of Sciences, 1960
D. magna (cladoceran)	45	900	Cairns, et al, 1978[1]
"	163	64	Debelak, 1975[2]
"	163	72	Debelak, 1975[2]
"	163	73	Debelak, 1975[2]
"	163	74	Debelak, 1975[2]
"	163	81	Debelak, 1975[2]
"	83	31	Debelak, 1975[2]
"	86	38	Debelak, 1975[2]
"	86	39	Debelak, 1975[2]
"	86	42	Debelak, 1975[2]
"	86	44	Debelak, 1975[2]
"	100	175	White, 1979[3]
"	92	157	White, 1979[3]
"	185	131	Call et al. 1981[4]
"	50	24.5	Call et al. 1981[4]
"	196	73.6	Call et al. 1981[4]
"	212	137	Call et al. 1981[4]
"	188	66.7	Call et al. 1981[4]
"	50	7.4	Call et al. 1981[4]
"	213	75.8	Call et al. 1981[4]
"	185	164	Call et al. 1981[4]
"	50	17.8	Call et al. 1981[4]
"	213	212	Call et al. 1981[4]
"	196	85.7	Call et al. 1981[4]
"	50	16.9	Call et al. 1981[4]
"	45	24.2	Mount, 1982[5]
"	100	130	Freeman & Fowler, 1953[6]
Goldfish	220	123	Adelman & Smith, 1976
"	220	123	Adelman & Smith, 1976
"	220	90	Adelman & Smith, 1976
"	220	125	Adelman & Smith, 1976
"	220	109	Adelman & Smith, 1976
"	220	135	Adelman & Smith, 1976
"	220	110	Adelman & Smith, 1976
"	220	129	Adelman & Smith, 1976
"	220	98	Adelman & Smith, 1976

"	220	133	Adelman & Smith, 1976
"	220	102	Adelman & Smith, 1976
"	220	133	Adelman & Smith, 1976
"	220	126	Adelman & Smith, 1976
"	220	126	Adelman & Smith, 1976
"	220	126	Adelman & Smith, 1976
"	220	133	Adelman & Smith, 1976
"	220	126	Adelman & Smith, 1976
"	220	124	Adelman & Smith, 1976
"	100	249	Dowden & Bennet, 1965
"	20	37.5	Pickering & Henderson, 1966
Fathead minnow	235	33.2	Broderius & Smith, 1979
"	209	39.7	Pickering, 1980
"	208	32.7	Pickering, 1980
"	209	37.7	Pickering, 1980
"	209	37	Pickering, 1980
"	209	35.9	Pickering, 1980
"	220	56	Adelman & Smith, 1976
"	220	51	Adelman & Smith, 1976
"	220	53	Adelman & Smith, 1976
"	220	49	Adelman & Smith, 1976
"	220	48	Adelman & Smith, 1976
"	220	60	Adelman & Smith, 1976
"	220	50	Adelman & Smith, 1976
"	220	53	Adelman & Smith, 1976
"	220	49	Adelman & Smith, 1976
"	220	37	Adelman & Smith, 1976
"	220	66	Adelman & Smith, 1976
"	220	55	Adelman & Smith, 1976
"	220	38	Adelman & Smith, 1976
"	220	34	Adelman & Smith, 1976
"	220	29	Adelman & Smith, 1976
"	220	34	Adelman & Smith, 1976
"	220	26	Adelman & Smith, 1976
"	20	17.6	Pickering & Henderson, 1966
"	360	27.3	Pickering & Henderson, 1966
"	20	45.6	Pickering & Henderson, 1966
"	400	24.1	Waheda, 1977[7]
"	400	22.6	Waheda, 1977[7]
Bluegill	20	118	Pickering & Henderson, 1966
"	360	133	Pickering & Henderson, 1966
"	45	110	Trama & Benoit, 1960
"	45	170	Trama & Benoit, 1960
"	120	213	Turnbull, et al. 1954
"	44	113	Cairns & Scheier, 1959[8]
"	44	113	Cairns & Scheier, 1959[8]
"	44	113	Cairns & Scheier, 1959[8]
"	44	120	Cairns & Scheier, 1959[8]
"	44	169	Cairns & Scheier, 1959[8]
"	44	147	Cairns & Scheier, 1959[8]
"	171	135	Academy of Sciences, 1960

"	171	130	Academy of Sciences, 1960
"	32	133	Cairns, et al. 1981[9]
"	32	133	Cairns, et al. 1981[9]

(1)Cairns, J. Jr. et al. 1978. Effects of temperature on aquatic organism sensitivity to selected chemicals. Bull. 106. Virginia Water Resour. Res. Ctr. Blackburg, VA.

(2)Debelak, R.W. 1975. Acute toxicity of mixtures of copper, chromium, and cadmium to _Daphnia magna_. Thesis, Miami Univ., Oxford, OH.

(3)White, B. 1979. Report of two toxicity evaluations conducted using hexavalent chromium. Michigan DNR.

(4)Call, D.J., et al. 1981. Aquatic Pollutant Hazard Assessment and Development of a Hazard Prediction Technology by Quantitative Structure-Activity Relationships. Second Quarterly Report to EPA. Center for Lake Superior Environmental Studies, University of Wisconsin-Superior.

(5)Mount, D.I. 1982. Memorandum to C.E. Stephan, U.S. EPA, Duluth, Minnesota.

(6)Freeman, L. and I. Fowler. 1953. Toxicity of combination of certain inorganic compounds to _Daphnia magna_. Sewage Ind. Wastes 25:1191.

(7)Waheda, M.F. 1977. Effect of size of fathead minnows and green sunfish on hexavalent chromium toxicity. Thesis, Wright State Univ., Dayton, OH.

(8)Cairns, J., Jr. and A. Scheier. 1959. The relationship of bluegill sunfish body size to tolerance for some common chemicals. Proc. 13th Ind. Waste Conf., Purdue Univ.

(9)Cairns, J., Jr. et al. 1981. Effects of fluctuating sublethal applications of heavy metals upon the gill ventilatory response of bluegills. EPA-600/3-81-003. NTIS, Springfield, Virginia.

Table D-2. Summary of Correlation Coefficients

Species	Hardness vs. C[1]	ln Hardness vs. ln C	Hardness vs. ln C	$Hardness^2$ vs. C
Physa heterostropha (snail)	.947	.972	.972	.947
Daphnia magna (cladoceran)	<0	.440	.435	<0
Goldfish	.053	.608	.426	<0
Fathead minnow	<0	.130	<0	<0
Bluegill	.119	.248	.135	.026

(1) where C = acute toxicity concentration (LC 50 values) for Cr VI

In the case of chromium VI, it was unnecessary to calculate a geometric mean of the r-factors, since only one of the four equations exhibited a positive relationship between hardness and toxicity (ln hardness vs ln H or $C = a (H)^b$). Therefore the SAE's developed were in the form of $C = a (H)^b$.

Utilizing this form of equation, acute chromium VI toxicity values were calculated at sample hardness endpoint values of 20 and, 400 mg/l. Table D-3 summarizes these calculated toxicity values along with additional information utilized to generate the Final Acute Equation (FAE).

Table D-3. Calculated Toxicity Values @ Endpoint Hardnesses

Species	Number of Data Points	Species Acute Equation, C in ug/l	C in ug/l @ Hardness = 20 mg/l	400 mg/l
Physa heterstropha (snail)	4	$C = 2172 (H)^{.545}$	11,100	56,900
Daphnia magna (cladoceran)	27	$C = 1.82 (H)^{.764}$	18.0	177.
Goldfish	19	$C = 17,340 (H)^{.365}$	51,800	155,000
Fathead minnow	28	$C = 27,930 (H)^{.064}$	33,800	41,000
Bluegill	15	$C = 106,200 (H)^{.058}$	126,000	150,000

The lowest values at the endpoint hardnesses of 20 and 400 mg/l were connected by the equation form of $C = a (H)^b$. *Daphnia magna* has the lowest values at both endpoints. Thus the Final Acute Equation for chromium VI was based on the following cladoceran curve from Table D-3:

$$C = 1.82 (H)^{.764}$$

where C = the acute criterion concentration in ug/l for chromium VI
and H = the average hardness value for Swamp Creek (94 mg/l)

Chronic Criterion

The chronic data base for hexavalent chromium is very limited compared to the amount of acute data available. Three species (fathead minnow, *Daphnia pulex*, and *Simocephalus serrulatus*) have one chronic test result apiece that was compared to an acute test at the same hardness condition. Acute/chronic (A/C) ratios were calculated for each of the three species. Only the fathead minnow has an SAE for direct application of an A/C ratio. In this case, a resulting species chronic equation was calculated for fathead minnow. Table D-4 summarizes the acute and chronic data that was utilized to calculate the A/C ratios.

Table D-4. Chronic Data Summary. References are taken from the EPA ambient water quality criteria document for chromium unless they are footnoted.

Species	Hardness (mg/l)	LC50 Value (ug/l)	Chronic Value (ug/l	A/C Ratio	Reference
Fathead minnow	209	36,525[1]	1990	18.4	Pickering, 1980
Daphnia pulex (cladoceran)	45	36.3[2]	6.1	5.95	Mount, 1982[3]
Simocephalus serrulatus (cladoceran)	45	40.9	19.9	2.05	Mount, 1982[3]

[1]The LC50 value for fathead minnow was based on a geometric mean of five acute test results at hardness 209 (39,700., 32,700., 37,700., 37,000., and 35,900).

[2]Although *Daphnia pulex* had five LC50 values at hardness 45, a geometric mean was not calculated because the acute test results were performed under different test conditions (5 separate references were cited).

[3]Mount, D.I. 1982. Memorandum to C.E. Stephan, U.S. EPA, Duluth, MN.

Since the most sensitive acute species (*Daphnia magna*) has no corresponding chronic data, the A/C ratio applied to the Final Acute Equation was the geometric mean of all the A/C ratios for the three species in Table Cr VI-4. The A/C ratio was calculated from the data in the above table as follows:

$$\text{A/C ratio} = (18.4 \times 5.95 \times 2.06)^{1/3} = 6.09$$

The above A/C ratio value was applied to the FAE. This yielded the Final Chronic Equation (FCE) for chromium VI that is listed below:

$$C = \frac{1.82}{6.09} (H)^{.764}$$

where C = the chronic criterion concentration in ug/l for chromium VI and H = the average hardness value for Swamp Creek (94 mg/l)

APPENDIX E

WATER QUALITY BASED LIMITS FOR TRIVALENT CHROMIUM

Criteria

11.1 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.105 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Chromium is a chemically complex metal which occurs in valence states ranging from -2 to +6. Both trivalent and hexavelent chromium are the environmentally significant forms of the element, but they have very different chemical characteristics. Trivalent chromium tends to form stable complexes with negatively charged organic or inorganic species. Its solubility and toxicity vary significantly depending on water quality characteristics such as hardness.

