

## CHAPTER 2. LITERATURE REVIEW

### Reservoir Eutrophication

Reservoirs are water bodies created specifically for the purposes of water management. They differ in many significant ways from natural lakes. Studies have shown, however, that reservoirs have many functional similarities to natural lakes. Furthermore, since much of our limnological understanding stems from the studies of natural lakes (Wetzel, 2001), it is reasonable to look at some studies on natural lakes in order to understand the processes of eutrophication in reservoirs.

The word “eutrophication” comes from the Greek word “eutrophos” that means nutrient-rich. By and large, a eutrophic lake is a lake with high production of phytoplankton, which is normally associated with high concentrations of nutrients—mainly phosphorus and nitrogen (Wetzel, 2001). Algae are microscopic single-cell plants, hence they require the same nutrients as do garden flowers and lawns. In the growing season, if they are richly fertilized, they thrive. A common characteristic of a eutrophic lake is a high number of green algae covering the water surface, thereby restricting the penetration of sunlight, and resulting in the limitation of photosynthesis, which, in turn, restricts the growth of other algae and rooted aquatic plants to shallow depths. Moreover, the algae often grow so fast that water fleas (the basic food of all larval fishes) cannot consume them at a sufficiently high rate to insure that their numbers are reduced significantly. Thus, a considerable amount die untouched. As a result, the ecology of the lake may become unbalanced. For example, the decomposition of the dead algae depletes the oxygen in the deep, cold water. Hydrogen sulfide could accumulate to poisonous levels as a result of further anaerobic decomposition of the dead algae. Noble fishes, such as whitefish, trout, and cisco, cannot survive under a condition of low oxygen and high hydrogen sulfide concentrations. Thus, they will die (Hassler, 1969). Furthermore, proliferation of algae also deteriorates quality of raw water for drinking water production. Decomposition products of dead algae and extracellular products of live algae may have a characteristically strong taste and odor, so a large amount of algae may cause raw water to have an unpleasant taste and odor. This would increase the operation cost of the treatment plant since their removal by any physical or chemical process is fairly expensive. Algal cells may also

clog the filter. This would decrease the length of time it may be used before backwashing is required (Fruh, 1967).

### **Nutrient Limitation**

A toxin that hinders or limits growth is not considered a limiting factor. A limiting factor is a nutrient or another growth or metabolism requirement that is inadequately available. If demand becomes greater than the supply of such a required element, it limits and controls growth or production regardless of the quantity of any other necessary elements present. When the limiting element is added to such a system, it will cause an increase in growth. In the case of algal growth, phosphorus, nitrogen, or silicon is usually the limiting factor (Cole, 1994). The single-limiting-factor concept is a simplified way to approach a complex system. Ultimately, one needs to consider the interactions of several factors in a given system. It has been found that availability or concentration of another substance could affect the way a deficient substance limits growth or production. For example, the zinc requirement of some plants lessens when they are in the shade and increases in sunlight. Therefore, the degree of limitation of zinc for these plants is less in the shade (Odum, 1959). Nevertheless, this literature review will not further explore the concept of multifactor interactions since the control of eutrophication presented here is based on the concept of single limitation.

Phosphorus has often been found to be the limiting nutrient in lakes. Shindler (1973) conducted whole lake experiments in northwestern Ontario to show that phosphorus limits the growth of undesirable algae, and that phosphorus removal alone can overcome eutrophication problems. He found that the addition of phosphorus and nitrate to a test lake caused rapid algal growth. Addition of phosphate ( $\text{PO}_4^-$ ), ammonia, and sucrose created the same result. However, the reduction in algal growth was almost immediate when phosphorus was removed from the nutrients added. When he added equal amounts of nitrate and sucrose to a lake that was divided into two basins and added phosphorus to one of the basins, only the phosphorus-enriched basin exhibited signs of accelerated algal growth. A similar result was obtained in Wahnbach Reservoir, where eliminating phosphorus without simultaneous elimination of nitrogen (the average N-concentration of all the tributaries was 5 mg/l) changed the trophic state of the reservoir from eutrophic to mesotrophic to oligotrophic within 3 years.

