8. WATER CHEMISTRY AND PHYSICS

INTRODUCTION

A great deal can be learned about a lake by examining the chemistry of its waters. Dissolved or suspended in the water are several elements, ions, and organic substances which can serve to characterize and classify the water. Knowing a lake's chemistry, a limnologist can deduce much about that lake without ever having seen it. Water chemistry is usually a part of the hydrographic study of a lake, which also includes physical parameters such as depth, shoreline development, surface area, and volume. The physical form of a lake greatly influences its chemical characteristics.

Pure water is biologically sterile. A lake's fertility is determined mainly by the same substances which create fertility in soils. In fact, a lake's fertility is usually correlated with the fertility of the soils in its watershed. Rainwater and groundwater wash materials from the soil downstream into lakes; therefore what is in a soil is also in the lake below. Clear, infertile, oligotrophic lakes are found in basins of insoluble bedrock, which are poor in carbonates and have little soil covering. Eutrophic lakes are usually found in watersheds where deep, fertile soils have been formed from carbonate rocks such as the limestones and dolomites of the Winona area. Man's activities can exert a strong influence upon a lake's fertility, generally by the addition of nutrients, making the lake more fertile. Sewage, even treated sewage effluent, and the runoff from agricultural lands are rich sources of nutrients which may accumulate to excessive levels in lakes, causing their eutrophication. The storm sewers of the city of Winona are an important source of nutrients entering Lake Winona.

Nitrogen exists in several forms useful to living organisms. Only plants and some bacteria take up nitrogen directly from the environment. Plants can absorb nitrogen in the form of ammonia (NH_3), nitrate (NO_3), and nitrite (NO_2). Nitrogen is abundant in the atmosphere (80%) in the form of N_2, and is also found in the protein molecules of living and dead organisms. Certain forms of bacteria and blue-green algae convert atmospheric nitrogen (N_2) to nitrate (NO_3) in a biologically important process called nitrogen fixation. Other bacteria decompose the bodies of dead organisms, converting the nitrogen in their proteins to ammonia, which is released into the water. Ammonia readily oxidizes to nitrite which easily oxidizes to nitrate, thereby recycling the nitrogen for use by living organisms. Ammonia is also produced as a waste product of the metabolic processes of living organisms, and is excreted into the environment.

Ammonia, nitrite, and nitrate are very soluble in water, and are readily taken up by active plants, so that dissolved nitrogen levels seldom reach high concentrations where plants thrive. Concentrations are highest in winter, when plant growth is least, and decomposing remains of the previous year's growth add nitrogen to the water. Nitrogen levels usually fall rapidly in spring and early summer when plant growth is maximum and nitrogen is removed from solution. The total nitrogen in a lake includes all these forms. The nitrogen contained in protein molecules may be called "organic N" or "Kjeldahl N". The other forms are all soluble in water and may be reported separately as N, NO_3, NH_3, or simply combined into a "soluble nitrogen" concentration. Since nitrate is usually much higher than nitrite or ammonia, sometimes only nitrate concentration is given. "Total nitrogen" means the sum of the soluble nitrogen and organic nitrogen, or the overall nitrogen fertility of the water. In natural, unpolluted waters, total N ranges from 0.1 to 3.0 ppm. Higher levels usually indicate the addition of nitrogen through man's activities, such as sewage input, agricultural runoff, or, as in Lake Winona, storm sewer runoff from city streets, lawns, and roofs. Polluted wells have been found with nitrate levels in excess of 50 ppm.

Plants require a variety of essential nutrients, and whichever one is used up first is called the limiting nutrient. In land ecosystems this is often nitrogen, but in surface waters the limiting nutrient is often phosphorus. It is used by living organisms as the phosphate ion, (PO_4). Phosphate is even more soluble than nitrogen, and is absorbed by plants directly from the water, so phosphate levels in surface waters are usually low, reaching a peak in winter, like nitrates, when plant growth is least. A little phosphate goes a long way, and levels in natural, unpolluted waters range from 0.002 to 0.1 ppm. Dissolved phosphates are very difficult to remove from water because of their high solubility, and much of man's effort to control eutrophication by limiting nutrients involves various methods of causing phosphates to precipitate from the water by the addition of various chemicals such as alum ($Al_2(SO_4)_3$) and certain iron compounds. This has been tried in lakes themselves, as well as wastewaters, and becomes quite expensive as removal of 80% or more of the phosphates is attempted.