Acute Criterion

The data base for trivalent chromium is less extensive than for hexavalent chromium. Three species have developed relationships between hardness and acute chromium III toxicity over a wide range of hardness values. Species acute equations were developed to predict acutely toxic chromium III concentrations for these species, namely *Daphnia magna* (a cladoceran), fathead minnow, and bluegill. Table E-1 summarizes the available acute data on chromium III toxicity.

Table E-1. Acute Data Summary. References are taken from the EPA ambient water quality criteria document for chromium.

Species	Hardness (mg/l)	LC50 Concentrations (ug/l)	Reference
Daphnia magna (cladoceran)	48	2.0	Beisinger & Christensen, 1972
"	52	16.8	Chapman, et al. Manuscript
"	99	27.4	Chapman, et al. Manuscript
"	110	26.3	Chapman, et al. Manuscript
"	195	51.4	Chapman, et al. Manuscript
"	215	58.7	Chapman, et al. Manuscript
Fathead minnow	203	29	Pickering, Manuscript
"	203	27	Pickering, Manuscript
"	20	5.1	Pickering & Henderson, 1966
"	360	67.4	Pickering & Henderson, 1966
Bluegill	20	7.7	Pickering & Henderson, 1966
"	360	71.9	Pickering & Henderson, 1966

Species acute equations (SAE's) were developed for each of the three species listed in Table E-1. Calculations were made to determine the best-fit relationship between acute chromium III toxicity and hardness among the four basic forms of equations. These calculations involved averaging the r-factors for those Wisconsin species where SAE's were developed. Table E-2 compares the r-factors for the four different types of equation.

Table E-2. Comparison of Correlation Coefficients

Equation Type	Geometric Mean ("r" factor)
Hardness vs C(1)	.982
ln hardness vs ln C	.939
Hardness vs ln C	.918
$Hardness^2$ vs C	.985

(1) where C = acute toxicity concentration (LC 50 values) for Cr III.

From the above table, the best relationship (determined from the geometric mean r value) was $hardness^2$ vs C (or $C = a + bH^2$).

Regression analyses performed for acute chromium III toxicity versus hardness resulted in the following equations and toxicity values at sample endpoint hardnesses of 20 and 400 mg/l.

Table E-3. Calculated Toxicity Values @ Endpoint Hardnesses

Species	Number of Data Points	Species Acute Equation, C in ug/l	C in ug/l @ Hardnesses = 20 mg/l	400 mg/l
Daphnia magna	6	$C = 10413 + 1.08H^2$	10,800	183,000
Fathead minnow	4	$C = 6958 + .474H^2$	7150	82,800
Bluegill	2	$C = 7260 + .499H^2$	7460	87,100

The lowest values at the endpoint hardnesses of 20 and 400 mg/l are connected by a curve with an equation of the form $C = a + b\ H^2$. Fathead minnow has the lowest values at both endpoints. Thus the Final Acute Equation for chromium III was based on the following fathead minnow curve from Table E-3.

$C = 6958 + .474\ H^2$
where C = the acute criterion concentration in ug/l for chromium III
and H = the average hardness value for Swamp Creek (94 mg/l)

Chronic Criterion

Two species, Daphnia magna and fathead minnow, have available data on chronic toxicity. From the chronic test results, an acute/chronic (A/C) ratio was calculated for the above species. Table E-4 summarizes the acute and chronic data that was utilized in developing the A/C ratios.

Table E-4. Chronic Data Summary. References are taken from the EPA ambient water quality criteria document for chromium unless they are footnoted.

Species	Hardness (mg/l)	LC50 Value (ug/l)	Chronic Value (ug/l)	A/C Ratio	Reference
Daphnia magna	100	16,800	66	255	Chapman, et al. Manuscript
" "		27,400	194(1)	141(2)	Chapman, et al. Manuscript(3)
Fathead minnow	203	28,000(4)	1020	27.4	Pickering, Manuscript

(1) Hardnesses for acute and chronic tests were not identical (99 and 100 respectively), but were close enough for the difference (1%) to be negligible.

(2) The A/C ratio for Daphnia magna is $(255 \times 141)^{1/2} = 190$.

(3) Chapman, G.A., et al. Manuscript. Effects of water hardness on the toxicity of metals to Daphnia magna. U.S. EPA, Corvallis, Oregon.

(4) The geometric mean of 27,000 and 29,000 ug/l is 28,000 ug/l at 203 mg/l hardness.

The species chronic equation (SCE) was developed by dividing the species acute equation by the A/C ratio. The species with the lowest values at the endpoints are connected by a curve with an equation of the form $C = a + bH^2$ Daphnia magna had the lower endpoint values of 57.1 and 965 ug/l compared to a fathead minnow with endpoint values of 261 and 3020 ug/l. Consequently the Final Chronic Equation for chromium III was based on the Daphnia magna curve as follows:

$$C = \frac{SAE}{A/C\ ratio} = \frac{10413 + 1.08\ H^2}{190} = 54.82 + .0057\ H^2$$

where C = the chronic criterion concentration in ug/l for chromium III

and H = the average hardness value for Swamp Creek (94 mg/l)

APPENDIX F

WATER QUALITY BASED LIMITS FOR COPPER

Criteria

0.025 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.013 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Copper occurs in two oxidation states: cuprous (+1) and cupric (+2). Copper (+1) is unstable in aerated water over the pH range of most natural waters (6 to 8). Consequently, copper occurs in surface waters primarily as the divalent cupric ion in free and complex forms. It is a minor nutrient to both plants and animals at low concentrations, but is toxic to aquatic life at concentrations not too much higher.

The cupric ion is highly reactive and forms moderate to strong complexes and precipitates with many inorganic and organic substances in natural waters (carbonate, phosphate, amino acids and humates). The proportion of copper present as the free cupric ion is generally low (less than one percent). The toxicity of copper is increased by reduction in water hardness, temperature, and dissolved oxygen, and decreased in the presence of humic acids, amino acids, and suspended solids. The criteria for copper was derived on the basis of toxicity tests conducted using soluble inorganic copper salts.

Acute Criterion

Of the aquatic life species indigenous to Wisconsin waters that have been tested for acute copper toxicity, five warmwater species have demonstrated relationships between hardness and LC50 concentrations over a wide range of hardness values. Equations have been developed to predict acutely toxic copper concentrations for these species (*Daphnia pulex*, *Philodina acuticornis*--rotifer, goldfish, fathead minnow, and bluegill). Test results for *Philodina acuticornis* and goldfish were available only in soft waters. Thus, for those two species, the predictive equations generated were utilized only at the low end of the hardness range typically found in Wisconsin surface waters.

Extensive data is available on two Daphnia species (D. pulex and D. pulicaria). U.S. EPA has concluded that the two species are extremely similar in their taxonomy and therefore are combining the data on the two species in their criteria determinations. The Department concurs with EPA by doing likewise in the determination of copper criteria. Data for both species in this appendix shall be listed as Daphnia pulex.

Carp has acute toxicity data over a wide hardness range, but there is no positive relationship evident between LC50 concentrations and hardness for this species. Thus a geometric mean of all 96 hour LC50 values was used to predict acutely toxic concentrations applicable at any water hardness.

Four warmwater species found in Wisconsin waters have acute copper toxicity data at more than one hardness value, but the range of hardnesses was too narrow to predict acute toxicity with any confidence. These species (bluntnose minnow, brown bullhead, banded killifish, and pumpkinseed) were not used in the calculations in the Final Acute Equation.

A number of species had only one acute copper toxicity test result reported, or had more than one test but all at the same hardness. Two or more test results must be reported, preferably from different references, to verify the accuracy of individual data for any given species. Since the single test results can not be verified as to their accuracy and since the data base is quite extensive for copper, those species with only one test result or more than one test at the same hardness were not used in determination of a copper criterion.

Table F-1 summarizes the data that was utilized in developing the acute criterion for copper.

Table F-1. Acute Data Summary. References are taken from the EPA ambient water quality criteria document for copper unless they are footnoted.

Species	Hardness (mg/l)	LC50 Concentrations (ug/l)	Reference
Daphnia pulex (cladoceran)	45	10	Cairns, et al. 1978
"	45	70	Cairns, et al. 1978[1]
"	45	60	Cairns, et al. 1978[1]
"	45	20	Cairns, et al. 1978[1]
"	45	5.6	Cairns, et al. 1978[1]
Daphnia pulicaria[2] (cladoceran)	48	11.4	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	48	9.06	Lind, et al. Manuscript

Daphnia pulicaria[2] (cladoceran)	48	7.24	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	44	10.8	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	45	9.3	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	95	17.8	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	145	23.7	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	245	27.3	Lind, et al. Manuscript
Daphnia pulicaria[2] (cladoceran)	31	55.5	Lind, et al. Manuscript[3]
Daphnia pulicaria[2] (cladoceran)	29	55.3	Lind, et al. Manuscript[3]
Daphnia pulicaria[2] (cladoceran)	28	53.3	Lind, et al. Manuscript[3]
Daphnia pulicaria[2] (cladoceran)	16	35.5	Lind, et al. Manuscript[3]
Daphnia pulicaria[2] (cladoceran)	151	78.8	Lind, et al. Manuscript[3]
Daphnia pulicaria[2] (cladoceran)	84	84.7	Lind, et al. Manuscript[3]
Philodina acuticornis (Rotifer)	40	160	Buikema, et al. 1977
"	25	700	Buikema, et al. 1974
"	81	1,100	Buikema, et al. 1974
Goldfish	20	36	Pickering & Henderson, 1966
"	52	300	Tsai & McKee, 1980
Carp	53	810	Rehwoldt, et al. 1971
"	55	800	Rehwoldt, et al. 1972
"	166	118	Deshmukh & Marathe, 1980[4]
"	166	530	Deshmukh & Marathe, 1980[4]

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Fathead minnow	202	460	Pickering, et al. 1977
"	202	490	Pickering, et al. 1977
"	200	790	Andrew, 1976
"	45	200	Andrew, 1976
"	360	1,140	Pickering & Henderson, 1966
"	360	1,760	Pickering & Henderson, 1966
"	20	23(4 times)	Pickering & Henderson, 1966
"	200	430	Mount, 1968
"	20	50	Tarzwell & Henderson, 1960[5]
"	400	1,400	Tarzwell & Henderson, 1960[5]
"	200	470	Mount & Stephan, 1969
"	31	84	Mount & Stephan, 1969
"	31	75	Mount & Stephan, 1969
"	200	440	Geckler, et al. 1976
"	200	490	Geckler, et al. 1976
"	48	114	Lind et al. Manuscript
"	45	121	Lind et al. Manuscript
"	46	88.5	Lind et al. Manuscript
"	30	436	Lind et al. Manuscript[3]
"	37	516	Lind et al. Manuscript[3]
"	84	550	Lind et al. Manuscript[3]
Bluegill	45	1,100	Benoit, 1975
"	200	8,300	Geckler, et al. 1976
"	200	10,000	Geckler, et al. 1976
"	43	1,250	Patrick, et al. 1968
"	20	660	Pickering & Henderson, 1966
"	360	10,200	Pickering & Henderson, 1966
"	35	2,400	O'Hara, 1971
"	100	6,970	Birge & Black, 1979
"	101	1,800	Turnbull, et al. 1954[6]
"	40	1,000	Thompson, et al. 1980[7]
"	46	740	Trama, 1954[8]
"	365	2,550	Inglis & Davis, 1972[9]
"	209	1,720	Inglis & Davis, 1972[9]
"	52	1,000	Inglis & Davis, 1972[9]
"	26	1,000	Cairns et al. 1981[10]
"	43	770	ANS, 1960[11]

(1) Cairns, J. et al. 1978. Effects of temperature on aquatic organisms sensitivity to selected chemicals. Bull. 106 - Virginia Water Resour. Res. Center, Blacksburg, VA.

