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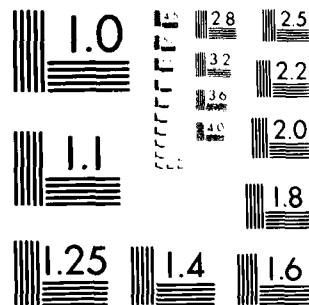
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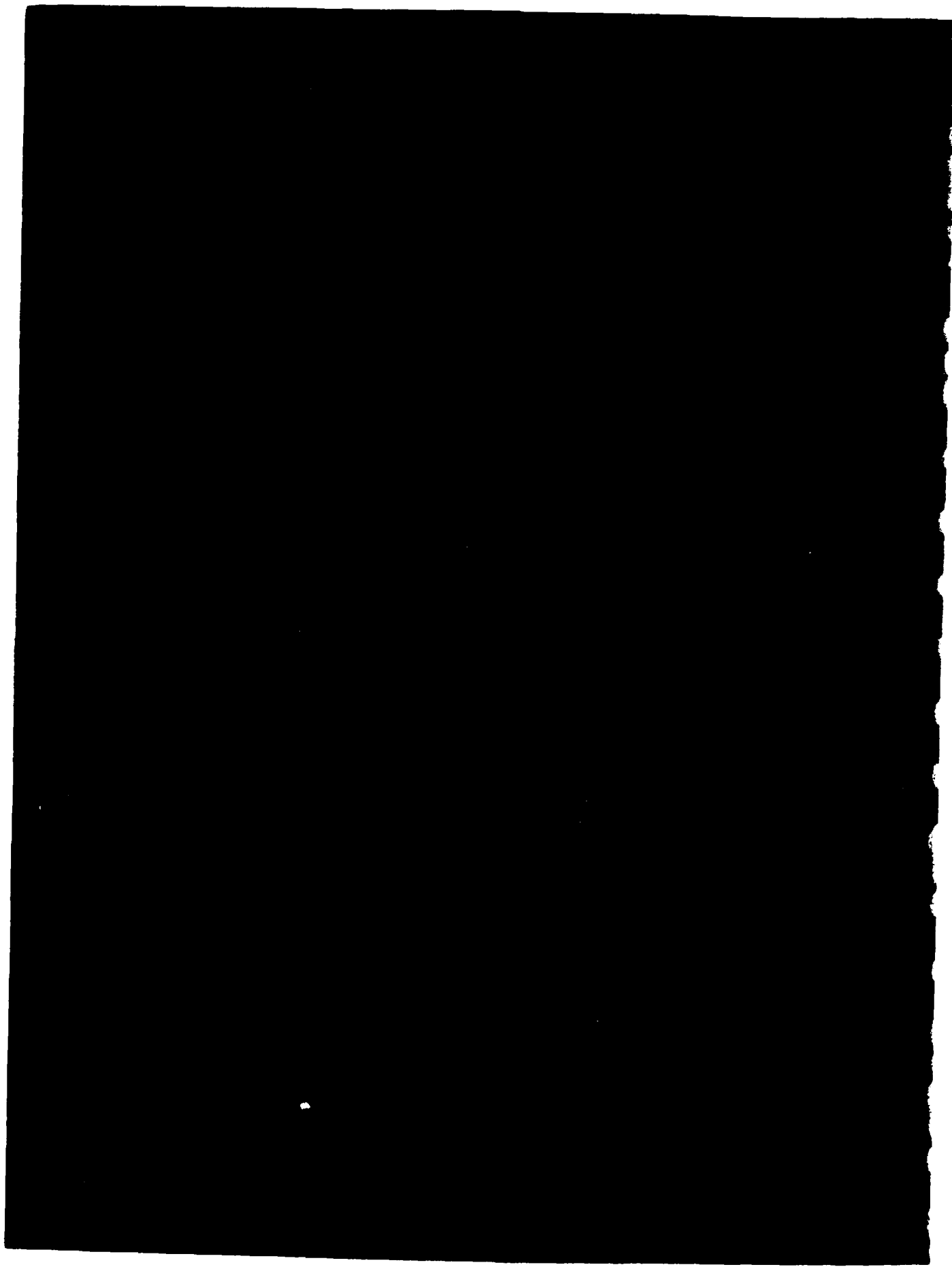
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indicates that the factors affecting oxidation of nutrients and metals are highly site specific. This report discusses oxidation pathways of chemicals and important environmental parameters that affect the transformation rate of selected nutrients and metals in lakes and reservoirs and presents a model for predicting the transition from anaerobic to aerobic conditions.