The chemical behavior of phosphates in water is quite complicated. Phosphates are absorbed by various suspended and bottom sediments, are complexed with various organic molecules and react with certain ions like aluminum and iron under certain conditions. Phosphate solubility increases with decreasing dissolved oxygen.

Phosphate analyses are also complex. Inorganic, water-soluble phosphate is called orthophosphate. This is the phosphate available for plants, including algae. Total phosphate is the orthophosphate plus the phosphate already contained in the bodies of living and dead organisms. To measure total phosphate, a sample is treated with heat and acid to convert organic phosphates to orthophosphates. Total phosphate minus orthophosphate gives organic phosphate. One must be careful when using or presenting phosphorus data to distinguish between phosphate (PO_4) and phosphorus (P).

Alkalinity refers to a water's ability to neutralize acid, and may be taken to mean the amount of dissolved mineral salts in the water. A number of ions may contribute to total alkalinity, but the major components of alkalinity in Minnesota waters are calcium and magnesium carbonates and sulfates. Determinations of alkalinity are measured by acid titration, and are often expressed "as calcium carbonate".

Waters with less than 20 ppm total alkalinity are very soft and unproductive. Waters with 100 ppm total alkalinity or more are considered hard, and are usually quite productive. Minnesota's best waterfowl lakes are found in the western prairies and are high in both carbonate and sulfate ions. Alkalinity in Minnesota lakes ranges up to about 1000 ppm. Lakes whose basins lie on limestone and dolomite derived soils such as those in the Winona area are high in total alkalinity and productivity. Seawater contains about 35,000 ppm total alkalinity.

A measurement sometimes made instead of total alkalinity is conductivity. Conductivity is measured with an electronic instrument, and the results are convertible to total alkalinity. The conductivity of a sample of water increases as ions are added to the water. Alkalinity is indicative of a water's productivity principally because the carbonate and bicarbonate dissolved in the water are the plants' source of carbon dioxide for use in photosynthesis.

Another measurement of conductivity and alkalinity is called total dissolved solids, or TDS. TDS is determined by evaporating a sample and weighing the residue.

By far the most important factor affecting the quality of water is dissolved oxygen, or DO. DO affects all forms of life in the water; it determines whether aerobic or anaerobic decomposition and respiration will occur; it influences most of the other chemical constituents in the water. DO concentrations range from 0.0 to almost 15.0 ppm, and solubility is limited by temperature. The solubility of oxygen, like other gases, increases as temperature decreases, and at 0 C water is saturated with 14.6 ppm. Supersaturated conditions sometimes occur, and measurements as high as 20 ppm may be encountered.

Oxygen enters water from two principal sources; the atmosphere and photosynthetic green plants. Under still conditions, the diffusion of oxygen into water from the atmosphere is very slow, and confined to a very thin surface layer. By the action of wind and waves, water and air are stirred and mixed; much oxygen is dissolved in this way. Oxygen also dissolves into the water directly from photosynthesizing plant cells, and on a sunny day this source may exceed the atmosphere in oxygen input. During the winter, when ice prevents oxygen from the atmosphere reaching the water, photosynthesis is the only source of DO in a lake.

DO levels are not uniform throughout a lake. DO levels are affected by the thermal stratification which occurs in many lakes during the summer. Layers of water at different temperatures separate and do not mix, with warmer water floating on colder water. During stratification, oxygen near the surface remains there and is not distributed to the depths of the lake. Thus, the deeper, colder layer of a eutrophic lake (the hypolimnion) will often be without oxygen. The upper layer (the epilimnion) will receive oxygen from the air and from photosynthesis, but this oxygen will not reach the hypolimnion because there is no mixing between the two. This creates in effect, two lakes within one basin, with very different chemical characteristics. Many ions, especially metals and also including sulfur and nitrogen compounds, are readily oxidized when oxygen is present. The oxidized forms tend to be less soluble than the reduced ions, precipitating from solution and settling to the bottom. In other words, many ions are soluble only in water which is very low in DO. When oxygen is present, the ions are removed from the solution. Sulfur oxidizes in aerobic conditions, becoming sulfate ion (SO_4). In anaerobic conditions it becomes hydrogen sulfide (H_2S), poisonous to many organisms. Ammonia is also poisonous to most animals; in the presence of oxygen it oxidizes to nitrate, a plant nutrient. Phosphates, a problem in excessively fertile lakes, are removed from solution by adsorption onto sediments when DO levels are high. Metal ions tend to be significantly soluble only in waters depleted of oxygen, such as the water in the hypolimnion of a thermally stratified, eutrophic lake.