[2]To be considered identical to Daphnia pulex.

[3]Lind, D., et al. Regional copper-nickel study. Aquatic toxicology progress report (Manuscript).

[4]Deshmukh, S.S. and V.B. Marathe. 1980. Size related toxicity of copper and mercury to Lebistes reticulata (Peter), Labeo rohita (Ham.) and Cyprinus carpio (Linn.). Ind. J. Exp. Biol. 18:421.

[5]Tarzwell, C.M. and C. Henderson. 1960. Toxicity of less common metals to fishes. Ind. Wastes. 5:12.

[6]Turnbull, H., et al. 1954. Toxicity of various refinery materials to freshwater fish. Ind. Eng. Chem. 46:324.

[7]Thompson, K.W., et al. 1980. Acute toxicity of zinc and copper singly and in combination to the bluegill. Bull. Environ. Contam. Toxicol. 25:122.

[8]Trama, F.B. 1954. The toxicity of copper to the common bluegill. Notulae Natur. No. 257. p.1.

[9]Inglis, A. and E.L. Davis. 1972. Effects of water hardness on the toxicity of several organic and inorganic herbicides to fish. U.S. Bur. Sport. Fish. Wildl. Tech. Paper #67.

[10]Cairns, J., et al. 1981. Effects of fluctuating, sublethal applications of heavy metal solutions upon the gill ventilation response of bluegills. EPA-600/3-81-003. NTIS, Springfield, Virginia.

[11]Academy of Natural Sciences. 1960. The sensitivity of aquatic life to certain chemicals commonly found in industrial wastes. Philadelphia, PA.

From the data listed in Table F-1, carp was the only species where an equation was not developed because no relationship was apparent between hardness and LC50 values for carp. A single concentration value that does not change with hardness was determined for carp from the geometric mean of the LC50 values (C = 449 ug/l).

For the rest of the species in Table F-1, relationships between acute copper toxicity and hardness exists, so species acute equations (SAE's) were determined. Calculations were made to establish the best fit relationship between copper toxicity and hardness among the four basic forms of equations. The best fit relationship of these four equations was found by calculating a geometric mean of the r-factors for those species that had SAE's developed. A summary of the r-factors for these species is listed in Table F-2.

Table F-2. Comparison of Correlation Coefficients

Equation Type	Geometric Mean ("r" value)
Hardness vs C(1)	.598
ln hardness vs ln C	.543
Hardness vs ln C	.613
$Hardness^2$ vs C	.558

(1) where C = acute toxicity concentrations (LC50 values) for copper

The best fit relationship from Table F-2, as determined from the geometric mean was of the equation from hardness vs ln C (or $C = a\ (b)^H$). Utilizing this type of equation, acute copper toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. The calculated toxicity values at these endpoint hardnesses, along with additional information used to generate the Final Acute Equation (i.e.: the geometric mean of the LC50 concentrations for carp) is summarized in Table F-3.

Table F-3. Calculated Toxicity Values at Endpoint Hardnesses

Species	Number of Data Points	Species Acute Equation (C in ug/l)	C (in ug/l) @ Hardness = 20 mg/l	400 mg/l
Daphnia pulex (cladoceran)	19	$C = 20.57\ (1.002)^H$	21.5	50.4
Philodina acuticornis (rotifer)	3	$C = 225\ (1.016)^H$	312	(1)
Carp	4	C = 448.7	449	449
Goldfish	2	$C = 9.567\ (1.068)^H$	36.0	(1)
Fathead minnow	21	$C = 98.88\ (1.008)^H$	115	2,070
Bluegill	16	$C = 1006\ (1.006)^H$	1,130	10,100

(1)Test results were available only in soft waters, thus the predictive equations were utilized only at the low end of the hardness range.

The lowest values at endpoint hardnesses of 20 and 400 mg/l are connected by a curve with an equation of the form $C = a\ (b)^H$. Daphnia pulex has the lowest values at both endpoints. Consequently, the acute criterion for copper was based on the following cladoceran curve from Table F-3:

$$C = 20.57\ (1.002)^H$$

where C = the acute criterion concentration in ug/l for copper
and H = the average hardness value for Swamp Creek (94 mg/l)

Chronic Criterion

The chronic data base for copper is significantly smaller compared to the amount of acute data available. Two species (fathead minnow and channel catfish) have demonstrated relationships between hardness and chronic toxicity over a wide range of hardness values such that equations can be developed to predict chronically toxic concentrations.

Bluegill has only one test result reported. However, since that test was done at the same hardness (45 mg/l) as six acute tests for bluegill, an acute/chronic (A/C) ratio was calculated for that species. Dividing the SAE for bluegill by the A/C ratio resulted in an equation to predict chronically toxic concentrations at any hardness.

Three species (a scud, a snail, and bluntnose minnow) had A/C ratios calculated similar to bluegill. However, since there are no SAE's for these three species, no chronic equations can be calculated. As a result, these species were not used in calculating a Final Chronic Equation (FCE) for copper.

Northern pike, white sucker, and walleye have chronic test results at just one hardness. For these three species, no acute tests were performed at the same hardness and thus no estimate of the chronic effects at other conditions can be made. Therefore, these data were not used in determining FCE's.

Table F-4 summarizes the data that was utilized in developing chronic toxicity criterion for copper.

Table F-4. Chronic Data Summary. References are taken from the ambient water quality document for copper unless they are footnoted.

Species	Hardness (mg/l)	Chronic Value (ug/l)	Reference
Fathead minnow	198	21.9	Mount, 1968
"	30	14	Mount & Stephan, 1969
"	200	27.7	Pickering, et al. 1977
"	274	75.4	Brungs, et al. 1976(1)
"	45	18.5	Lind, et al. Manuscript
Channel catfish	36	14.7	Sauter, et al. 1976
"	186	15.7	Sauter, et al. 1976
Bluegill	45	29	Benoit, 1975

(1)Brungs, W.A., et al. 1976. Acute and chronic toxicity of copper to the fathead minnow in a surface water of variable quality. Water Res. 10:37.

For the species listed in Table F-4, species chronic equations (SCE's) were developed for fathead minnow and channel catfish using regression analyses while an A/C was calculated for bluegill. The A/C for bluegill at 45 mg/l hardness was 37.9 (1100/29 = 37.9). The SAE for bluegill was divided by the A/C ratio to yield a SCE. The SCE's for all three species in Table F-4 were of the form $C = a\ (b)^H$ because this was the form of the SAE's proven to have the best overall fit.

Utilizing the SCE in the form $C = a\ (b)^H$, chronic copper toxicity values were calculated at sample endpoint hardness values of 20 and 400 mg/l. Table F-5 summarizes these calculated toxicity values.

Table F-5. Calculated Chronic Values at Endpoint Hardnesses

Species	Number of Data Points	Species Chronic Equation (C in ug/l)	C (ug/l) @ Hardness = 20 mg/l	400 mg/l
Fathead minnow	5	$C = 11.96\ (1.005)^H$	13.3	95.6
Channel catfish	2	$C = 14.47\ (1.0004)^H$	14.6	17.2
Bluegill	1	$C = \frac{1006\ (1.006)^H}{37.9}$	29.8	268

The lowest values at the hardness endpoints are connected by a curve with an equation of the form $C = a\ (b)^H$. The lowest value at 20 mg/l hardness is 13.3 ug/l (fathead minnow) and at 400 mg/l hardness it is 17.2 ug/l (channel catfish).

The chronic criterion for copper can be calculated based on the following Final Chronic Equation:

$C = 13.08\ (1.0007)^H$
where C = the acute criterion concentration in ug/l for copper
and H = the average hardness value for Swamp Creek (94 mg/l)

APPENDIX G

WATER QUALITY BASED LIMITS FOR CYANIDE

Criteria

0.096 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.011 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Cyanide commonly occurs in water as HCN, CN-, simple cyanides, in metal complexes, or as simple chain and complex ring organic compounds. The extent of HCN formation is mainly dependent on water temperature and pH. The cyanide ion (CN^-) can combine with various heavy metal ions to form metallocyanide complex ions. The toxicity to aquatic organisms of most simple cyanides and metallocyanide complexes is due mostly to the presence of HCN derived from ionization or dissociation of cyanide-containing compounds. Both HCN and CN^- are toxic to aquatic life and the majority of free cyanide usually exists as the more toxic HCN. Thus the cyanide criterion established in this appendix is expressed in terms of free cyanide expressed as CN.

Acute Criterion

A relationship between hardness and LC50 concentrations has not been demonstrated for cyanide from the acute toxicity data available. Therefore, the cyanide criterion was based on the geometric mean of the LC50 values. Data from five species with two or more test results on acute cyanide toxicity were utilized in developing the water quality criterion for this parameter. Four species with single test results were excluded from the criterion determination because the validity of the test results was uncertain. Table G-1 provides a summary of the data utilized to generate an acute standard for cyanide.

Table G-1. Acute Data Summary. References are taken from the ambient water quality criteria document for cyanide unless they are footnoted.