The predominating blue green algae disappeared and diatoms grew again every spring. The Secchi-depth increased to an average of 6 m annually (Bernhardt and Clasen, 1982).

### **Eutrophication Prevention and Reservoir Restoration**

The nutrient enrichment of lakes comes mainly from human activities, such as population growth, industrial activity, intensified agriculture, river basin development, recreational use of waters, and domestic and industrial exploitation of shore properties. Such enrichment results in undesirable changes in plant and animal life, and diminishes the aesthetic qualities and economic value of the water body. Although the diversion of sewage around lakes and into streams does not cause as much damage to the streams (flowing water does not favor the attachment of algae and rooted aquatic plants), it places a burden on the receiving water downstream. Many large streams in modern times have dams for impounding water. If an impounded water used for water supply is eutrophic, the cost for purifying and controlling its taste and odor will increase. Therefore the permissible nutrient input to water bodies and streams must be controlled (Hassler, 1969).

Generally, the control of eutrophication in lakes has been limited to the control of phosphorus loading, because of the role of phosphorus as the main limiting nutrient. In addition, the phosphorus-controlling strategy has often been found to be a cost-effective technique. Bernhardt (1981) stated that nitrogen does not play any particular part in creating a certain trophic state if P is the limiting factor. He believed that lake and reservoir trophic state could be predicted from ambient phosphorus concentrations only. Bernhardt also concluded that a desired trophic state could be reached by controlling P-input to a lake or reservoir. Bernhardt further described several ways to reduce phosphorus loads to lakes by removing it from the effluents of urban sewage treatment plants by chemical precipitation, adsorption of P-compounds on alumina, seepage trenches, phosphorus elimination plants, and biological sewage treatment.

The objective of the present study was not, however, to investigate eutrophication prevention and restoration by controlling phosphorus inputs of water bodies from an external source, but to investigate prevention and restoration by the phosphorus adsorption capacity of sediments. The important role of phosphorus adsorption capacity of sediments in lake restoration has long been recognized. Fitzgerald (1970) found that phosphorus-limited

*Selenastrum* and *Cladophora sp.* responded with increased growth to changes in extractable PO<sub>4</sub>-P as small as 0.02 mg/L in solution. However, when lake mud was present, these same species did not respond to the addition of as much as 2 mg/L PO<sub>4</sub>-P under aerobic conditions. A mass of 0.4 g of mud was found to adsorb about 0.05 mg PO<sub>4</sub>-P in less than 30 minutes, resulting in his conclusion that lake muds under aerobic conditions may be used to remove phosphorus from the water column. A recent example, a moderate reduction of the external phosphorus load (45-50 %) of Lake Balaton, Hungary, resulted in a drastic improvement of water quality. The unexpected improvement was attributed to the rapid immobilization of the mobile phosphorus at the sediment surface (Istvanovics and Somlyódy, 2001).

The sediments could act as a phosphorus store, though, and if the sediment-bound phosphorus is released back to the water columns, the reduction of external phosphorus input might not reduce concentrations sufficiently to mitigate eutrophication problems (Higgins *et al.*, 1976). When lakes and reservoirs stratify in summer or winter, the hypolimnetic waters become thermally isolated from the layers in contact with the atmosphere, thereby limiting the amount of oxygen that is available to support respiration. Once oxygen is depleted, and if no other inorganic electron acceptors are present, the hypolimnion may become anaerobic. Under this condition, phosphorus may be released back to the overlying water (Wetzel, 2001). For example, it was found that the reduction of the annual phosphorus load to Lake Finjasjon, Sweden from 65 tons to 5 tons by removal from wastewater could not help improve the trophic state of the lake. The problem was ultimately identified to stem from phosphorus-leaking black sediments (Annadotter *et al.*, 1999).

