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# WATER QUALITY AND CHEMICAL MODELS

*By James N. Butler\**

## INTRODUCTION

A model is any representation of a real system which is easier to manipulate than the real system itself. For a long time, the traditional model was a mechanical one, but the extension of this concept to the mathematical model operational on a computer has become much more popular in the past decade as the capability of computers has increased and the cost of computations has decreased.

This paper will discuss chemical models of natural and polluted water systems. These are distinct from hydrodynamic models, which treat all groundwater and surface water as a simple fluid with no chemical properties. Hydrodynamic factors, which depend on such characteristics as density, temperature, geometry of surface channels, and porosity of aquifers, are essentially separable from chemical interactions, which are either homogeneous point properties of the fluid or are localized at the sediment-water or air-water interface.

This paper will further explain how chemical models form a basis for water quality criteria, and how strongly these chemical models have been influenced by the availability of convenient analytical methods. As a result, many water quality parameters are measured which are of only marginal significance, and others which are of much more direct significance are rarely measured. Finally, it will point out that the setting of water quality standards cannot be separated either from the purpose for which the water is to be used or from the natural processes active in the region where water quality is monitored.

## CHEMICAL MODELS

Some examples of chemical models are the following:

1. Elemental composition and stoichiometry model. In this

model, one considers only what elements are present, in what quantities they are present, and whether the ratios are constant. For pure inorganic compounds, this leads to the concept of the chemical formula and the stoichiometric chemical reaction.

2. Structural models of organic compounds. Here one distinguishes between different isomers of the same elemental composition, and the molecule is the distinctive unit. Molecules of a given type can be separated by a physico-chemical method such as chromatography, and identified by a spectroscopic or other physical method.

3. Oxidation state models of transition metals and non-metals. Here an essentially arbitrary system is used to divide up the bonding electrons between atoms on the basis of their electronegativity. So long as a particular oxidation number system is used consistently, meaningful statements can be made about the number of electrons transferred in a reaction.<sup>1</sup>

4. Sodium chloride in water as a model of salinity. This works fairly well for predicting the vapor pressure, electrical conductivity or density of sea water, but whenever chemical processes involving other materials than sodium chloride are involved, one must take account of the other elemental components of sea water—which may include virtually all elements of the earth's crust.<sup>2</sup> When one considers biological phenomena, the innumerable trace qualities of various organic materials must also be considered.

5. Calcium carbonate-carbon dioxide-water as a model of alkalinity and groundwater effects. This model provides the standard method for measuring alkalinity<sup>3</sup> as well as numerous important correlations between dissolved carbon dioxide and pH of groundwaters.<sup>4</sup> An insight into how the chemical composition of the aqueous environment is regulated by rapid equilibria can be gained from this relatively simple system.<sup>5</sup>

6. A focus on certain constituents of complex systems has provided a model useful with respect to recent environmental concern. Examples are phosphates, mercury, and chlorinated hydrocarbon pesticides such as DDT.<sup>6</sup> Such a focus may be useful, particularly if the material is persistent and toxic; but it also tends to ignore the numerous other factors in a natural system which may be of greater importance.

7. Multiple equilibria which take place rapidly in aqueous solution can be modeled in some detail, now that extensive com-

pilations of equilibrium constants are available.<sup>7</sup> Reactions which fall into this class are protonation (acid-base), coordination (complex formation), and ion-pairing. Perhaps the best known examples are the series of chemical models for sea water.<sup>8</sup> However, many biochemical reactions, and biochemically mediated oxidation-reduction reactions, require more complex kinetic models, and little has been done yet along this line.<sup>9</sup>

#### WATER QUALITY CRITERIA AND STANDARDS

Once the harmful effect of a particular material added to the environment has been recognized, it is labeled "pollutant" and legal sanctions are set up to attempt to minimize harm. The distinction is made between water quality *standards*, which are plans established by governmental authority as a program for water pollution prevention and abatement, *criteria*, which are scientific requirements on which a decision or judgment may be based concerning the suitability of water quality to support a designated use,<sup>10</sup> and *indices*, quantitative measures of water quality which may consist of a single criterion or several in combination.