Species	LC50 (ug/l)	Geometric Mean (ug/l)	Reference
P. heterostropha (snail)	432	431	Patrick, et al. 1968
P. heterostropha (snail)	431		Cairns & Scheier, 1958
Daphnia pulex (cladoceran)	83	95.5	Lee, 1976
"	110		Cairns, et al. 1978(1)
Fathead minnow	120	133	Smith, et al. 1978
"	98.7		Smith, et al. 1978
"	81.8		Smith, et al. 1978
"	110		Smith, et al. 1978
"	116		Smith, et al. 1978
"	119		Smith, et al. 1978
"	126		Smith, et al. 1978
"	81.5		Smith, et al. 1978
"	124		Smith, et al. 1978
"	137		Smith, et al. 1978
"	121		Smith, et al. 1978(2)
"	137		Smith, et al. 1978(2)
"	129		Smith, et al. 1978(2)
"	131		Smith, et al. 1978
"	131		Smith, et al. 1978
"	122		Smith, et al. 1978
"	161		Smith, et al. 1978
"	105		Smith, et al. 1978
"	188		Smith, et al. 1978
"	119		Smith, et al. 1978
"	175		Smith, et al. 1978
"	163		Smith, et al. 1978
"	169		Smith, et al. 1978
"	230		Douderoff, 1956
"	120		Broderius, et al. 1977
"	113		Broderius, et al. 1977
"	128		Broderius, et al. 1977
"	83		Broderius, et al. 1977(3)
"	117		Broderius, et al. 1977(3)
"	128		Broderius, et al. 1977
"	350		Henderson, et al. 1961
"	230		Henderson, et al. 1961

Bluegill	364	138	Smith, et al. 1978
"	232		Smith, et al. 1978
"	279		Smith, et al. 1978
"	273		Smith, et al. 1978
"	81		Smith, et al. 1978
"	85.7		Smith, et al. 1978
"	74		Smith, et al. 1978
"	100		Smith, et al. 1978
"	107		Smith, et al. 1978
"	83		Smith, et al. 1978(2)
"	87.1		Smith, et al. 1978(2)
"	120		Smith, et al. 1978(2)
"	99		Smith, et al. 1978
"	113		Smith, et al. 1978
"	121		Smith, et al. 1978
"	126		Smith, et al. 1978
"	180		Cairns & Scheier, 1958
"	180		Cairns & Scheier, 1959
"	150		Henderson et al. 1961
"	160		Cairns & Scheier, 1963
Yellow perch	288	118	Smith et al. 1978
"	330		Smith et al. 1978
"	88.9		Smith et al. 1978
"	93		Smith et al. 1978
"	74.7		Smith et al. 1978
"	94.7		Smith et al. 1978
"	101		Smith et al. 1978
"	107		Smith et al. 1978
"	90.4		Smith et al. 1978(2)
"	102		Smith et al. 1978(2)

(1)Carins, J. Jr. et al. 1978. Effects of temperature on aquatic organism sensitivity to selected chemicals. Bull. 106, Virginia Water Res. Center, Virginia Polytechnic Inst. and State Univ., Blacksburg, VA.

(2)Smith, L.L., Jr., et al. 1978. Acute toxicity of hydrogen cyanide to freshwater fishes. Arch. Environ. Contam. Toxicol. 7:325.

(3)Broderius, S., et al. 1977. Relative toxicity of free cyanide and dissolved sulfide forms to the fathead minnow. Jour. Fish. Res. Board Can. 34:2323.

The lowest species mean acute value (SMAV) from Table G-1 was utilized as the Final Acute Value (FAV). Of the five species with two or more test results, Daphnia pulex had the lowest SMAV. Therefore, the FAV for cyanide was based on the cladoceran number of 95.5 ug/l.

Chronic Criterion

Three species had a single chronic test result reported for cyanide. A scud, Gammarus pseudolimnaeus, had a chronic test result that was performed by the same reference source as the acute test. Thus, an acute/chronic (A/C) ratio was calculated for the scud. The other two species with one chronic test result, fathead minnow and bluegill, do not have common reference sources between acute and chronic data bases. Normally, these species would not be used in the determination of the Final Chronic Value (FCV) because there is no guarantee of similar test conditions between acute and chronic tests. However, due to the lack of chronic cyanide data, especially for fish species, A/C ratios were calculated for these species and the data was used in determination of the FCV.

Table G-2 summarizes the data that was utilized in developing a chronic criterion for cyanide.

Table G-2. Chronic Data Summary. References are taken from the ambient water quality criteria document for cyanide.

Species	Acute Value (ug/l)	SMAV (ug/l)	Chronic Value (ug/l)	A/C Ratio	Reference
Gammarus pseudolimnaeus (scud)	167	NA(1)	18.3	9.1	Oseid & Smith, 1979
Fathead minnow	NA(1)	133	16.4	8.1	Lind, et al. 1977
Bluegill	NA(1)	138	14.6	9.5	Kimball, et al. 1978

(1)NA = Not Applicable

Acute/chronic (A/C) ratios were calculated by dividing either the acute value or the SMAV (geometric mean of all the acute data for a species) by the chronic test result value for that species.

Since the most sensitive acute species (Daphnia pulex) had no corresponding chronic test data, a geometric mean of all the A/C ratios in Table G-2 was determined. The Final Acute Value (95.5 ug/l) was then divided by the geometric mean of the A/C ratios (8.9) to yield a Final Chronic Value (FCV). The FCV applicable for cyanide is 10.7 ug/l (95.5 ug/l/8.9 = 10.7 ug/l).

APPENDIX H

WATER QUALITY BASED LIMITS FOR LEAD

Criteria

1.0 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.042 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

The solubility of lead compounds in water depends on the pH. Lead exists in the plus two or plus four valence states with inorganic Pb^{+2} compounds being the most stable. Lead can be removed from the water column by absorption to solids or chemical precipitation. Lead is acutely and chronically toxic to aquatic organisms with toxicity being affected by water hardness.

Acute Criterion

Of the aquatic organisms that have been tested for acute lead toxicity, three species have demonstrated relationships between hardness and lead LC50 concentrations. These species (*Daphnia magna*, fathead minnow, and bluegill) have data available over a wide range of hardness conditions such that equations were developed to predict acutely toxic lead concentrations.

Three other species have acute lead toxicity available. But since the range of hardnesses were too narrow or only one acute lead toxicity test result was reported, the data for these species were not utilized in determining the acute criterion for lead. Table H-1 summarizes the data that was utilized in developing the acute toxicity criterion for lead.

Table H-1. Acute Data Summary. References are taken from the ambient water quality criteria document for lead.

Species	Hardness (mg/l)	LC50 Concentrations (ug/l)	Reference
Daphnia magna (cladoceran)	45	450	Biesinger & Christensen, 1972
"	54	612	Chapman, et al. Manuscript
"	110	952	Chapman, et al. Manuscript
"	152	1910	Chapman, et al. Manuscript
Fathead minnow	20	2400	Tarzwell & Henderson, 1960
"	20	5580	Pickering & Henderson, 1966
"	20	7480	Pickering & Henderson, 1966
"	20	7330	Pickering & Henderson, 1966
"	360	482,000	Pickering & Henderson, 1966
Bluegill	20	23,800	Pickering & Henderson, 1966
"	360	442,000	Pickering & Henderson, 1966

Because a relationship exists between water hardness and acute lead toxicity for the species in Table H-1, species acute equations (SAE's) were determined. Calculations were made to establish the best fit relationship between lead toxicity and hardness among the four basic forms of equations. The best fit relationship of these four equations was found by calculating a geometric mean of the r-factors for all Wisconsin species that had SAE's developed. Table H-2 summarizes the correlation coefficient "r" for each type of equation.

Table H-2. Summary of Correlation Coefficients

Equation Type	Geometric Mean ("r" value)
Hardness vs C(1)	.977
ln hardness vs ln C	.985
Hardness vs ln C	.984
Hardness^2 vs C	.970

(1) where C = acute toxicity concentration (LC50 values) for lead.

The best fit relationship from Table H-2, as determined from the geometric mean, was of the equation form ln hardness vs ln C ($C = a (H)^b$). Utilizing this type of equation, acute lead toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. The calculated toxicity values at these endpoint hardnesses, along with additional information used to generate the Final Acute Equation, is summarized in Table H-3.

Table H-3. Calculated Toxicity Values at Endpoint

Species	Number of Data Points	Species Acute Equation (C in ug/l)	C (ug/l) @ Hardnesses 20 mg/l	Hardness = 400 mg/l
Daphnia magna (cladoceran)	4	$C = 8.40 (H)^{1.05}$	196	4580
Fathead minnow	5	$C = 47.66 (H)^{1.57}$	5210	569,000
Bluegill	2	$C = 1152 (H)^{1.01}$	23,800	492,000

The lowest values at the endpoint hardnesses of 20 and 400 mg/l were connected by a curve with an equation of the form C = a + bH. Daphnia magna has the lowest values at both endpoints. Consequently, the acute criterion for lead was based on the Daphnia magna curve from Table H-3.

$C = 8.40 (H)^{1.05}$
where C = the acute criterion concentration in ug/l for lead
and H = the average hardness value for Swamp Creek (94 mg/l)

Chronic Criterion

A small amount of chronic data exists for lead. Of those species with data, Daphnia magna has a demonstrated relationship between hardness and chronic lead toxicity over a wide range of hardness values. Thus an equation was developed for this species to predict chronically toxic lead concentrations at various hardnesses.

One species, bluegill, has only one chronic test result reported, but it was not performed at the same hardness as the acute tests used in generating the SAE. Since no other warmwater fish species have chronic lead toxicity results that can be used, an acute value was calculated from the SAE at the same hardness condition at which the chronic test was performed (41 mg/l). An acute/chronic (A/C) ratio was then generated for bluegill. Dividing the bluegill SAE by the A/C ratio results in an equation to predict chronically toxic concentrations at any hardness.

Three other species (Lymnaea palustris (a snail), channel catfish, and white sucker) have chronic test results at just one hardness. Since no acute tests were performed on these species, no estimate of the chronic effects of lead could be made. Therefore, the chronic test results for these species were not used in determining the Final Chronic Equation. Table H-4 summarizes the data that was utilized in developing the chronic toxicity criterion for lead.

Table H-4. Chronic Data Summary. References are taken from the ambient water quality criteria document for lead.

Species	Hardness (mg/l)	Chronic Value (ug/l)	Reference
Daphnia magna (cladoceran)	52	12.3	Chapman, et al. Manuscript
"	102	119	Chapman, et al. Manuscript
"	151	128	Chapman, et al. Manuscript
Bluegill	41	92	Sauter et al. 1976

Species chronic equations (SCE's) were developed using regression analysis (for Daphnia magna) and an A/C ratio (for bluegill). To be consistent with the equation form of the SAE's for acute toxicity, the SCE utilized for lead was of the same form ($C = a\ (H)^b$). For bluegill, the SCE was determined by dividing the SAE by the A/C ratio (A/C ratio = 49,200/92 = 534).

Using the SCE of the form $C = a\ (H)^b$, chronic lead toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. Table H-5 summarizes the calculated toxicity values at the endpoint hardnesses for Daphnia magna and bluegill.

Table H-5. Calculated Chronic Values at Endpoint Hardnesses

Species	Number of Data Point	Species Chronic Equation (C in ug/l)	C (ug/l) @ Hardness = 20 mg/l	400 mg/l
Daphnia magna (cladoceran)	3	$C = .0014\ (H)^{2.35}$	1.54	1750
Bluegill	1	$C = \frac{1152}{534} [(H)^{1.01}]$	44.6	921

The lowest values at the hardness endpoints for each species (*Daphnia magna* at 20 mg/l and bluegill at 400 mg/l) were connected by a curve with an equation of the form $C = a\ (H)^b$. The chronic criterion for lead can be calculated based on following Final Chronic Equation:

$$C = 0.0026\ (H)^{2.134}$$

where C = the chronic criterion concentration in ug/l for lead and H = the average hardness value for Swamp Creek (94 mg/l).