There are several ways to cope with this problem. The failure to recover Lake Finjasjon was solved by a combination of a constructed wetland and food-web manipulation program (Annadotter *et al.*, 1999). Fruh (1967), citing Knight (1965) stated that the hypolimnetic waters rich with phosphorus released from the sediments could be removed before fall or spring circulations to prevent algal blooms. This method may, however, impair water quality and waste assimilative capacity of downstream waters. Citing Bryan (1965), Fruh (1967) stated that, for generally small and relatively shallow lakes, destroying the thermal stratification or improving the hypolimnetic oxygen condition with aeration could prevent the phosphorus release from the sediments. Higgins *et al.* (1976) applied fly ash, which is an

industrial waste material, over the sediment surface of Lake Charles East, TX as a barrier between the nutrient rich sediment and the overlying water. The fly ash effectively sealed the sediment surface, preventing the release of phosphorus. Simple removal of the nutrient rich sediment from the water bodies, while costly, could also solve the problem. Bengtsson *et al.* (1975) successfully restored lake Trummen in the South Swedish Uplands by sediment suction dredging and the restitution of shoreline. The nitrogen and phosphorus concentrations in the lake decreased drastically and the role of sediment in recycling nutrients was minimized.

Nitrate is the only compound of nitrogen that has been found to occur in water supplies at sufficiently high concentrations to create a health hazard (McCarty, 1966). As a species with the potential to change the oxidation-reduction balance of an aquatic system, it has been studied as another method to control phosphorus release from sediments. Currently, the MCL of nitrate is 10 mg/l as N (USEPA, 2001). The standard was last reviewed by the National Research Council (NRC, 1995) consistent with the requirement for periodic review of U.S. EPA standards to ensure continuing protection of public health. The NRC concluded that the current standard is adequate to protect human health. Furthermore, the NRC agreed with the 1990 U.S. EPA conclusion that there is no convincing evidence that nitrate or nitrite is associated with any adverse effect other than methemoglobinemia. Bruning-Fann and Kaneene (1993), citing Bodansky (1951), Greenberg (1943), and Marshall (1945), stated that the nitrate consumed with food or drink does not directly cause methemoglobinemia. The nitrate is reduced in the upper gastrointestinal tract to nitrite, which may be absorbed into the blood stream. In the bloodstream, the nitrite will combine with the hemoglobin to form methemoglobin. The methemoglobin lacks the ability to carry oxygen, thereby, at adequately high levels, it will cause low blood oxygen content and cyanosis (unusual bluish-grey or brownish-grey color of skin).

As indicated in the introduction, UOSA does not operate its denitrification process as long as the ambient nitrate concentration in the vicinity of the FWCA intake is below 5 mg/l as N. One major reason is that the nitrate in the effluent has been shown to have a role in the maintenance of good water quality in the Occoquan Reservoir. To (1974) studied the phosphorus release from the sediment in the Occoquan Reservoir before the UOSA WRF was put in operation. He speculated that, after UOSA WRF started, the Occoquan Reservoir

sediment would continue releasing phosphorus to the overlying water for a long period of time. To did not foresee that nitrate from UOSA effluent would help keep the sediment-bound phosphorus in the sediment. Following UOSA start-up, the nitrate concentrations in Bull Run increased due to the highly nitrified UOSA effluent. The additional nitrate is believed to help delay the onset of phosphorus release by delaying the onset of iron reduction in the sediment (OWML, 1998). As a result, studies conducted on the reservoir after the UOSA start-up have been focusing on the reservoir conditions during the stratification.

McLaughlin (1981) measured anaerobic phosphorus release rates and aerobic uptake rates of the Occoquan Reservoir sediments. He found that the mean total phosphate release rates ranged from 0.05 to 12.19 milligram per square meter per day (mg/sq. m/d), and the mean orthophosphate release rates ranges from -0.64 to 12.12 mg/sq. m/d under anaerobic conditions. The mean uptake rates of total phosphorus and orthophosphate were found to range from 7.09 to 13.57 mg/sq. m/d and from 5.64 to 13.39 mg/sq. m/d, respectively, under aerobic conditions.