Although this process of measuring, quantifying, and monitoring pollutants has been going on for centuries, most of the emphasis until recently was on water-borne pathogenic bacteria and viruses, and little attention was paid to identifying specific chemical substances which might be persistent or toxic in themselves. Still less attention was paid to their long-term non-toxic influence on the ecosystem into which they were introduced.<sup>11</sup>

A general framework for pollution and environmental quality models is shown in Figure 1.<sup>12</sup> This diagram attempts to illustrate the various factors affecting the decision-making processes in pollution control. Beginning at the top, the first step is to quantify the pollutants in some way. Usually this is a chemical characterization, such as the quantity of sulfur dioxide in polluted air, the amount of bacteria or organic matter in polluted water, the amount of lead, mercury, or pesticide in a stream or lake. It also can be a physical characterization, such as temperature change as a measure of thermal pollution, or turbidity as a measure of suspended matter.

If there is a simple source for the pollutant, such as a sewage outfall or a power plant stack, the extent of pollution may be expressed as an emission: so many grams per day of the pollutant. Alternatively, the amount released may be expressed as an ambient

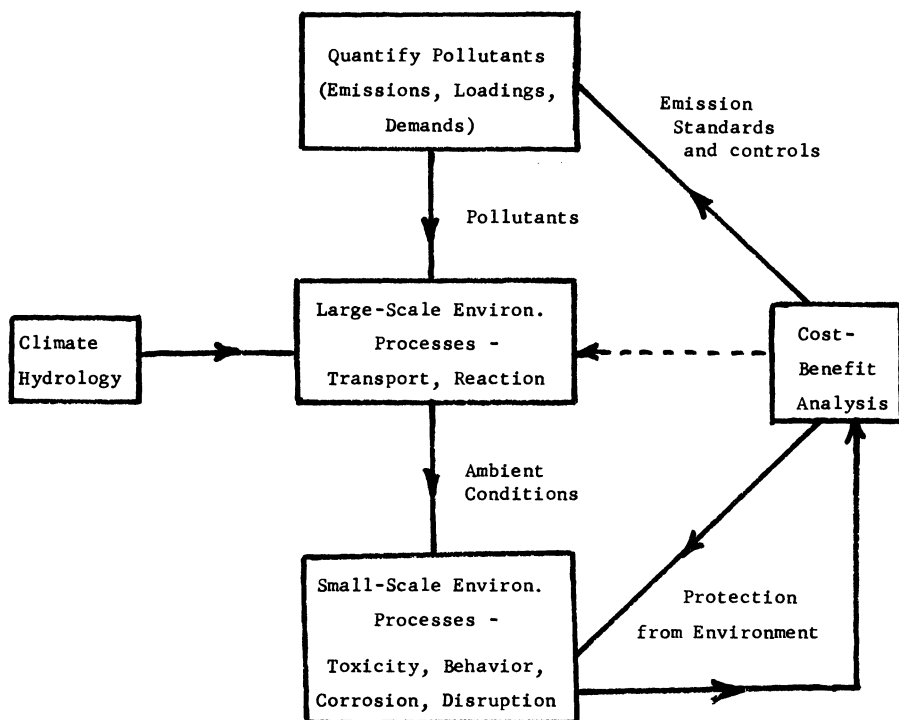


FIGURE 1

loading: so many parts per million in the environment near the source of pollution. If the pollution source is not easily located, as for example the drainage of fertilizer from cultivated fields into rivers and lakes, then it is not easily possible to assign an emission value, but an ambient loading (so many parts per million of nitrate in the stream at a particular point) is easy to quantify. Most of our air quality standards are now expressed in terms of ambient loadings.