APPENDIX I

WATER QUALITY BASED LIMITS FOR MERCURY

Criteria

0.002 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.0002 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Mercury has been recognized as one of the more toxic metals in the aquatic environment. It can exist in three oxidation states: elemental, mercurous, and mecuric, and it can be part of both inorganic and organic compounds. Mecuric salts are more commonly found in aqueous solution than mercurous salts, because they are more soluble in water. Due to their insolubility in water, mercurous salts are much less toxic than the mecuric forms. Thus the criterion established for mercury was based on the short and long term toxicity of mecuric, rather mercurous compounds, to aquatic life.

In addition to adversely affecting aquatic life through direct toxicity, mercury is one of the few pollutants that impacts aquatic organisms through bioaccumulation. Consequently, in establishing a criterion value for mercury, a Final Residue Value (FRV) was calculated (from the bioconcentration factor and maximum permissible tissue level) and was compared to The Final Chronic Value (FCV). The lowest of the two values (either FRV or FCV) was applied as the criterion for monthly average for mercury.

Acute Criterion

Eleven indigenous Wisconsin organisms that are warmwater species have acute toxic data on mercury. Of those species that had two or more data points (only three species -- <u>Philodina acuticornis</u> (a rotifer), <u>Daphnia pulex</u> (a cladoceran), and fathead minnow), no relationship between hardness and LC50 concentrations was demonstrated. Normally only those organisms that had two or more test results would be utilized in determination of the Final Acute Value (FAV). However, due to the importance of mercury toxicity in the aquatic environment, species with single test results were included in consideration of the acute, chronic, and residue criteria. Either a geometric mean of the LC50 concentrations (for species with two or more test results) were calculated and expressed as a species mean acute value (SMAV), or a species acute value (SAV) (when only single test results were available) was determined. The lowest of the SMAV's and SAV's of the eleven species with acute data was utilized as the FAV.

Table I-1 provides a summary of the acute data utilized in generating the acute criterion for mercury.

Table I-1. Acute Data Summary. References are taken from the ambient water quality criteria document for mercury unless they are footnoted.

Species	LC50 (ug/l)	SMAV or SAV (ug/l)	References
Rotifer (Philodina acuticornis)	518	783	Buikema, et al. 1974
"	1185		Buikema, et al. 1974
Bristleworm (Nais sp.)	1000	1000	Rehwoldt, et al. 1973
Snail (Amnicola sp.)	80	80	Rehwoldt, et al. 1973[1]
Cladoceran (Daphnia pulex)	2.22	2.22	Canton & Adema, 1978[2]
"	2.22		Canton & Adema, 1978[2]
Scud (Gammarus sp.)	10	10	Rehwoldt, et al. 1973
Mayfly (Ephemerella subvaria)	2,000	2,000	Warnick & Bell, 1969
Stonefly (Acroneuria lycorius)	2,000	2,000	Warnick & Bell, 1969
Caddisfly (Hydropsyche betteni)	2,000	2,000	Warnick & Bell, 1969
Midge (Chironomus sp.)	20	20	Rehwoldt, et al. 1973[1]
Fathead minnow	150	168	Call, et al. 1982[3]
"	168		Snarski & Olson, 1982[4]
"	190		Curtis & Ward, 1981[5]
Bluegill	160	160	Holcombe et al. Manuscript[6]

(1)Rehwoldt, R., et al. 1973. The acute toxicity of some heavy metal ions toward benthic organisms. Bull. Environ. Contam. Toxicol. 10:291.

(2)Canton, H. and D.M.M. Adema. 1978. Reproducibility of short-term and reproduction toxicity experiments with Daphnia magna and comparison of the sensitivity of Daphnia magna with Daphnia pulex and Daphnia cucullata in short-term experiments. Hydrobid. 59:135.

(3)Call, D.J., et al. 1982. Toxicity and metabolism studies with EPA priority pollutants and related chemicals in freshwater organisms. Center for Lake Superior Environmental Studies, Univ. of Wisconsin-Superior.

(4)Snarski, V.M. and G.F. Olson. 1982. Chronic toxicity and bioaccumulation of mercuric chloride to the fathead minnow. Aquat. Toxicol. 2:143.

(5)Curtis, M.W., and C.H. Ward. 1981. Aquatic Toxicity of 40 Industrial Chemicals - Testing in Support of Hazardous Substance Spill Prevention Regulation. J. Hybrd. 51:359.

(6)Holcombe, G.W., et al. Manuscript. The toxicity of selected priority pollutants to various aquatic organisms.

From Table I-1, it is apparent that Daphnia pulex is much more sensitive to acute mercury toxicity than most other aquatic life species. The data for a non-indigenous daphnid (Daphnia magna) was very close to the mean value for Daphnia pulex. Based on seven test results, the SMAV for Daphnia magna was 2.44 ug/l. Therefore, to adequately protect the cladoceran species, the acute criterion value for mercury is 2.22 ug/l based on the SMAV for Daphnia pulex.

Chronic Criterion

No fish and aquatic life species that are indigenous to Wisconsin surface waters have data reported on chronic mercury toxicity. The only available data are for the non-indigenous, Daphnia magna, which has three data points with a geometric mean of 1.32 ug/l. Since this was the only chronic data available for mercury, an acute/chronic (A/C) ratio was determined for this species.

The acute and chronic Daphnia magna results did not come from common sources, so the A/C ratio was calculated using the mean and chronic values. Table I-2 summarizes the cladoceran data that was utilized in generating the chronic criteria for mercury.

Table I-2. Chronic Data Summary

Species	Acute Value ug/l	SMAV (ug/l)	Chronic Value (ug/l)	SMCV (ug/l)	A/C Ratio	Reference
Daphnia magna	5	2.44	0.96	1.32	1.85	Biesinger, et al. Manuscript, 1982[1]
	3.18		1.29			
	3.18		1.87			
	1.33					
	1.63					
	2.29					
	2.07					

(1)Biesinger, K.E., et al. 1982. Chronic effects of inorganic and organic mercury on Daphnia magna: toxicity, accumulation, and loss. Arch. Environ. Contam. Toxicol. 11:769.

An A/C ratio was calculated by dividing the SMAV for Daphnia magna by the SMCV. The resulting A/C (1.85) was then divided into the Final Acute Value (2.22 ug/l) to yield a Final Chronic Value for mercury of 1.2 ug/l.

Residue Criteria

A Final Residue Value (FRV) was calculated by dividing a maximum permissible tissue concentration (MPTC) by an appropriate bioconcentration factor (BCF). For mercury, the most stringent MPTC is 1.0 part per million (ppm) for man which is an FDA action level. The only data available for BCF is for fathead minnow (4994). The FRV for mercury then was 0.2 ug/l (MPTC/BCF or 1 ppm/4994 = 0.2 ug/l).

In comparing the FRV with the FCV, the FRV was the lower of the two values. Thus, the FRV of 0.2 ug/l is the monthly average criterion for mercury.

APPENDIX J

WATER QUALITY BASED LIMITS FOR SELENIUM

Criterion

1.0 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.077 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Selenium exists in four oxidation states (-2, 0, +4 and +6). Selenium in the +6 oxidation state (selenate) is stable in alkaline and oxidizing conditions. Of the compounds in which selenium is in the +4 oxidation state (selenate), ferric selenate is one of the most important. It has a very low solubility and absorbs on soil particles, consequently lowering the availability of selenium to biota. Selenate has a very limited toxic data base; therefore the water quality criterion established for selenium was based on the toxicity of selenate to aquatic life.

Acute Criterion

Based on the acute data available for selenium +4, no relationship between hardness and LC50 concentrations was found to exist. Thus, the criterion for selenium was based on the geometric mean of the LC50 values. Only those species with more than one test result on acute selenium +4 toxicity (Daphnia magna and fathead minnow) were utilized in developing the water quality criterion for this parameter. Seven species with single test results were excluded from the criterion determination because the validity of the test results was uncertain. Table J-1 provides a summary of the data that was utilized in generating an acute standard for selenium.

Table J-1. Acute Data Summary. References are taken from the ambient water quality criteria document for selenium.

Species	LC50 (mg/l)	Geometric mean (mg/l)	Reference
Daphnia magna (cladoceran)	2.50	1.03	Bringman & Kuhn, 1959
"	0.71		Halter, et al. 1980
"	1.22		Kimball, Manuscript
"	1.22		Kimball, Manuscript
"	0.43		EPA, 1978
Fathead minnow	10.5	3.1	Adams, 1976
"	11.3		Adams, 1976
"	6.0		Adams, 1976
"	7.4		Adams, 1976
"	3.4		Adams, 1976
"	2.2		Adams, 1976
"	2.1		Cardwell et al. 1976
"	5.2		Cardwell et al. 1976
"	1.0		Halter, et al. 1980
"	0.62		Kimball & Manuscript
"	0.97		Kimball & Manuscript

The lowest species mean acute number from Table J-1 was used as the Final Acute Value (FAV). Daphnia magna had a lower geometric mean value than fathead minnow. Consequently, the FAV for selenium was based on the cladoceran number of 1.0 mg/l.

Chronic Criterion

For selenium +4, two species with acute data (Daphnia magna and fathead minnow), had one reported chronic test result each. Since each chronic test was performed by the same reference source as at least one acute test on that species, an acute/chronic (A/C) ratio was calculated for both Daphnia magna and fathead minnow. Table J-2 summarizes the data that was utilized in developing a chronic criterion for selenium.

Table J-2. Chronic Data Summary. References are taken from the ambient water quality criteria document for selenium.

Species	Acute Value (mg/l)	Chronic Value (mg/l)	A/C Ratio	SMCV(1) (mg/l)	Reference
Daphnia magna	1.22	.092	13.3	.077	Kimball, Manuscript
Fathead minnow	.775	.113	6.9	.45	Kimball, Manuscript

(1) SMCV = species mean chronic value

The Final Chronic Value (FCV) is calculated for each species by dividing the FAV by the A/C ratio. The most stringent species mean chronic value listed in Table J-2 (0.077 mg/l for *Daphnia magna*) was utilized as the FCV for selenium.

APPENDIX K

WATER QUALITY BASED LIMITS FOR SILVER

Criterion

0.007 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

No recommended value as a monthly average.

Introduction

Silver exhibits oxidation states of 0, +1, +2, and +3, but only 0 and +1 states occur to any extent in the environment. In natural waters, the form of silver that causes environmental concerns is the monovalent species. Monovalent silver ions may exist in various degrees of association with a large number of inorganic ions, such as sulfate, bicarbonate, and nitrate to form numerous compounds with a range of solubilities. Silver may also exist as metal organic complexes in natural waters or be absorbed by organic materials.

