

WATER QUALITY CRITERIA

General Discussion

Population growth combined with increased per capita use of water, expanding industrial requirements, and the mounting emphasis placed on recreational use of surface water, all contribute to the importance of maximum protection and utilization of Pennsylvania's water resources. Certain constituents may affect a given water use at one concentration and affect another water use at a different concentration. Also, certain characteristics or compounds may be synergistic with each other. For instance, the toxicity to fish of various elements or compounds varies substantially with pH.

Other constituents found in mine drainage are produced by secondary reactions of sulfuric acid with minerals and organic compounds in the mine and along the stream valleys. Such secondary reactions produce concentrations of aluminum, manganese, calcium, sodium, and other constituents in the drainage water. These mine drainage constituents, along with iron and sulfate, are indicators of mine drainage pollution that may persist long after the acid in the drainage has been neutralized.

During the early stages of this report it had been our intention to use as a criteria those set forth on Page 16a, Attachment A, ("Stream Pollution by Coal Mine Drainage in Appalachia") to Appendix C ("The Incidence and Formation of Mine Drainage Pollution in Appalachia") to "Acid Mine Drainage in Appalachia", a report, prepared by the U.S. Army Corps of Engineers in cooperation with the U.S. Dept. of Interior, 1969 shown in Table 5. However, the Department of Environmental Resources determined that the water quality criteria to be used for the identification of acid mine drainage is as follows:

pH - less than 6.0

Acidity - any amount of net acidity; net acidity
equals acidity minus alkalinity.

Total Iron - greater than 7.0 parts per million.

These parameters have been incorporated in this report and are used in making the priority analysis.

General Discussion (contd.)

TABLE 5
CRITERIA SIGNIFICANT IN EVALUATING
AMD POLLUTION IN APPALACHIA

<u>Parameter</u>	<u>Range of Values of Concern</u>	<u>Major Water Uses Protected</u>	<u>Usual Values in Unpolluted Waters in Appalachia</u>
pH	less than 6.0	uses involving aquatic life	6.0 - 9.0
Acidity	sufficient to lower alkalinity below 20 mg/l	uses involving aquatic life	less than alkalinity
Alkalinity	<20 mg/l	uses involving aquatic life	>20mg/l
Sulfates	>250 mg/l	domestic and industrial water supply	<20 mg/l
Hardness	>250 mg/l	domestic and industrial water supply	<150 mg/l
Total Iron	>1.0 mg/l	uses involving aquatic life, domestic and industrial water supply	<0.3 mg/l
Manganese	>1.0 mg/l	uses involving aquatic life, domestic and industrial water supply	<0.05 mg/l
Aluminum	>0.5 mg/l	uses involving aquatic life	absent

Effects of Parameters on Aquatic Biota

Temperature affects the metabolic levels of fish. When excessively high, the respiration rate increases to the point that all available energy is used for respiration instead of being distributed among several processes such as food intake, behavior patterns, etc. Fish become increasingly sluggish, lose equilibrium generally followed by death.

Excessive amounts of acids or alkalies cause a great increase in the mucous layer covering the skin. This adversely affects movements, metabolic levels, respiration rate, and food gathering ability.

Acids and the heavy metals also coagulate mucous within the gill structure. This cuts off the fish's oxygen supply.

Dissolved oxygen is essential for respiration and one of the most critical parameters.

Chemical parameters generally affect fish on the organ level (gills, liver, intestines, etc.). Effects may be on only one organ but usually multiple organs are affected. Additionally, toxic levels and target organs may vary from species to species. Interspecies variation and a multitude of primary and secondary effects preclude discussion of each parameter.

The effects of the parameters on the aquatic ecosystem is equally as important as the effects on the fish themselves. When considering the whole environment, the parameters become critical at every level of organization. While the organization level is generally the most important in fish, the target organization level varies down to the sub-cellular in the primary producers.

While most of these effects are not documented, and enumerating those that are known would be a great task, the following guideline is helpful in obtaining a desirable ecosystem. A less extreme environment has a greater diversity of species; and the greater the species diversity, the greater the stability. Therefore, the less extreme the parameters, the more stable the ecosystem.

Classes of Water Quality

(1) DOMESTIC Criteria for this class are officially established by the U.S. Public Health Service. Parameter values in the subsection titled "Table of Parameters and Classes" are the maximum permitted for this class, with the exception of dissolved oxygen. 2 mg/l. D.O. was selected as minimum concentration to prevent nuisance. It is assumed that parameters not established by USPHS are not critical or are correctable by ordinary water treatment.

(2) INDUSTRIAL Parameter values for this class are not established. The important parameters and values will vary greatly with different industries. Parameter values must be established for specific industries, rather than a general class.

(3) FISH Parameter limits have not all been determined for all game and pan fish. This is due, primarily, to the following reasons: 1) amount of time needed to investigate a parameter, eliminating all other variables. 2) great number of important commercial game and pan fish. 3) many game and pan fish do not lend themselves to laboratory investigations.