A third method by which pollution may be quantified is by its demand on the resources of the environment. The classic example of this is the biological oxygen demand<sup>13</sup> of organic waste introduced into streams. Because the stream is being constantly re-aerated, oxygen is supplied continually to the microorganisms which degrade most organic sewage wastes, and eventually these materials (possibly pathogenic) are converted to non-toxic carbon dioxide, nitrogen, and inorganic salts. If oxygen is supplied too slowly, or the waste is supplied too rapidly, or in too concentrated a stream, the oxygen content of the water will drop to zero. The

anaerobic processes which take over will not only fail to degrade the waste as rapidly, but will produce noxious hydrogen sulfide. Thus, it is desirable not to load a stream too heavily with waste; otherwise its assimilative capacity will be exceeded. Unfortunately, this capacity depends on the flow rate of the stream, the temperature of the water, the amount of turbidity, and other factors and will be greatest when the spring floods are running, least when the summer drought depletes the river. A laboratory test of biological oxygen demand (performed in a closed bottle by measuring the rate at which oxygen is taken up by the natural microbial population of the waste) together with a mathematical model of the stream reaeration process<sup>14</sup> can be used to predict how much waste can be added to a stream while maintaining a satisfactory oxygen level.

Regardless of how the pollutants are quantified, they enter the large scale environmental processes of stream flow, lake circulation, rain, wind, waves, and ocean currents and are transported through the environment. As the transport occurs, various chemical processes also occur, changing the character of the pollutants. The oxidation of organic wastes in streams by microorganisms as a mode of self-purification has already been noted. The current alarm about chlorinated hydrocarbon pesticides and plasticisers has risen because they are *not* degraded during their transport to the seas and through the air, and because they have begun accumulating to levels which may be dangerous. For a long time, the motto for waste disposal was "the solution to pollution is dilution," expressing the fact that natural regenerative and degradation processes were rapid compared to the rate at which pollutants were being admitted to water systems or to the air. Indeed, simple dispersal is still the disposal method of choice when tall smokestacks or ocean outfalls are used; in most cases these are quite adequate means for keeping the ambient pollution level tolerable.

Should the large-scale processes be inadequate to remove the pollutants, or should we find ourselves too close to the source, then small-scale processes closer to man will be affected, and the pollution will be felt in various ways: as toxicity to man, animals, or plants, as corrosion of machines and structures, as disruption of ecological balances, or as subacute modifications of behavior. Each of these has its own costs. In principle, the benefit of the process producing a given kind of pollution could be balanced against these disruptive costs, although one might argue about the cost of some of the more subtle effects. Corrosion of machinery or acute

toxicity to man can be translated into monetary terms without too much disagreement. The question of who should bear the costs is quite another matter<sup>15</sup> which is beyond the scope of this paper.

Thus, the effects of pollution lead ultimately to a cost-benefit analysis of *some kind*. We would like to believe that this analysis is logical, straightforward, and accurate, but we know that it is not. It is capricious, emotional, and influenced less by scientific fact than by forceful statement of opinion, influence with powerful agencies, and manipulation of the mass media.

Nevertheless, by whatever means the analysis is made, it is reflected primarily in two types of response to the existence of pollution. One response is to set up emission standards and controls, based on criteria for ambient pollutant levels which are considered acceptable. In setting these standards and monitoring the level of pollutants, the techniques used to quantify pollutants are, as we have mentioned, largely chemical. We may thus make the significant point that standards and controls are primarily based on chemical models of the environment. Furthermore, most of these models are relatively primitive, as we shall see below.

An alternative way of responding to pollution is to protect those people or things likely to be damaged by the polluted environment. Airconditioning as a response to smog is one example. Chlorinating drinking water<sup>16</sup> to kill water-borne pathogens is another. However, protection from widespread pollution is usually much more expensive in the long run than prevention.

### WATER QUALITY INDICES

Any mode of quantifying the extent of pollution can be used as an index of pollution intensity. In this context, we may imagine a water quality index analogous to a price in economics, and in principle, any index could be converted to a price by measuring the cost of achieving a certain value of the index.