Acute Criterion

Silver is one of the most toxic metals to freshwater aquatic life. Of the aquatic organisms that have been tested for acute silver toxicity, two species have demonstrated relationships between hardness and LC50 concentrations. These two species (Daphnia magna and fathead minnow) have data over a wide range of hardness values such that equations can be developed to predict acutely toxic silver concentrations.

One species, a scud (Gammarus pseudolimnaeus), has data at more than one hardness. However, the range of hardness values were too narrow to predict acute silver toxicity with any confidence over the range of hardnesses found in Wisconsin waters. Consequently this species was not used in calculations of the Final Acute Equation for silver.

Four other species (a rotifer, an unidentified form of midge, bluegill, and carp) have one acute test result reported apiece. Two of more test results must be reported to verify the accuracy of the individual data. Consequently, those species with only single test results were not used in determining the acute criteria for silver.

Table K-1 summarizes the data that was utilized in developing the acute toxicity criterion for silver.

Table K-1. Acute Data Summary. References are taken from the ambient water quality criteria document for silver unless they are footnoted.

Species	Hardness (mg/l)	LC50 (ug/l)	Reference
Daphnia magna (cladoceran)	40	1.5	EPA, 1978
"	48	0.66	Lemke, Manuscript
"	48	0.39	Lemke, Manuscript
"	255	45	Lemke, Manuscript
"	255	49	Lemke, Manuscript
"	54	2.2	Lemke, Manuscript
"	54	2.9	Lemke, Manuscript
"	46	0.9	Lemke, Manuscript
"	46	1.0	Lemke, Manuscript
"	38	1.1	Lemke, Manuscript
"	40	0.64	Lemke, Manuscript
"	75	15.0	Lemke, Manuscript
"	75	8.4	Lemke, Manuscript
"	47	0.25	Chapman, et al. Manuscript
Fathead minnow	48	11	EPA, 1980
"	33	3.9	Goettl & Davies, 1978
"	274	4.8	Goettl & Davies, 1978
"	48	11	Lemke, Manuscript
"	48	12	Lemke, Manuscript
"	48	30	Lemke, Manuscript
"	48	23	Lemke, Manuscript
"	255	150	Lemke, Manuscript
"	255	110	Lemke, Manuscript
"	255	230	Lemke, Manuscript
"	255	270	Lemke, Manuscript
"	54	11	Lemke, Manuscript
"	54	14	Lemke, Manuscript
"	54	20	Lemke, Manuscript
"	46	5.3	Lemke, Manuscript

"	46	3.9	Lemke, Manuscript
"	46	6.7	Lemke, Manuscript
"	46	12	Lemke, Manuscript
"	38	5.8	Lemke, Manuscript
"	40	5.6	Lemke, Manuscript
"	25	12	Lemke, Manuscript
"	39	9.7	Lemke, Manuscript
"	75	6.3	Lemke, Manuscript
"	75	5	Lemke, Manuscript
"	75	10	Lemke, Manuscript
"	75	8.7	Lemke, Manuscript
"	36	7.4	Nebeker, et al. Manuscript
"	38	16	EG&G Bionomics, 1979
"	44.3	10.7	Lima, et al. 1982[1]

[1]Lima, et al. 1982. Acute toxicity of silver to selected fish and invertebrates. Bull. Environ. Contam. Toxicol. 29:184.

Species acute equations (SAE) were determined for Daphnia magna and fathead minnow based on the data listed in Table K-1. Calculations were made to establish the best fit relationship between silver toxicity and hardness among the four basic forms of equations. The best fit relationship of these four equations was found by calculating a geometric mean of the r-factors for all Wisconsin species that had SAE's developed. Table K-2 summarizes the correlation coefficient "r" for each type of equation.

Table K-2. Summary of Correlation Coefficients

Equation Type	Geometric Mean ("r" value)
Hardness vs C[1]	.856
ln hardness vs ln C	.786
Hardness vs ln C	.762
Hardness^2 vs C	.822

[1]where C = acute toxicity concentration (LC50 values) for silver

The best fit relationship from Table K-2, as determined from the geometric mean, was of the form hardness vs C. However, a plot of hardness versus LC50 concentration for silver for Daphnia magna results in acutely toxic concentrations less than zero over a portion of the hardness range (20-400 mg/l) found in Wisconsin waters. Consequently, the second best-fit relationship was utilized of the equation form hardness^2 vs C (or $C = a + b H^2$).

Utilizing the above equation type, acute silver toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. The calculated toxicity values at these endpoint hardnesses, along with additional information used to generate the Final Acute Equation, is summarized in Table K-3.

Table K-3. Calculated Toxicity Values at Endpoint Hardnesses

Species	Number of Data Points	Species Acute Equation (C in ug/l)	C (ug/l) @ Hardness = 20 mg/l	400 mg/l
Daphnia magna (cladoceran)	14	$C = .896 + .00072\ H^2$	1.2	115
Fathead minnow	29	$C = 6.58 + .0021\ H^2$	7.4	343

The lowest values at the endpoint hardnesses of 20 and 400 mg/l were connected by a curve with an equation of the form $C = a + b\ H^2$. *Daphnia magna* has the lowest values at both endpoints. Thus, the acute criterion for silver was based on the cladoceran curve from Table K-3.

$C = .896 + .00072\ H^2$
where C = the acute criterion concentration in ug/l for silver
and H = the average hardness value for Swamp Creek (94 mg/l)

Chronic Criterion

Very little chronic data exists for silver. *Daphnia magna* is the only species with chronic toxicity data available over a wide range of hardness conditions. However, there was no significant relationship between chronic values and hardness for that species. Thus, a geometric mean was calculated of all the chronic values reported for *Daphnia magna.*

The following data listed in Table K-4 was utilized to generate a chronic value for silver.

Table K-4. Chronic Data Summary. The reference for *Daphnia magna* was taken from the ambient water quality criteria document for silver.

Species	Hardness (mg/l)	Chronic Value (ug/l)	Geometric Mean (ug/l)	References
Daphnia magna (cladoceran)	60	2.6	7.9	Nebeker et al. Manuscript
"	75	13		Nebeker et al. Manuscript
"	180	5.2		Nebeker et al. Manuscript
"	48	3.2		Nebeker et al. Manuscript
"	70	15		Nebeker et al. Manuscript
"	70	29		Nebeker et al. Manuscript

The geometric mean of the six available chronic values for *Daphnia magna* is 7.9 ug/l, so the Final Chronic Value (FCV) for silver is also 7.9 ug/l. The acute criterion value for silver is 7.2 ug/l based on a hardness of 94 mg/l for Swamp Creek. In this particular case, the acute criterion value for silver (7.2 ug/l) is more stringent than the chronic value (7.9 ug/l). Therefore, no chronic value was recommended for silver for the discharge to Swamp Creek.

APPENDIX L

WATER QUALITY BASED LIMITS FOR ZINC

Criterion

0.44 mg/l as a daily maximum to protect fish and aquatic life against acute toxicity effects.

0.071 mg/l as a monthly average to protect fish and aquatic life against chronic toxicity effects.

Introduction

Zinc exists in nature in a valence state of +2. Compounds of zinc are soluble in most natural waters, so that zinc is readily transported in the aquatic environment. Zinc forms complexes with a variety of organic and inorganic compounds. Water quality has been shown to affect zinc toxicity. Predicting the toxicity of a given zinc concentration in water is complicated by physical-chemical factors which alter the form of zinc and change its toxicity. However, of the factors affecting zinc toxicity, water hardness is the most significant. Consequently, hardness has been uncorporated into the criterion for the protection of aquatic life.

Acute Criterion

About twenty aquatic life species indigenous to Wisconsin waters have been tested for acute zinc toxicity. Four species have demonstrated relationships between hardness and zinc toxicity over a wide range of hardness values. Equations were developed to predict acutely toxic zinc concentrations for the following species, namely Physa heterostropha (a snail), Daphnia magna (a cladoceran), fathead minnow, and bluegill.

Another species, goldfish, exhibited an acute toxicity relationship with hardness, but the test results were only conducted in soft waters. Since the data was only for soft water conditions, the predictive equation for goldfish was considered only at the low end of the hardness range.

Three species (carp, banded killifish, and pumpkinseed) had acute zinc toxicity data over a narrow range of hardness values. Since the range of hardness values was too narrow to predict acute toxicity with any degree of confidence, these species were not used in the calculation of the Final Acute Equation.

Several other species had only one acute zinc toxicity test result reported or had more than one test result at the same hardness. To verify the accuracy of these data, results must be reported at two or more hardness conditions, preferably from different reference sources. Consequently, these species were not included in the determination of the Final Acute Equation.

Data that were utilized to derive acute water quality criteria for zinc are summarized in Table L-1.

Table L-1. Acute Data Summary. References are taken from the ambient water quality criteria document for zinc unless they are footnoted.

Species	Hardness (mg/l)	LC50 Concentrations (ug/l)	Reference
P. heterostropha (snail)	43	900	Cairns & Scheier, 1958
"	41	600	Cairns & Scheier, 1958
"	163	3,300	Cairns & Scheier, 1958
"	178	4,400	Cairns & Scheier, 1958
"	45	100	Biesinger & Christensen, 1972
"	45	280	Cairns, et al. 1978
"	54	334	Chapman, et al. Manuscript
"	105	525	Chapman, et al. Manuscript
"	196	655	Chapman, et al. Manuscript
"	130	799	Attar & Maly, 1982(1)
Goldfish	20	6440	Pickering & Henderson, 1966
"	45	7500	Cairns, et al. 1969
Fathead minnow	46	600	Benoit & Holcombe, 1978
"	200	2610	Broderius & Smith, 1979
"	203	8400	Brungs, 1969
"	203	10,000	Brungs, 1969
"	203	12,000	Brungs, 1969
"	203	13,000	Brungs, 1969
"	203	9,200	Brungs, 1969(2)
"	45	3,100	Judy & Davies, 1979
"	50	12,500	Mount, 1966
"	50	13,800	Mount, 1966

"	100	18,500	Mount, 1966
"	100	25,000	Mount, 1966
"	200	29,000	Mount, 1966
"	200	35,500	Mount, 1966
"	50	13,700	Mount, 1966
"	50	6,200	Mount, 1966
"	100	12,500	Mount, 1966
"	100	12,500	Mount, 1966
"	200	19,000	Mount, 1966
"	200	13,600	Mount, 1966
"	50	4,700	Mount, 1966
"	50	5,100	Mount, 1966
"	100	6,400	Mount, 1966(3)
"	100	8,100	Mount, 1966
"	100	9,900	Mount, 1966
"	200	8,200	Mount, 1966
"	200	15,500	Mount, 1966
"	20	870	Pickering & Henderson, 1966(4)
"	20	960	Pickering & Henderson, 1966
"	20	780	Pickering & Henderson, 1966
"	360	33,400	Pickering & Henderson, 1966
"	20	2,550	Pickering & Henderson, 1966
"	20	2,330	Pickering & Henderson, 1966
"	20	880	Pickering & Henderson, 1966(4)
"	186	870	Pickering & Vigor, 1965
"	166	7,630	Rachlin & Perimutter, 1968
Bluegill	46	9,900	Cairns, et al. 1971
"	46	12,100	Cairns, et al. 1971
"	46	10,600	Cairns, et al. 1971(5)
"	52	7,450	Cairns & Scheier, 1959
"	52	7,200	Cairns & Scheier, 1959
"	52	6,910	Cairns & Scheier, 1959
"	20	5,460	Pickering & Henderson, 1966
"	20	4,850	Pickering & Henderson, 1966
"	20	5,820	Pickering & Henderson, 1966
"	20	5,370	Pickering & Henderson, 1966
"	360	40,900	Pickering & Henderson, 1966
"	20	6,440	Pickering & Henderson, 1966
"	45	3,840	Cairns & Scheier, 1957
"	45	3,750	Cairns & Scheier, 1957
"	45	3,430	Cairns & Scheier, 1957
"	174	12,390	Cairns & Scheier, 1957
"	174	12,120	Cairns & Scheier, 1957

[(1)]Attar and Maly. 1982. Acute toxicity of cadmium, zinc, and cadmium-zinc mixtures to Daphnia magna. Arch. Environ. Contam. Toxicol. 11:291.