Information is scattered through the reference literature and often concerns non-harvestable fish which are more easily studied in the laboratory. Much research has been done in Europe on species not native to North America.

Parameter values in the following subsection

Classes of Water Quality (contd.)

represents general maximum limits which appear to be safe for a number of fish species and food organisms. Many fish species exhibit a very high tolerance to one or a few parameters; however, these exceptions are not included in the class values.

The three fish classes considered are significantly separated by only two parameters, temperature and dissolved oxygen. While there is sometimes great interspecies variation within and between classes, it appears that the same general chemical parameter values apply to all three classes.

Pumpkinseeds (Lepomis gibbous) and bull heads (Ictalurus sop.) are the most tolerant to mine water pollution. pH4 and an acidity of about 100 mg/l. CaCO₃ will probably support populations of these fish.

It is recommended that bio-assays be performed on all species considered for stocking with pilot plant treated water. This is necessary for the following reasons: 1) to determine that individual species are tolerant to class parameter values; 2) may include those parameters not considered in the following subsection; 3) possible synergistic effect of several parameters.

(4) WILDLIFE

This is matter of taste, comfort, and toxicity. The broad range of animals for consideration and research limitations preclude definite criteria. Parameter values for this class are those which are most critical and taken from domestic or fish classes.

Classes of Water Quality (contd.)

(5) NON-
HARVESTABLE
BIOTA

A biota of sorts will develop under most conditions except when parameter values are so extreme they prevent vital cellular life processes.

NOTE:

Low concentrations of heavy metals are very important (such as mercury and lead). These are very toxic and often become highly concentrated in some areas of the food chain. When this happens, predator species (such as man) are subject to lethal doses.

TABLES OF PARAMETERS AND CLASSES

CLASS PARAMETER	DOMESTIC	INDUSTRIAL	COLD WATER SPORT FISH	WARM WATER SPORT FISH	COARSE FISH	WILDLIFE	NON-HARVESTABLE BIOTA
TEMPERATURE	-	-	70	85	87	87	90
COLIFORM MPN (#/100 ml)	USPHS criteria varying upon spl size, spl freq., & sequence of positive results.		70	70	70	70	-
CONDUCTIVITY mho $\times 10^{-6}$	-	-	400	400	400	400	-
SUSPENDED SOLIDS mg/l	-	-	20000	20000	20000	-	-
DISSOLVED SOLIDS mg/l	2000	-	-	-	-	-	-
DISSOLVED OXYGEN mg/l	2	2	6	5	3	2	2
pH	6.5	-	6.0	6.0	6.0	6.0	-
ACIDITY mg/l CaCO_3	20	-	50	50	50	50	-
ALKALINITY M.O. mg/l	-	-	180	180	180	180	-
HARDNESS mg/l	-	-	50	50	50	50	-
ALUMINUM mg/l	-	-	5	5	5	0.07	-
CALCIUM mg/l	-	-	300	300	300	-	-
IRON mg/l	0.3	-	71.0	71.0	71.0	0.3	-
MAGNESIUM mg/l	-	-	.05	1	1	-	-
MANGANESE mg/l	0.05	-	50	50	50	-	-
SULFATE mg/l	250	-	400	400	400	-	-

Testing Methods and Discussion

Once the samples were collected, they were shipped to the Seewald Laboratories in Williamsport, Pennsylvania via Greyhound Bus. On March 1, 1972, we were directed by the Department of Environmental Resources to submit all further samples to Microbac Laboratories in Pittsburgh, Pennsylvania. Until this time no analysis for ferrous iron had been made on the samples.

In September, 1972, Microbac was directed to revise their sampling procedure as set out on page 438 of Standard Methods, 12th Edition; in that all samples analyzed for acidity from the first of October, 1972, were to be analyzed to hot titration.

This, of course, left us with two separate values that could not be correlated, and, as such, we have noted them separately in this report. A listing of the laboratory testing methods are discussed and shown herein.

In January, 1973, our firm was directed to submit all samples to Gwin, Dobson and Foreman, Inc. located in Altoona, Pennsylvania.

We were also directed to utilize two bottles for the collection of samples. One 16 oz. bottle for pH, acidity, alkalinity, sulfate and hardness, and one 8 oz. bottle for the ferrous and total iron which was to be acidified by adding 10 drops of concentrated Hydrochloric acid (HCL) to the sample bottle.

After a discussion with the Department of Environmental Resources (D.E.R.) concerning the preliminary watershed study report, it was determined that our sampling had progressed to a point where the continuation of hot titration testing of the acid would be a hindrance in analyzing the priorities. It was therefore established that starting with the sampling January, 1973 acid sampling would be analyzed without bringing the sample to a boiling point.

It was also determined, at this meeting, that the laboratory testing for hardness would be eliminated. The following is the method of testing used by each of

Testing Method and Discussion (contd.)

the required parameters.

1. pH

Method - Glass electrode pH meter

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 276.