In practice, this is not so easy, since any index used to measure water pollution depends on many things, not the least of which is the water use. Thus, an acceptable water for boating may not be acceptable for drinking. An acceptable water for drinking may not be acceptable for irrigation (because of copper content, for example) and an acceptable water for irrigation may not be acceptable for drinking (because of bad odor or taste). Furthermore, since much pollution is not readily visible or even easily measur-

able, the price mechanism of a free market is not closely analogous.

To a large extent, the public applies an aesthetic criterion to determine the extent of pollution. Sometimes this is useful, but often it is irrelevant to the more primary question of public health. For example, sulfide in natural mineral spring water smells bad, creates unsightly incrustations on wells, but is considered healthy; nitrate is colorless, odorless, and tasteless, but can cause infant mortality (methemoglobinemia) if it reaches too high a level (greater than 15 milligrams per liter) in drinking water.<sup>17</sup> Beer cans, broken bottles, junk automobiles, and plastic bags are the most visible and most publicized form of waste, but probably the least harmful to public health in the long run.

Of course, the most important water quality index is whether man, using the water in the way he wants to use it, manages to survive and be healthy. This is not such a useful index, however, because we would not like to require proof of an epidemic before employing disinfection to drinking water. Nevertheless, we should retain this perspective, since the survival of man in the long run is indeed the ultimate consideration in establishing all environmental quality standards.

Like the miner's canary, who died of asphyxiation before the miner did, and therefore warned him in time to escape, we have often used the death of sensitive indicator organisms as a criterion of water quality. Massive fish kills are a familiar example. Growth of undesired organisms is also used as an obvious water quality criterion: blue-green algae, as a visible manifestation of a potentially toxic situation, are such indicators in eutrophic lakes and ponds.

Perhaps one of the most important groups of indicator organisms is coliform bacteria. Although *Escherichia coli* and related organisms do not in themselves cause disease, they are found in the feces and urine of warmblooded animals, and thus their presence indicates the possible presence of intestinal pathogens which may cause cholera, typhoid, hepatitis, and other water-borne diseases. The bacteria and viruses actually responsible for these diseases are much more difficult to identify routinely, and thus the coliform test is almost universally used.<sup>18</sup>

Turning to chemical criteria of water quality, the most important is the dissolved oxygen content. Survival of aquatic life, as well as the self-purification processes mentioned earlier that occur in natural waters, depend on maintaining an adequate supply of



dissolved oxygen. The 5-day biological oxygen demand test, long the most important measure of the quantity of pollution emitted by sewage treatment plants, is based on the oxygen requirements of the natural population of microorganisms and organic substrate in the water.<sup>19</sup> Indeed, for many purposes, oxygen is the only chemical criterion which really matters, and important economic decisions have been based primarily on this simple chemical model.<sup>20</sup>

Many chemical properties of natural waters which are easy to measure have no particular relation to pollution and thus cannot be used as indices: hardness, sodium, sulfate, chloride, dissolved solids, suspended solids, conductance, pH, are all much more dependent on the geological environment than on any pollution. One important exception is the increase in salinity of groundwater due to winter salting of roads.<sup>21</sup>

More specialized chemical models of pollution have led to the proliferation of chemical standards applied to drinking water quality. As recently as 1946 the U.S. Public Health Service chemical drinking water standards specified only 7 items. In 1962, these standards<sup>22</sup> included 21 items.<sup>23</sup> Only four years later, in 1968, the Federal Water Pollution Control Administration published a revised set of criteria<sup>24</sup> for public water supplies which had expanded the list of trace metals, as well as including fifteen specific chlorinated organic pesticides and herbicides, and three types of radioactivity measurements (see Table I). Further revisions of these criteria are in progress.