[(2)]Brungs, W.A. 1969. Chronic toxicity of zinc to fathead minnow. Trans. Am. Fish Soc. 98:272.

[(3)]Mount, D.I. 1966. The effect of total hardness and pH on acute toxicity of zinc to fish. Int. Jour. Air Water Pollut. 10:49.

[(4)]Pickering, Q.H. and C. Henderson. 1966. The acute toxicity of some heavy metals to different species of warm water fishes. Air/Water Pollut. 10:453.

[(5)]Cairns, J., Jr., et al. 1971. The effects of pH, solubility and temperature upon the acute toxicity of zinc to bluegill sunfish. Trans. Kans. Acad. Sci. 74:81.

For those species listed in Table L-1, relationships between water hardness and acute zinc toxicity exists, so species acute equations (SAE's) were determined. Calculations were made to establish the best fit relationship between zinc toxicity and hardness among the four basic forms of equations. The best fit relationship of these four equations was found by calculating a geometric mean of the r-factors for those species that had SAE's developed. A summary of the r-factors for these species is listed in Table L-2.

Table L-2. Comparison of Correlation Coefficients

Equation Type	Geometric Mean ("r" value)
Hardness vs C[(1)]	.877
ln hardness vs ln C	.868
Hardness vs ln C	.842
$Hardness^2$ vs C	.857

(1) where C = acute toxicity concentrations (LC50 values) for zinc

The best fit relationship from Table L-2, as determined from the geometric mean, was of the equation form hardness vs C (or C = a +bH). Utilizing this type of equation, acute zinc toxicity values were calculated at sample hardness endpoint values of 20 and 400 mg/l. The calculated toxicity values at these endpoint hardnesses, along with additional information used to generate the Final Acute Equation, is summarized in Table L-3.

Table L-3. Calculated Toxicity Values at Endpoint Hardnesses

Species	Number of Data Points	Species Acute Equation (C in ug/l)	C (ug/l) @ Hardness = 20 mg/l	400 mg/l
P. heterostropha (snail)	4	C = 24.5 H - 300	189	9490
Daphnia magna (cladoceran)	6	C = 110 + 3.54 H	180	1530
Goldfish	2	C = 5592 + 42.4 H	6440	NA
Fathead minnow	36	C = 2911 + 63.2 H	4170	28,200
Bluegill	17	C = 2724 + 90.7 H	4540	39,000

(1) SAE's were applicable only in soft water for goldfish for reasons explained above. Consequently no calculation was made at 400 hardness.

The lowest values at endpoint hardnesses of 20 and 400 mg/l are connected by a curve with an equation of the form C = a + bH. Daphnia magna has the lowest values at both endpoints. Consequently, the acute criterion for zinc can be calculated based on the following cladoceran curve from Table L-3:

C = 110 + 3.54 H
where C = the acute criterion concentration in ug/l for zinc
and H = the average hardness value for Swamp Creek (94 mg/l)

Chronic Criterion

The chronic data base for zinc is significantly smaller compared to the amount of acute data available. One species, Daphnia magna, has chronic zinc toxicity data over a wide range of hardness values, but no relationship is apparent between the two parameters. Thus, a geometric mean of the chronic values was calculated for Daphnia magna to determine a chronically toxic zinc concentration applicable at any hardness.

One other species, fathead minnow, had only one chronic zinc test result reported. Since the results were generated by the same reference source and at the same hardness as the acute test, an acute/chronic (A/C) ratio was calculated for this species. By dividing the species acute equation for fathead minnow by the A/C ratio, an equation was generated that predicted chronically toxic concentrations at any hardness.

No other warmwater species had chronic toxicity test results for zinc. Table L-4 summarizes the data that was utilized in developing chronic toxicity criterion for zinc.

Table L-4. Chronic Data Summary. References are taken from the ambient water quality criteria document for zinc.

Species	Hardness (mg/l)	Chronic Value (ug/l)	Reference
Daphnia magna (cladoceran)	45	85	Biesinger & Christensen, 1972
"	52	136	Chapman et al. Manuscript
"	104	47	Chapman et al. Manuscript
"	211	47	Chapman et al. Manuscript
Fathead minnow	46	106	Benoit & Holcombe, 1978

For Daphnia magna a geometric mean of the four chronic test results in Table L-4 was calculated resulting in a single chronic value (71.1 ug/l). For fathead minnow, an A/C ratio was determined at the same hardness conditions. The A/C ratio was calculated at a hardness of 46 (A/C ratio = 600/106 = 5.66). The acute value was taken from Table L-1 and the chronic value of 106 was obtained from Table L-4. A species chronic equation (SCE) of the form C = a +bH was utilized because that was the form of the SAE with the best-fit. The SAE was divided by the A/C ratio of 5.66 to yield the SCE for fathead minnow.

Utilizing the species chronic equation in the form C = a + bH, chronic zinc toxicity values were calculated at sample hardness endpoint values. Table L-5 summarizes the calculated toxicity values at the endpoint hardnesses for Daphnia magna and fathead minnow.

Table L-5. Calculated Chronic Values at Endpoint Hardnesses

Species	Number of Data Points	Species Chronic Equation (C in ug/l)	C (ug/l) @ Hardness = 20 mg/l	400 mg/l
Daphnia magna (cladoceran)	4	C = 71.1	71.1	71.1
Fathead minnow	1	$C = \frac{2911 + 63.3\,H}{5.66}$	738	4980

The lowest values at the hardness endpoints are for Daphnia magna. Thus, the applicable chronic criterion value for zinc is 71.1 ug/l over the entire range of hardness values (20-400 mg/l).

APPENDIX M

WATER QUALITY BASED LIMITS FOR BOD

Effluent Limits for BOD:

BOD of 20 mg/l (summer) and 40 mg/l (winter) as a weekly average when $Q_E \leq$ 2000 gpm.

BOD of 15 mg/l (summer) and 30 mg/l (winter) as a weekly average when Q_E = 2000-3000 gpm.

Introduction

Biochemical oxygen demand (BOD) is the result of the activity of heterotrophic and autrophic bacteria feeding on the organic material and ammonia and oxidizing it to carbon dioxide, water and nitrate. Factors such as pH, temperature, type of bacteria and type of waste are important in determining how fast the organic material will be stabilized and the amount and rate of oxygen demand exerted. Water quality models attempt to predict dissolved oxygen levels in a stream or river based on the oxygen demand of the wastewater, in addition to other factors.

Rationale for Criteria

In the case of the proposed discharge to Swamp Creek, a simpler, empirical model was used to determine effluent limits for BOD. Studies performed by the Wisconsin Committee on Water Pollution on the Fox, Wisconsin, Oconto, and Flambeau Rivers form the original basis for this model (Lueck, et al. 1957). Further studies on small streams in Wisconsin in the 1970's (Wisconsin Department of Natural Resources, unpublished data) showed that this model could reasonably be applied to municipal waste treatment facilities discharging to small, water quality limited streams such as Swamp Creek. Studies by Velz (1970) on critical BOD-dissolved oxygen relationships also result in almost the exact same loading function to maintain 5 mg/l of oxygen in the stream.

The empirical model, known as the "26 Pound Rule", relates the allowable effluent BOD level to the design flow of the treatment facility and the seven day, ten year low flow of the receiving stream (15 cfs for Swamp Creek).

A major problem with this model is that of applying a generalized formulation to a large number of streams of varying character. Assumptions must be made in order to insure similar initial conditions in all cases. These assumptions are:

1. The ambient dissolved oxygen concentration in the stream is 7 mg/l.

2. Twenty-six pounds of BOD_5 per day per cfs of stream flow will lower the dissolved oxygen concentration in the stream to the 5 mg/l standard.

3. The above relationship is temperature dependent and an appropriate temperature correction is applied.

The 26 Pound Rule can be expressed mathematically as:

$$BOD = 4.8 \left(\frac{(Qs)(.65) + Qe}{Qe}\right) .967^{T-24}$$

where BOD = allowable effluent BOD_5 in mg/l
Qs = seven-day, ten-year low flow in cubic feet per second (15 cfs for Swamp Creek)
Qe = design flow of the discharge in millions of gallons per day (2.88 MGD based an average treatment plant flow of 2000 gpm and 4.32 MGD based on average treatment plant flow of 3000 gpm)
T = critical (maximum) stream temperature in degrees centigrade

The coefficients in this equation are derived as follows:

1. 4.8 is the correction factor for converting pounds per day per cfs to units of mg/l, times the anticipated 2 mg/l drop in dissolved oxygen concentration

2. .65 is the correction factor converting cfs to mgd

3. .967 is the temperature correction factor based on the work of the Wisconsin Committee on Water Pollution. The 26 pound rule was initially calibrated at a temperature of 24°C

Effluent Limits

Effluent limits determined from the 26 Pound Rule are applied as weekly average values in order to be consistent with the use of the seven-day, ten-year low flow in this analysis.

Limits were calculated for both summer and winter conditions based on the difference in stream temperature between the two seasons. For summer conditions 25°C is used in the analysis, while for winter conditions 5°C is utilized. Upon application of the temperature correction factor in the 26 Pound Rule, the above choice of temperatures results in winter BOD_5 limits which are about twice the summer limits.

The weekly average effluent limits for BOD_5 for the proposed Exxon discharge to Swamp Creek (based on an average treatment plant flow of 2000 gpm) are 20 mg/l in the summer months (May 1 through October 31) and 40 mg/l in the winter months (November 1 through April 30). Based on treatment plant flow of between 2000-3000 gpm, the weekly average effluent limits for BOD_5 are 15 mg/l in the summer months and 30 mg/l in the winter months.