Discussion - pH is the negative common logarithm of the hydrogen-ion concentration. The pH of most natural waters falls within the range of 4 to 9. The majority of waters are slightly basic due to the presents of carbonate and bicarbonate. pH enters into the calculations of carbonate, bicarbonate and carbon dioxide, as well as of the corrosion or stability index, and into the control of water treatment processes.

2a. Acidity

Method - Phenolphthalein Titration

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 50.

Discussion - The carbonate and bicarbonate can be estimated by titrating the alkalinity with standard acid to the bicarbonate equivalence point of pH 8.3 and then to the carbonic acid equivalence point in the pH range of 4 to 5.

A fading and impermanent endpoint characterizes the phenolphthalein acidity titration performed at room temperature on a sample containing iron and aluminum sulfate.

2b. Hot Acidity

Method - Potentiometric titration to pH 8.3

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 370 (modified).

Testing Methods and Discussion (contd.)

Discussion - The hot acidity test as modified consists of preliminary oxidation with 2 ml of 30% hydrogen peroxide solution followed by boiling for not less than two minutes and titration while at 90°C or higher to pH 8.3, using a thermally compensated pH meter or an uncompensated meter standardized with an appropriate buffer at 90°C to 95°C. Preoxidation and boiling are used to insure complete hydrolysis of the acid producing salts. Boiling, however, also drives off carbon dioxide. The method, therefore, determines the acidity due to free mineral acids and acid salts, but does not measure the contribution to acidity of carbon dioxide. Acidity is reported as milligrams per liter of calcium carbonate (CaCO₃). The molecular weight ratio CaCO₃/H₂SO₄ is 1.02.

2c. Reported as Net Acidity

Discussion - Net acidity is the acidity that is present in excess of alkalinity.

3. Net Alkalinity

Method - Potentiometric titration to pH 4.5.

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 52.

Discussion - The alkalinity of a water is the capacity of that water to neutralize a standard acid. When alkalinity is present in excess of acidity there is a net alkalinity. In most waters of Appalachia alkalinity is essentially bicarbonate and/or carbonate in origin.

4. Iron (total)

Method - Phenanthroline Method

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 189.

Testing Methods and Discussion (contd.)

Discussion - Mine drainage generally contains iron in both ferrous and ferric states. At pH values less than 3, ferric and ferrous iron are both in solution and the hydrolyzable acid salts of both forms can contribute to acidity. At pH values above 3, ferric iron is found in solution only as part of complexes formed with organic chelates, phosphates, and other anions. Acid salts of ferrous iron provide the contribution to acidity. Unpolluted streams in Appalachia have iron concentrations of less than 0.3 mg/l. Mine drainage influence may raise iron concentration in excess of 100 mg/l.

5. Ferrous iron

Method - Same as 4 (Total Iron) except deletion of 1 ml of sodium sulfite solution.

Discussion - Ferrous iron is rapidly oxidized to ferric iron after mine drainage enters an aerated stream, therefore high concentrations of ferrous iron generally are not found very far downstream from the last mine drainage source.

6a. Sulfate

Method - Turbidimetric method. The photometer used is a Coleman Junior.

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 334.

Discussion - A mole of sulfate accompanies each mole of sulfuric acid and sulfate is, therefore an excellent indicator of the amount of mine drainage acidity formed. This is particularly true because calcium sulfate, the most common sulfate salt, is relatively soluble. Unpolluted waters in Appalachia have been observed

Testing Methods and Discussion (contd.)

to have concentrations of generally less than 20 mg/l; polluted waters frequently have concentrations of several hundred milligrams per liter.

6b. Sulfate

Method - Ion Exchange - Titrimetric method

Reference - Environmental Science and Technology, article by George W. Dollman.

Discussion - The method involves evaporation of the column effluent under conditions which drive off all ordinary acids while quantitatively retaining all the sulfuric acids. The result is then determined by titration with a standard base.

The sample is placed in an oven for two hours at 75°C to eliminate the water and volatile acids.

Three categories of organics have been considered: filterable sediment (as in sewage), oils and greases, and water-soluble organics, partially or wholly oxidizable by bromine. Elimination of these sources is by filtration or benzene extraction and boiling with bromine water.

Sulfate in an aqueous media can be accurately determined as sulfuric acid after passage of the sample through a hydrogen-form cation exchange resin

7. Manganese

Method - Persulfate method

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 206.

Discussion - Concentrations of manganese in unpolluted streams do not usually exceed 0.05 mg/l. This indicator is usually associated with mine drain-

Testing Methods and Discussion (contd.)

age pollution. Concentrations in the order of 5 mg/l to 20 mg/l are not uncommon in mine drainage.

8. Aluminum

Method - Aluminum reagent

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 57.

Discussion - High concentrations of aluminum are usually found as a result of the leaching of deposits of clays or clayish soils by acid mine waters.

9. Hardness

Method - EDTA Titration

Reference - Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971, p. 179.

Discussion - Hardness is defined as a characteristic of water which represents the total concentration of the calcium and magnesium ions expressed as calcium carbonate. Other hardness producing ions commonly present in significant amounts in mine drainage are iron, manganese, and aluminum.