In essence, each of the criteria in Table I represents the quantification of some aspect of pollution, and each implies a corresponding water quality index. The important point here is that water quality is a multidimensional concept whose dimensions are imposed by the complexity of the chemical model used to establish the criteria. This chemical model, in turn, depends on a detailed understanding of the various factors which may affect a given use for the water. Much of the survey work on water quality in the past has concentrated on those parameters which are easy to measure in the field, and only recently has there been a serious attempt to obtain widespread data which cover all of the parameters presently considered relevant. As analytical methods become more advanced, a more complex model is possible, and more parameters will certainly be included.<sup>26</sup>

TABLE I  
SURFACE WATER CRITERIA FOR PUBLIC WATER SUPPLIES<sup>25</sup>

Constituent or characteristic	Permissible criteria	Desirable criteria
<b>Physical:</b>		
Color (color units) .....	75 .....	<10 .....
Odor .....	Narrative .....	Virtually absent .....
Temperature* .....	do .....	Narrative .....
Turbidity .....	do .....	Virtually absent .....
<b>Microbiological:</b>		
Coliform organisms .....	10,000/100 ml <sup>1</sup> .....	<100/100 ml <sup>1</sup> .....
Fecal coliforms .....	2,000/100 ml <sup>1</sup> .....	<20/100 ml <sup>1</sup> .....
<b>Inorganic chemicals:</b>		
	(mg/l)	(mg/l)
Alkalinity .....	Narrative .....	Narrative .....
Ammonia .....	0.5 (as N) .....	<0.01 .....
Arsenic* .....	0.05 .....	Absent .....
Barium* .....	1.0 .....	do .....
Boron* .....	1.0 .....	do .....
Cadmium* .....	0.01 .....	do .....
Chloride* .....	250 .....	<25 .....
Chromium,* hexavalent .....	0.05 .....	Absent .....
Copper* .....	1.0 .....	Virtually absent .....
Dissolved oxygen .....	≧4 (monthly mean) .....	Near saturation .....
	≧3 (individual sample)	
Fluoride* .....	Narrative .....	Narrative .....
Hardness* .....	do .....	do .....
Iron (filterable) .....	0.3 .....	Virtually absent .....
Lead* .....	0.05 .....	Absent .....
Manganese* (filterable) .....	0.05 .....	do .....
Nitrates plus nitrites* .....	10 (as N) .....	Virtually absent .....
pH (range) .....	6.0-8.5 .....	Narrative .....
Phosphorus* .....	Narrative .....	do .....
Selenium* .....	0.01 .....	Absent .....
Silver* .....	0.05 .....	do .....

Sulfate*	250	< 50
Total dissolved solids* (filterable residue).	500	< 200
Uranyl ion*	5	Absent
Zinc*	5	Virtually absent
Organic chemicals:		
Carbon chloroform extract* (CCE)	0.15	< 0.04
Cyanide*	0.20	Absent
Methylene blue active substances*	0.5	Virtually absent
Oil and grease*	Virtually absent	Absent
Pesticides:		
Aldrin*	0.017	do
Chlordane*	0.003	do
DDT*	0.042	do
Dieldrin*	0.017	do
Endrin*	0.001	do
Heptachlor*	0.018	do
Heptachlor epoxide*	0.018	do
Lindane*	0.056	do
Methoxychlor*	0.035	do
Organic phosphates plus carbamates.*	0.1 <sup>2</sup>	do
Toxaphene*	0.005	do
Herbicides:		
2,4-D plus 2,4,5-T, plus 2,4,5-TP*	0.1	do
Phenols*	0.001	do
Radioactivity:		
	(pc/l)	(pc/l)
Gross beta*	1,000	< 100
Radium-226*	3	< 1
Strontium-90*	10	< 2

\* The defined treatment process has little effect on this constituent.

<sup>1</sup> Microbiological limits are monthly arithmetic averages based upon an adequate number of samples. Total coliform limit may be relaxed if fecal coliform concentration does not exceed the specified limit.

<sup>2</sup> As parathion in cholinesterase inhibition. It may be necessary to resort to even lower concentrations for some compounds or mixtures. See par. 21.