In order to better demonstrate the necessary components for an aerobic predictive model, consideration was given to the basic concepts of the most commonly available equilibrium models for predicting water quality in lakes. Evaluation of the practicality of available models revealed that, although equilibrium models provide the flexible and comprehensive approaches necessary for water quality prediction, rate models are more precise and reliable in their depiction of the transition from anoxic to aerobic conditions in reservoirs.

Oxidation rates of selected nutrients and metals in U. S. Army Corps of Engineers reservoirs were determined in environmentally controlled laboratory investigations; field measurements of the fate of reduced iron and manganese in the anoxic bottom water of Eau Galle Reservoir, Wisconsin, during destratification corroborated the laboratory results. These oxidation rate coefficients will form the basic input variables for RE-AERS, a reaeration subroutine of the water quality evaluation model CE-QUAL-R1.

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PREFACE

This study was sponsored by the Office, Chief of Engineers (OCE), U. S. Army, as a part of the Environmental Water Quality and Operational Studies (EWQOS) Work Unit 31594 (IB.2) entitled Develop and Verify Descriptions for Reservoir Chemical Processes. The OCE Technical Monitors for EWQOS were Mr. Earl Eiker, Mr. John Bushman, and Mr. James L. Gottesman.

The work was conducted during the period September 1978-June 1981 by the Environmental Laboratory, U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, under the direction of Dr. J. Harrison, Chief of the Environmental Laboratory (EL), and under the general supervision of Mr. D. L. Robey, Chief of the Ecosystem Research and Simulation Division (ERSD), and Dr. R. M. Engler, Chief of the Ecological Effects and Regulatory Criteria Group. Program Manager of EWQOS was Dr. J. L. Mahloch, EL. Some of the foundation work for this study was performed as part of a U. S. Army Corps of Engineers In-House Laboratory Independent Research Program (ILIR) Work Unit 111 06 entitled Mechanisms That Regulate the Degree of Oxidation-Reduction in Anaerobic Sediments and Natural Water Systems.

This study was conducted by Drs. R. L. Chen and D. Gunnison and Mr. J. M. Brannon, ERSD. Messrs. I. Smith, Jr., and T. C. Sturgis, ERSD, assisted with the laboratory experimentation. This report was written by Drs. Chen and Gunnison and Mr. Brannon and was reviewed by Drs. R. H. Kennedy, Engler, and M. Zimmerman, ERSD.

Director of WES during this study and the preparation and publication of this report was COL Tilford C. Creel, CE. Technical Director was Mr. F. R. Brown.

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CONTENTS

	<u>Page</u>
PREFACE	1
LIST OF TABLES	3
LIST OF FIGURES	3
PART I: INTRODUCTION	5
Background	5
Purpose	7
PART II: AEROBIC CHEMICAL TRANSFORMATIONS IN REAERATED OR DESTRATIFIED RESERVOIR ECOSYSTEMS	8
Literature Review	8
Equilibrium Models Depicting Aerobic Processes	32
PART III: RE-AERS--REAERATION SUBROUTINE.	37
Model Organization and Function	37
Interrelationships Among Reduced Chemicals as the Anoxic Water Column Is Aerated	41
PART IV: EVALUATION OF RELEVANT RATE DATA	54
PART V: LABORATORY AND FIELD STUDIES	55
Materials and Methods	55
Results	59
PART VI: SUMMARY AND CONCLUSIONS	70
REFERENCES	71
TABLES 1-9	