Studies of both To (1974) and McLaughlin (1981) showed evidence that much sediment-bound phosphorus may be kept in the sediment as long as there is some free molecular oxygen present in the water column. In other words, when the water column contains molecular oxygen, the rate of phosphate release from sediment is relatively low, compared to the rate of release when the oxygen in the water column is depleted. It is well known that after oxygen in water is depleted, microorganisms will utilize nitrate to oxidize organic matter before ferric oxides (Stumm, 1996). Since phosphorus-bound sediment is postulated to adsorb into ferric oxides (Holdren and Armstrong, 1980; Song and Muller, 1999; Bonanni *et al.*, 1992; and Jensen *et al.*, 1992), it is likely that phosphorus releases from sediments under low oxygen conditions will be retarded by the presence of nitrate. Furthermore, the reservoir monitoring data showed that when the nitrate concentrations in the reservoir were high, the phosphorus concentrations were low and vice versa as shown on Figure 2-1. Therefore, the presence of nitrate in the reservoir may effectively prohibit the release of sediment-bound phosphate.

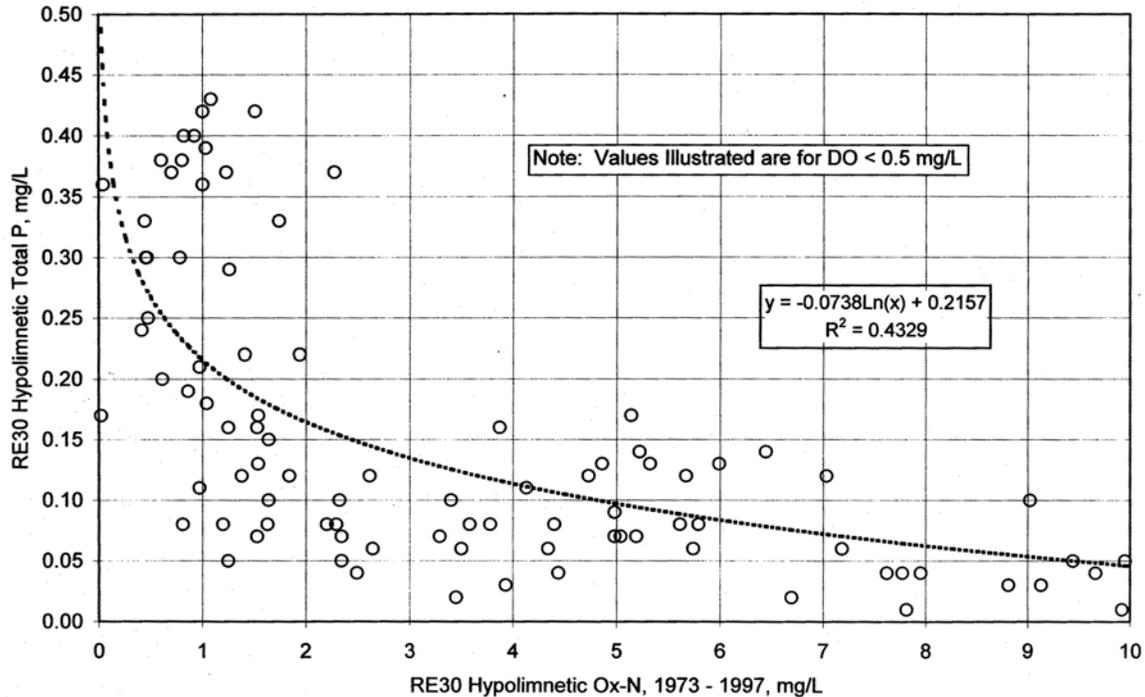


Figure 2-1. The hypolimnetic total phosphorus as a function of Ox-N (nitrate and nitrite) for low DO at RE30, 1973 – 1997. (Taken from OWML, 1998)

As a result, Sherman (1983) conducted a study to determine the effect of nitrate on an anaerobic water-sediment system, and to determine whether nitrate can prevent the release of sediment-bound phosphorus. She used microcosm studies to investigate these issues. The microcosm reactors were comprised of 1.5 liters (L) of sediment from the Occoquan Reservoir and 8.5 L of deionized distilled water. The reactors were airtight and were unsealed only during her routine sampling. Air could leak into the reactor during this period. Therefore, Sherman sparged the reactors with nitrogen gas for at least two hours after each sampling event to strip away any dissolved oxygen. She also frequently added dextrose as an organic carbon source throughout her experiment.

