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 characeristics 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 others 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.

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 by the ARC, prepared by the U.S. Army Corps of Engineers in cooperation with the U.S. Dept. of Interior, 1969 shown in Table 1, could be used. 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 1

CRITERIA SIGNIFICANT IN EVALUATING

AMD POLLUTION IN APPALACHIA

<u>Parameter</u>	Range of Values of Concern	Major Water Uses(s) Protected	Usual Values in Unpolluted Waters in Appalachia
рН	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	>20 mg/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 aqua tic 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. 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 fish themselves. When considering the whole environment, the parameters become critical at every level of organization. While the organ 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, except dissolved oxygen. 2 mg/l. D.O. 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.

Classes of Water Quality (contd.)

Parameter values in the following sub-section 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 inter-species variation within and between classes, it appears that the same general chemical parameter values apply to all three classes.

Pumpkinseeds (Lepomis qibbosus) and bull heads (Ictalorus spp.) are the most tolerant to mine water pollution. pH 4.0 and an acidity of about 100 mg/l CaC03 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 sub-section; 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, etc.) are subject to lethal doses.

TABLES OF PARAMETERS AND CLASSES

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CLASS	DOMESTIC	INDUSTRIAL	COLD WATER SPORT FISH	WARM WATER SPORT FISH	COARSE FISH	WILDLIFE	NON-HARVESTABLE BIOTA
PARAMETER TEMPERATURE	L-J		70	85	87°	87	90 🐇
SUSPENDED SOLIDS mg/1			20,000	20,000	20,000		\$4 \$2 \$2
DISSOLVED SOLIDS mg/l	2000				1.		
DISSOLVED OXYGEN mg/l	2	2	6	5	3	2	2
рН	6.5		60	6.0	6.0	6.0	
ACIDITY mg/1 CaCO ₃	20			50 150	50	50	
ALKALINITY M.O. mg/l			180	180	180	180	3 .4.
HARDNESS mg/l			.50	50	50	50), i = 1
CARBON DIOXIDE: mg/l			20	20	20		
ALUMINIM mg/l			5	5	. 5	0.07	
CALCIUM mg/l			300	300	300		
CHLORIDE mg/1	250		1500	1500	1500		
COD mg/l			100	100	100		
FLUORIDE mg/1	1.2		1.5	1.5	1.5		
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TABLE 2
TABLES OF PARAMETERS AND CLASSES (contd.)

PARAMETER	DOMESTIC	INDUSTRIAL	COLD WATER SPORT FISH	WARM WATER SPORT FISH	COARSE FISH	WILDLIFE	NON-HARVESTABLE
IRON mg / l	0.3		71.0	71.0	71.0	0.3	·
MAGNESIUM mg/l			• 05	1.	1		
MAGNGANESE mg/l	0.05		50	50	50		
NITRATE mg/1	45		• 1	•1			
NITROGEN mg/l			1.3	1.3	1.3		
PHOSPHATE mg/l			• 5	•5	•5		
PHOSPHORUS mg / l			0.04	0.04	0.04		
POTASSIUM mg/1			50	50	50		
SODIUM mg/1			500	500	500		
SULFATE mg/l	250		400	400	400		

Testing Methods and Discussion

Once the samples were collected, they were shipped via Greyhound Bus to Gwin, Dobson and Foreman, Inc. located in Altoona, Pennsylvania for analysis. In September 1973 We were directed by the Department of Environmental Resources to submit all further samples to Buchart-Horn Laboratories in York, Pennsylvania.

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

The following methods of testing were used by each of the laboratories.

I. 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.

2. 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 hydrolisis 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.

3. 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 - <u>Standard Methods for the Examination of Water</u> and Wastewater, Thirteenth Edition, 1971, p. 189.

Testing Methods and Discussion (contd.)

Discussion - Mine drainage generally contains iron n 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 are not, generally, found very far downstream from the last mine drainage source.

6. Sulfate

Method - Ion Exchange - Titremetric 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

Testing Methods and Discussion (contd.)

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 hydrogenform cation exchange resin.