LIST OF TABLES

No.		Page
1	Summary of Previous Results on Oxygenation Kinetics of Ferrous Iron	80
2	Oxidation and Transformation of Various Reduced Components in Aerated Reservoirs and Other Freshwater Environments	81
3	Summary of Methods Used to Obtain Data	82
4	Characteristics of Selected Sediments and Soils Used in the Laboratory Studies	83
5	Changes in Concentrations of DO in the Overlying Water During Aeration Study	84
6	Concentration of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in Waters Overlying Sediments from Selected CE Reservoir Systems Incubated Under Aerobic Conditions at 20°C , $\mu\text{gN/ml}$	85
7	The Rate of N Transformations in CE Reservoir Systems Incubated Under Aerobic Conditions at 20°C for 3 weeks in the Dark	86
8	Changes of Inorganic Phosphate (Ortho-P) Concentration in the Overlying Waters of Selected CE Reservoir Systems Under Aerobic Conditions at 25°C in the Laboratory	86
9	Concentration of Reduced Fe and Mn in Waters Overlying Sediments from Selected CE Reservoir Systems Incubated Under Aerobic Conditions at 20°C , $\mu\text{g/ml}$	87

LIST OF FIGURES

1	Thermally stratified reservoir and associated conditions of low dissolved oxygen	10
2	Alternatives for air or oxygen injection in hydropower projects	11
3	Outline of pathways of carbon in aquatic environments	15
4	Outline of pathways of nitrogen in aquatic environments	18
5	Interchange between water and sediment P compartments	20
6	Outline of pathways of iron and manganese in aquatic environments	22
7	Redox potential-pH diagram indicating the stability field of common iron compounds	25
8	Changes in O_2 and soluble Mn concentrations with time in the overlying waters in a stratified CE reservoir	28

LIST OF FIGURES

No.		Page
9	Thermal stratification cycle	38
10	After hypolimnetic aeration: thermal stratification continues in the reservoir; hypolimnion DO level is maintained at approximately 5-6 mg/L	39
11	Major chemical changes and pathways associated with anaerobic conditions in the hypolimnion	42
12	Major chemical changes and pathways associated with the destratification period in anoxic hypolimnion	49
13	Sediment-water reactor for studying aerobic conditions in reservoirs	56
14	Changes in organic and inorganic carbon contents of the overlying water in Beech Fork Reservoir under aerobic and anaerobic conditions	61
15	Changes in organic and inorganic carbon contents of the overlying water in Browns Lake under aerobic and anaerobic conditions	61
16	Changes in organic and inorganic carbon contents of the overlying water in Browns Lake (small column) under aerobic and anaerobic conditions	62
17	Changes in organic and inorganic carbon contents of the overlying water in Eagle Lake under aerobic and anaerobic conditions	62
18	Changes in organic and inorganic carbon contents of the overlying water in Eau Galle Reservoir under aerobic and anaerobic conditions	63
19	Changes in organic and inorganic carbon contents of the overlying water in Eau Galle Reservoir (small column) under aerobic and anaerobic conditions	63
20	Changes in organic and inorganic carbon contents of the overlying water in Richard B. Russell Reservoir under aerobic and anaerobic conditions	64
21	Map of Eau Galle Reservoir, Wisconsin	68

CHARACTERIZATION OF AEROBIC CHEMICAL PROCESSES IN RESERVOIRS:
PROBLEM DESCRIPTION AND MODEL FORMULATION

PART 1: INTRODUCTION

Background

1. Many Corps of Engineers (CE) reservoirs have within the hypolimnion low concentrations of dissolved oxygen and high concentrations of products of anaerobic transformation; consequently, these concentrations occur in waters released from projects having bottom withdrawal. Adverse impacts of low dissolved oxygen in reservoirs and their releases have included harmful effects on aquatic biota, such as fish kills; loss of project benefits from excessive growth of aquatic vegetation and algae; increased operation and maintenance costs, especially as a result of corrosion; and increased costs to downstream water users due to increased requirements for water treatment.