## THE CONTEXT OF WATER QUALITY

The Water Quality Criteria published by the Federal Water Pollution Control Administration in 1968<sup>27</sup> distinguishes five categories of water use: (1) recreation and aesthetics, (2) public water supplies, (3) fish, other aquatic life, and wildlife, (4) agriculture and livestock, and (5) industry. These distinctions reflect the point made above that criteria for water quality, and to some extent the legally established standards, depend on the context in which the water is used. We shall discuss here only one context: the recreational use of an urban lake.

For boating and bathing, the essential quality parameters are that swimmers should not contract disease or be poisoned, and that the visibility be sufficient to allow rescue of those likely to drown. The corresponding water quality criteria recommended are<sup>28</sup> fecal coliforms as a measure of waterborne disease (as discussed above) and pH, which should be neither too acidic nor too basic (6.5 to 8.2) to prevent eye irritation. The visibility of a target (Secchi disk) at four feet depth is a criterion of water clarity. In addition, general recommendations are made that "optimum conditions for recreation based on utilization of fish, other aquatic life, and wildlife should apply. . . ."

A lake or pond is not a swimming pool in which the water can be filtered and disinfected mechanically; and it is customary to rely on natural purification processes to take care of these functions. In most urban and suburban areas, however, the most serious problem is not waterborne disease but rather the excessive fertilization of the algae and aquatic plants (eutrophication). Although this is to a large extent an aesthetic problem, since water having the consistency of pea soup is not considered attractive for swimming and boating, there are also health hazards involved, particularly from the blue-green algae (e.g. anacystis) which release toxins into the water and can cause substantial fish kills. Furthermore, if the algal growth is excessive, a cycle of growth and decay occurs several times during the spring and summer, and whereas the growing algae may be a mild aesthetic nuisance, the decaying algae, creating noxious odors on hot summer days, are a major aesthetic nuisance, and can substantially discourage recreation on a lake.

Several questions may thus be asked: What are the most impor-

tant factors causing eutrophication? How may algal blooms be controlled? How may the extent of algal growth be predicted? What management practices yield the greatest recreational value without excessive cost?

From a chemical viewpoint, the most interesting aspect of eutrophication is the role played by specific nutrients in controlling the rate of growth and the ultimate quantity of algae and aquatic plants. Of the numerous elements required for plant growth, phosphorus is the element most frequently limiting algal growth in fresh waters,<sup>29</sup> and as a result, much emphasis has been placed in legislation and the popular media on control of phosphate in detergent formulations and on tertiary wastewater treatment to remove phosphorus from sewage. It is important to note in this connection that only where the wastewater ultimately drains into a lake, pond, or other impoundment, is phosphorus control of any special value. In an area where individual cesspool-leaching field waste treatment is practiced, and these leaching fields are more than a few hundred yards from a lake or pond, there is little to be gained by avoiding the use of phosphate in detergents. Similarly, where ocean outfalls are used for sewage disposal, tertiary treatment to remove nitrogen is probably more important than the removal of phosphorus and can be done at less expense.<sup>30</sup>

However, the concentration of dissolved inorganic phosphate determined by the standard methods is not necessarily a good indicator of the potential for eutrophication in a lake. At any given time, most of the phosphorus present is in the sediments, or in growing fish, plants and algae, and very little is present in the water itself. Thus, particularly in shallow lakes and ponds, the reaction and transport of phosphorus in the sediment and its interstitial waters can control to a large extent the amount available to aquatic life.<sup>31</sup>

Although a portion of the phosphorus introduced into a lake is lost to the sediments over the course of a year, the release of phosphorus from sediments also occurs and is undoubtedly an important part of the mechanism by which the spring turnover (when the ice melts and the lake mixes by convection) triggers the spring algal blooms. In deeper stratified lakes, the sediments may have relatively less influence because of limited circulation between the upper waters and bottom waters. Nevertheless, the

detritus of algae and other aquatic organisms eventually finds its way down to the sediments and tends to be removed from circulation.<sup>32</sup>