References Cited

Lueck, B. F. et al. 1957. Determination of stream purification capacity. Sewage and Industrial Wastes, 29, 9.

Velz, C. J. 1970. Applied stream sanitation. Wiley - Interscience, p. 442.

Wisconsin Department of Natural Resources. Studies on small streams in Wisconsin in the 1970's. Unpublished.

APPENDIX N

WATER QUALITY BASED LIMITS FOR BARIUM

Criterion

5.0 mg/l as a monthly average to protect fish and aquatic life against chronic effects.

Introduction

Barium is an alkaline earth metal that is rapidly decomposed by water to form barium ions. In the aquatic environment, barium ions combine with salts, many of which are soluble. Two of the highly insoluble salts of barium, $BaCO_3$ and $BaSO_4$ are precipitated and removed by absorption or sedimentation. Consequently, barium is not usually present in measurable concentrations in surface waters.

Rationale for Criterion

Barium toxicity to aquatic life is not usually a problem because most surface waters have sufficient quantities of sulfate and/or carbonate to precipitate the barium present in the water as a insoluble non-toxic compound. The literature is lacking in information on the toxicity of soluble barium salts on aquatic organisms. Due to insufficient knowledge about chronic barium toxicity, recommended guidelines have not been established by EPA for this parameter. The Red Book (EPA, 1976) states the following on barium toxicity: "Recognizing that the physical and chemical properties of barium generally will preclude the existence of the toxic soluble form under usual marine and freshwater conditions, a restrictive criteria for aquatic life appears unwarranted."

A review of the EPA Red Book (American Fishery Society, 1979) concluded that a criterion for barium should be provided for both freshwater and marine environments. California Water Quality Criteria (1971) does suggest limits for barium based on very limited data. The recommended criterion for barium contained in that document for the protection of fish and aquatic life is 5.0 mg/l. Studies conducted by Bijan and Deschiens (1956) showed that barium chloride was lethal to aquatic life at the following concentration levels:

Organism	Lethal Concentration (mg/l)
Snail (*Bulinus contortus*)	14.3
Snail (*Planorbis glabratus*)	11.1
Goldfish (*Carassius auratus*)	200
Aquatic plant (*Elodea canadensis*)	10.0

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The limit of 5.0 mg/l established for barium is conservative in its protection for fish and aquatic life. This value (5.0 mg/l) was utilized in calculating the average effluent limits for the proposed discharge to Swamp Creek.

References Cited

American Fisheries Society, 1979. A review of the EPA red book: Quality Criteria for Water.

Bijan, H. and Deschiens, R. 1957. Effect of barium salts on the mollusk vectors of schistosomiasis. Bull. Soc. Pat. exot. 49, 455.

Environmental Protection Agency, 1976. Quality Criteria for Water.

Resources Agency of California, 1971. Water Quality Criteria. State Water Resources Control Board.

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APPENDIX O

WATER QUALITY BASED LIMITS FOR FLUORIDE

Criterion

6.8 mg/l on a monthly average to protect fish and aquatic life against chronic effects.

Introduction

Fluoride is a very reactive element. Consequently, it is not usually found free in nature and is not a common element in natural surface waters. However, fluoride is found as a constituent of salts such as sodium fluoride in the aquatic environment.

Rationale for Criterion

Toxicity effects of fluoride on aquatic life have not been extensively studied. Plants can accumulate fluoride in their tissues through uptake in their root system. Only in extreme cases will the levels be high enough to cause direct damage to plants.

Review of the data in the literature provides some information for determining the toxicity of fluoride to fish and fish food organisms. Neuhold and Sigler (1960) found that sodium fluoride LC50 values ranged from between 7.5 and 9.1 mg/l for juvenile carp in a 20-day exposure. The EPA National Water Quality Laboratory (1975) conducted studies on the effect of sodium fluoride toxicity to fathead minnows. Results showed that the 96-hr LC50 value for the 4-day-old larvae was 80 mg/l and for the 14-week-old fathead minnows the 96-hr LC50 was 200 mg/l. At fluoride concentration levels of 57 mg/l, all the fathead minnows died within 8 weeks. At sodium fluoride concentrations of between 27.5 and 13.6 mg/l, egg production and larvae survival of fathead minnows were significantly reduced due to chronic exposure. This study recommended a criterion value of 6.8 mg/l in soft waters for the protection of fish and aquatic life against chronic toxicity effects of fluoride.

Based on the EPA National Water Quality Laboratory (1975) recommendations, the criterion value required for protection of fish and aquatic life against chronic toxicity effects of fluoride is 6.8 mg/l for Swamp Creek.

References Cited

National Water Quality Laboratory, 1975. Sodium fluoride toxicity to fathead minnows (Pimephales promelas).

Neuhold, J. M. and Sigler, W. F. 1960. Effects of sodium fluoride on carp and rainbow trout. Trans. Amer. Fish Soc. 89: 358-369.

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APPENDIX P

WATER QUALITY BASED LIMITS FOR IRON

Criterion

1.0 mg/l on a monthly average to protect fish and aquatic life against chronic effects.

Introduction

The primary forms of iron in the aquatic environment are ferrous (Fe^{+2}) and ferric (Fe^{+3}) irons. Very little iron is in solution in the water column because any iron salts present (in the form of chlorides, nitrates, or sulfates) usually dissociate. The ferrous or ferric ions then combine with hydroxyl ions to form precipitates.

Rationale for Criterion

The toxicity of iron and iron salts depends on whether the iron is present in the ferrous or ferric state and whether it is in solution or suspension. In waters that are not strongly buffered, addition of a soluble iron salt can lower the pH of the water to a toxic level. In addition, the deposition of iron hydroxides on the gills of fish can cause an irritation and blocking of the respiratory channels (California Water Quality Criteria, 1971). The smothering effects of settled iron precipitates may be particularly detrimental to fish eggs and bottom dwelling fish food organisms (EPA, 1976).

With time, flocs of iron can consolidate to form cement-like materials, thus consolidating bottom gravels into parement-like areas that are unsuitable as spawning sites for nest-building fishes.

Warnick and Bell (1969) obtained 96-hour LC 50 values for iron of 0.32 mg/l for mayflies, stoneflies, and caddisflies, all of which are important fish food organisms. Brandt (1948) found iron toxic to carp at concentrations of 0.9 mg/l when the pH of water was 5.5. In studies conducted by Doudoroff and Katz (1953), iron was found to be lethal to pike (Esox lucius) at concentrations of 1 to 2 mg/l.

The European Inland Fisheries Advisory Commission (1964) recommended that iron concentrations not exceed 1.0 mg/l for the protection of aquatic life. EPA (1976) also recommends a water quality criterion value of 1.0 mg/l for the protection of freshwater aquatic life, based primarily on field observations. Data obtained under laboratory conditions suggest a greater toxicity for iron than that obtained in natural ecosystems. However, the toxicity of this element varies in ambient waters due to the valence state and solubility, both of which are influenced by parameters such as alkalinity, pH, hardness and temperature. Consequently, the criterion value applicable for iron is 1.0 mg/l based on the recommendations from the European Inland Fisheries Advisory Commission (1964) and EPA (1976).

References Cited

Brandt, H. H. 1948. Intensified injurious effects on fish, especially the increased toxic effects produced by a combination of sewage poisons. Beitr. Wass. Abwass. Fishereichemi. 15.

Doudoroff, P. and Katz, M. 1953. Critical review of literature on the toxicity of industrial wastes and their components to fish. II. The metals, as salts. Sew. Ind. Wastes, 25:802.

Environmental Protection Agency, 1976. Quality Criteria for Water.

European Inland Fisheries Advisory Commission, 1964. Water quality criteria for European freshwater fish. Report on finely divided solids and inland fisheries. Tech. Paper I.

Resources Agency of California, 1971. Water Quality Criteria. State Water Resources Control Board.

Warnick, S. L. and Bell H. L. 1969. The acute toxicity of some heavy metals to different species of aquatic insects. Jour. Water Poll. Cont. Fed. 41(2):280.

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APPENDIX Q

WATER QUALITY BASED LIMITS FOR TOTAL DISSOLVED SOLIDS

Effluent limits for total dissolved solids:

1,055 mg/l as a daily maximim when $Q_E \leq$ 2000 gpm.

915 mg/l as a daily maximum when Q_E = 2000-3000 gpm.

Introduction

Total dissolved solids (TDS) is a term associated with freshwater systems and consists of inorganic salts, small amounts of organic matter and dissolved materials (Sawyer, 1960). The principal inorganic anions dissolved in water include the carbonates, chlorides, sulfates, and sodium, potassium, calcium and magnesium. Dissolved solids concentrations can influence the toxicity of heavy metals to fish and other aquatic organisms because of the antagonistic effect of hardness toward metals.

Rationale for Criterion

The main concern of TDS with respect to aquatic life is its effect on an organism's ability to regulate the intake and elimination of water in such a manner so as not to either dilute or concentrate its body fluids. Sudden changes of TDS can have negative impacts by creating an osmotic stress in aquatic organisms. Fish and other aquatic life become acclimated to certain concentrations, and abrupt changes in the dissolved solids can be expected to alter the species composition of an aquatic population.

The literature does not provide substantial documentation for total dissolved solids which must be maintained to sustain an indigenous population of freshwater aquatic life. Specific criteria for sulfates and chlorides necessary for the protection of aquatic life is also lacking in the literature. However, it is necessary that some control be placed on the rate of discharge of TDS into receiving waters.

To prevent osmotic stress in aquatic life caused by abrupt changes in TDS concentrations, the maximum desired TDS change in a stream should not exceed 500 mg/l. The TDS concentration acceptable in the discharge to Swamp Creek was calculated using a mass balance equation as follows:

$$(Q_S)\ (TDS_S) + (Q_E)\ (TDS_E) \leq (Q_S + Q_E)\ (TDS_S + \Delta TDS)$$

where Q_S = upstream flow in Swamp Creek (1/4 Q7,10)
TDS_S = background TDS level in Swamp Creek
Q_E = effluent flow
TDS_E = effluent TDS concentration
TDS = allowable change in TDS in Swamp Creek

Summary

The allowable TDS in the proposed discharge to Swamp Creek was calculated from the mass balance equation above, based on an average and maximum effluent flow from the treatment plant. Using an average flow from the treatment plant of 2000 gpm, the daily maximum TDS allowed in the discharge is 1055 mg/l. If the flow is between 2000-3000 gpm from the treatment plant, then the daily maximum TDS value that applies is 915 mg/l.

Specific criteria for sulfates and chlorides were not established due to a lack of toxicity information on these parameters in the literature. However, these particular anions (sulfates and chlorides) will be controlled as part of TDS limit in the WPDES permit.

References Cited

Sawyer, C. N. 1960. Chemistry for sanitary engineers. McGraw-Hill Book Co., New York.