In a stratified lake, a substance may be rendered insoluble in the oxygenated waters near the surface, settle toward the bottom, and return to solution in the anoxic waters near the bottom. One of the major lake reclamation techniques in use today, and described elsewhere in this document as used in Lake Winona, is the mechanical mixing and aeration of lake waters, eliminating stratification and the anoxic bottom conditions associated with it.

Oxygen is necessary for the respiration of most living organisms, including all animals. Warm water fishes can tolerate DO levels down to about 5.0 ppm, and lower levels for short periods, especially if water temperatures are low and respiration slow. Cold water fishes like trout require at least 6.0 ppm to live. Individual species of fish have lower tolerances; some species of rough fish can survive lower levels than game fish. Bullheads, for example, can tolerate DO as low as 1.0 ppm, and can gulp oxygen from the air. Air is much richer in oxygen than the most highly oxygenated water.

Temperature - DO profiles are a common method of evaluating a lake's suitability for various forms of life. Temperature and DO are measured at regular intervals from surface to bottom and presented in a graph or table. Such a profile reveals if and where stratification occurs, and how much of the lake can support animal life. A lake can be huge in water volume, but if it is very deep and the lower layers are without oxygen, the fish and zooplankton will be confined to the upper layer, drastically reducing the 'size' of the lake.

When organic material decomposes it oxidizes, consuming oxygen. If too much material decomposes too fast, it may consume enough oxygen to render the water unfit for fish. This potential for oxygen consumption is measured as BOD (biochemical oxygen demand). It is a measure of how much oxygen is consumed in a certain period of time by decomposition of non-living material. BOD is an indicator of the non-living organic matter content of water and high levels may be a sign of pollution, such as by sewage or other wastewaters. Another high BOD situation may occur in late summer in highly fertile lakes when large crops of algae and rooted plants reach the end of their life cycles and die, creating a large amount of organic matter which then begins to decompose rapidly in the warm water. This situation may result in a 'summerkill' of fish if the DO in the lake is reduced below what they can tolerate.

Turbidity is a measure of the cloudiness of the water resulting from suspended particles of all kinds. These include plankton, as well as suspended sediments. A simple and common method of measuring turbidity is with a Secchi disc. A light colored disc is lowered into the water to the point where it just disappears from sight. This depth is one half the depth to which light penetrates, because light has to travel to the disc and back to the eye to be seen.

METHODOLOGY

Winona State University students have been monitoring the chemistry and physics of Lake Winona, Gilmore Creek, Boller Lake and springs within the watershed for about 20 years. Some of their work has been done as field studies in limnology classes and as special problems in biology, but much has been done on a volunteer basis. Monitoring methodology has become increasingly sophisticated as the years have passed. Dissolved oxygen and temperature measurements are made with Yellow Springs Instrument Co. meters which are calibrated before each use. In winter when D.O. levels are very low, high sensitivity membranes are used and the meters are calibrated in deoxygenated ice water. Nitrogen and phosphorus determinations are made with Hach Co. prepackaged chemicals. Readings are then made via a calibrated Coleman Jr. spectrophotometer. Conductivity is measured with a P-H TAMM meter. Turbidity is measured with a Hach turbidometer. Hardness is determined by titration with Hach chemicals. Coliform bacteria testing is done with Millipore procedures. Student workers are divided into teams so that replicate sets of data make it easy to detect errors.

Because the compiled chemical and physical data are voluminous and may be of interest mainly to specialists, it is included as Appendix 8.