The problem of predicting the time of an algal bloom can to some extent be attacked by developing detailed dynamic mathematical models of nutrient transport between plant species and predators (bacteria are more important than fish) and work is proceeding along this line.<sup>33</sup> Measurement of surface water phosphorus content in the late winter has some predictive value, particularly in deeper lakes. For shallow lakes, measurement of nutrient concentration in the sediment's interstitial water is perhaps more relevant.<sup>34</sup>

Prediction does not necessarily imply the ability to control. The most effective method of controlling eutrophication is to limit the input of nutrients to the lake: but this is almost never easy, and sometimes it is virtually impossible. If the primary sources are wastewater outfalls, then diversion of the wastewater to a special impoundment where algae are grown and harvested, or tertiary treatment to remove phosphate by chemical reaction (e.g. with lime) is called for. If the primary source of nutrient is over-fertilization of the surrounding land, control of the fertilizer composition and degree of fertilization is sometimes helpful, but the most effective remedy is to provide a wide belt of unfertilized meadow or forest around the lake. Unfortunately, in an already developed area this is seldom possible, but in areas which are still being developed this should be an important consideration in land use planning.

An alternative approach is to attempt to remove the offensive algae and plants. The most common technique is application of a herbicide (such as copper sulfate or 2,4-D) to the lake just before the spring bloom is expected. This technique actually *increases* the concentration of nutrients in the surface water, and unless the herbicide is applied at fairly frequent intervals, as it decomposes or is dispersed, the algal bloom which then occurs will be even more severe than if the herbicide had not been used. Harvesting aquatic plants is not too difficult, but microscopic algae tend to form scums which are difficult to filter and thus machines for this purpose have not been widely used. A direct approach which could be employed more is to stock the lake with fish species which are specific algae eaters;<sup>35</sup> this has the advantage of providing a more

stable ecological balance to the lake, and avoiding the possible long-term toxic effects of herbicides.

Another approach which is particularly effective in deep lakes where the water is dark-colored and light penetration is low, is to stir the lake by forcing air bubbles up from the bottom of a deep part of the lake. This disperses the algae and even though the total amount of nutrients available is larger, the lack of access to light limits the photosynthetic process. Thus the growth of algae becomes light-limited instead of nutrient limited, and a steady crop is maintained at a relatively low level all summer long, and the cycles of bloom and decay are largely avoided.

Dredging is not recommended as a method of removing the sediment reservoir of nutrients, since much of the sediment binding capacity is associated with the layers closest to the top, and dredging not only upsets the lake ecology but is actually likely to provide more nutrients than it removes.<sup>36</sup>

In considering the example of the urban recreational lake, we have seen that not only are chemical models required in evaluating and controlling water quality, but that biological and hydrological phenomena are also important. Furthermore, adequate management of such a resource is bound to involve political and institutional constraints, as well as economic factors. If I leave you with a single message it is this: the more complete and relevant one's mental model of an environmental situation is, the better the decisions will be regarding that situation.



#### FOOTNOTES

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<sup>21</sup> R. C. Bubeck, W. Diment, *et al.*, SCIENCE, 172, 1128 (1971).

<sup>22</sup> WATER DRINKING STANDARDS, *supra* n.17.

<sup>23</sup> 1946 Standards: As, Cl, Cr, Cu, Fe, Mn, Phenols. 1962 Standards: As, Cl, Cu, F, Fe, Mn, Zn, Ba, Cd, Cr, Pb, Se, Ag, CN, NO<sub>3</sub>, SO<sub>4</sub>, Alkylbenzenesulfonates (ABS, referred to as 'methylene blue active substances' in Table I), phenols, carbon chloroform extract (CCE).

<sup>24</sup> WATER QUALITY CRITERIA, *supra* n.10.