Her study was divided into two experiments. In the first experiment, she allowed anaerobic conditions to develop in the reactors for 36 days. She did not take any samples during this period. Then she added potassium nitrate ( $\text{KNO}_3$ ) to the reactors to provide nitrate concentrations in the water columns of 10 – 15 mg/L  $\text{NO}_3^-$ -N and collected samples twice a day for two days. She found that nitrate addition could rapidly raise the oxidation-reduction potential of an anaerobic system to the level of an oxidized system. The concentrations of phosphorus decreased sharply after the addition and continued to decrease for the remainder

of the experiment. The nitrate concentrations decreased slowly. The nitrate was still present at the end of the experiment.

She started the second experiment with the nitrate concentrations in the water columns of approximately 10 mg/L  $\text{NO}_3^-$ -N and continuously sparged the reactors with nitrogen gas. Samples were taken from the reactors every 3 to 10 hours. She found that the nitrate concentrations were initially stable when molecular oxygen was present in the water columns. After the oxygen was depleted, the nitrate concentrations started to decline and disappear within 4 days. She attributed the decrease of nitrate concentrations to denitrification, which will be discussed later. The phosphorus was first detected approximately 50 hours after the nitrate disappearance. Then the phosphorus concentrations had an increasing trend until the end of the experiment. She concluded that very low nitrate concentrations (0 to 0.2 mg/l  $\text{NO}_3^-$ -N) were required to prevent releases of sediment-bound phosphorus in oxygen-void waters.

Ripl (1976) successfully restored highly eutrophic Lake Lillesjon, Sweden, with the addition of calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), slaked lime ( $\text{Ca}(\text{OH})_2$ ), and ferric chloride ( $\text{FeCl}_3$ ). Ripl started the restoration about two months after the lake had stratified at the end of April 1975. He added one chemical at a time to the lake sediment, beginning with the trivalent iron-chloride. He found that the lake had low iron (Fe) content compared to the nearby lakes (9-23 milligrams as iron per gram dry matter (mg Fe/g dry matter) versus 30-50 mg Fe/g dry matter). He explained that phosphorus normally co-precipitates with ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) in sediment. The added ferric chloride will precipitate as  $\text{Fe}(\text{OH})_3$ , increasing the iron content and the binding capacity of phosphorus. The solution was, however, acidic, and hence lowered the lake pH. Therefore, following the ferric chloride addition, Ripl adjusted pH of the lake by adding slaked lime solution. This increased the pH from *ca.* 3 to between 7 and 7.5. Ripl said that this was the range of optimum denitrification. Then  $\text{Ca}(\text{NO}_3)_2$  was added to the sediment. He explained that nitrate promotes the oxidation of organic matter in sediment as well as increases the redox potential of sediment.

After the treatment, Ripl observed that the added nitrate disappeared within about seven weeks, indicating rapid denitrification. The phosphorus concentration in the hypolimnion dropped from more than 3 milligram as phosphorus per liter (mg P/L) to about

40 micrograms as phosphorus per liter ( $\mu\text{g P/L}$ ). The duckweed that normally covered the lake early in the spring disappeared. The sediment biochemical oxygen demand decreased by *ca.* 50 percent. The sediment oxygen uptake also decreased. He stated that at post-treatment uptake rates, the oxygen content of the lake would last longer than the stratification during the ice period (3 - 4 months). He concluded that chemical additions are valuable means in lake restoration and may be more cost effective than sediment dredging methods.