<sup>25</sup> F. Morel and J. J. Morgan, *supra* n.9.

<sup>26</sup> Some of the important new analytical methods are atomic absorption spectroscopy (for trace metal analysis), gas chromatography (for pesticide analysis) and selective electrodes (for pH, fluoride, lead, cadmium, nitrate, sulfide, calcium, magnesium, sodium, dissolved oxygen, and ammonia). An important reference is STANDARD METHODS FOR WATER AND WASTEWATER ANALYSIS, American Public Health Association, 13th Ed., 1971. Current bulletins by the Environmental Protection Agency continually update these methods. For the most advanced techniques, consult the annual review issue of ANALYTICAL CHEMISTRY. For a concise review of pesticide analysis, see D. J. List, SCIENCE, 170, 589 (1970).

<sup>27</sup> WATER QUALITY CRITERIA, *supra* n.10.

<sup>28</sup> *Id.*

<sup>29</sup> W. Stumm and E. Stumm-Zollinger, in WATER POLLUTION MICROBIOLOGY, *supra* n.13.

<sup>30</sup> J. H. Ryther and W. M. Dunstan, SCIENCE, 171, 1008-1013 (1971).

<sup>31</sup> In attempting to understand the role of sediments, the interaction with soluble iron and insoluble iron phosphate minerals is important, since the reduction of iron to the ferrous form in anaerobic sediments tends to release phosphate, whereas the oxidation of iron to the ferric form at an aerobic sediment water interface tends to precipitate phosphate from the interstitial waters as strengite (FePO<sub>4</sub> · 2H<sub>2</sub>O) and related minerals.

Closely related is the adsorption of phosphate on limestone and clay minerals, as well as the precipitation of phosphate by calcium (as hydroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) or aluminum (as variscite AlPO<sub>4</sub> · 2H<sub>2</sub>O and related minerals) in the interstitial water. These processes have been studied at our laboratory in some detail. The kinetics of phosphate removal by calcite (CaCO<sub>3</sub>) were investigated quantitatively by Stumm and Leckie (see references *infra*). Both a fast adsorption process and a slow nucleation and growth of hydroxyapatite on the surface of calcite were distinguished. Adsorption of phosphate on gamma alumina (a synthetic Al<sub>2</sub>O<sub>3</sub>) is strongly affected by the presence of organic acid anions and fluoride, which apparently complex with aluminum atoms

either on the surface or as ions in the interstitial aqueous phase, diminishing the affinity of alumina for phosphate. Similar effects are observed on alpha-alumina (corundum,  $\text{Al}_2\text{O}_3$ ; gibbsite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), although the total amount of phosphate adsorbed by these minerals is less than on gamma-alumina.

This work is reported in the following publications: W. Stumm and J. O. Leckie, PROCEEDINGS 5TH INTERNATIONAL WATER POLLUTION RESEARCH CONFERENCE, Pergamon, 1971; J. O. Leckie and W. Stumm, in WATER QUALITY IMPROVEMENT BY PHYSICAL AND CHEMICAL PROCESSES, E. F. Gloyna and W.W. Eckenfelder, eds., Univ. Tex. Press, 1970; W. Stumm, C. P. Huang, and S. R. Jenkins, CROATIA CHEMICA ACTA, 42, 223 (1970). Y. S. Chen, J. N. Butler, W. Stumm, submitted to J. COLLOID SCI.

<sup>32</sup> W. Stumm and E. Stumm-Zollinger, *supra* n.29.

<sup>33</sup> In particular, the work of D. O'Connor and co-workers at Manhattan College, H. Rice, G. McLeod, and R. Patterson at the New England Aquarium, F. H. Verhof at Notre Dame University, and G. F. Lee at the University of Wisconsin has dealt with this solution.

<sup>34</sup> See n.29, 31 *supra*.

<sup>35</sup> J. M. Hubschman, SCIENCE, 171, 536 (1971).

<sup>36</sup> See n.29, 31 *supra*.