2. Adding oxygen to an anoxic hypolimnion, either through natural or mechanical destratification, will rapidly alleviate many water quality problems caused by reduced chemical substances. Improvement in water quality during the change from anaerobic to aerobic conditions is a consequence of the oxidation of metals and nutrients, which produces speciation and solubility changes that benefit water quality. In some CE reservoirs suffering from severe anaerobic conditions, mechanical aeration may be an acceptable means of alleviating the associated water quality problems.

3. Artificial mixing and/or destratification of the anoxic hypolimnion to improve water quality has been attempted in a number of stratified waterbodies. Several researchers have studied the effect of aeration on nutrient availability in reservoir water (Bernhardt 1967; Cooley et al. 1980; Strecker et al. 1977). Results indicate that increasing the dissolved oxygen content of the anoxic water results in decreases in the concentrations of manganese, iron, ammonia, hydrogen

sulfide, and phosphorus. The transformation rates of iron, manganese, and phosphorus in reservoir waters are dependent upon the effects of pH and oxidation state. High concentrations of organic matter in surface waters also affect soluble iron levels due to the formation of organic complexes.

4. Several attempts have been made to quantify oxidation rates of reduced species found in water. However, with the exception of redox potential, the effects of various environmental factors on the transformation rates of iron, manganese, phosphorus, sulfur, and nitrogen have not been well established. Effects of mixing, redox potential, temperature, sediment type, and other environmental parameters on transformation rates of nutrients and other contaminants must be known prior to evaluation of any theoretical model.

5. Existing modeling approaches do not adequately predict the many chemical ramifications of aerobic processes that occur in reservoirs, although several models of pertinent individual processes do exist. Moreover, present techniques give an ineffective characterization of the sources and extent of reaeration, the development of aerobic conditions in a previously anaerobic hypolimnion, the mobilization and immobilization of nutrients and contaminants, and the rates at which these processes occur. Managers lack the capability to evaluate various alternative methods for encouraging or reducing these processes or to determine the amount of reaeration required for improvement of impoundment water quality.

6. Field and laboratory investigations of chemical processes associated with low oxygen concentration and anoxic conditions in reservoirs have been conducted by the Environmental Laboratory, Waterways Experiment Station (WES). Results of these studies have been compiled and used to formulate a description of anaerobic conditions (Gunnison and Brannon 1981). The present report offers a description of the transition from anaerobic to aerobic conditions in reservoirs and proposes the chemical equilibrium model GEOCHEM and a reaction rate model, RE-AERS, as basic models which function according to this description. The models will be incorporated into the WES one-dimensional

reservoir water quality model CE-QUAL-R1 (Environmental Laboratory 1982) as a part of the Environmental and Water Quality Operational Studies (EWQOS) Task IB.2.

Purpose

7. The objectives of this study were: (1) to compile and organize existing information on aerobic processes occurring in lakes and reservoirs; (2) to identify important aerobic chemical processes, particularly those dealing with oxidation of reduced chemical species that were accumulated during periods of anaerobic conditions and also those that were important in shifting chemical species from the dissolved to the particulate phase; (3) to incorporate these processes into a unified format of aerobic subroutine; and (4) to provide representative rate data for the various processes, as obtained in laboratory and field studies. The proposed aerobic model is intended for use in conjunction with the previously developed anaerobic subroutine (Gunnison and Brannon 1981) to deal with water quality problems in reservoirs.

PART II: AEROBIC CHEMICAL TRANSFORMATIONS IN REAERATED OR
DESTRATIFIED RESERVOIR ECOSYSTEMS

Literature Review

Dissolved oxygen and the oxidation-
reduction system in reservoirs

8. Oxygen solubility is directly proportional to the partial pressure of oxygen in the gas phase and decreases in a nonlinear manner as temperature increases. To date, most measurements of the oxidation-reduction status of the water-sediment system have involved redox potential, Eh or E_7 (Eh corrected to pH 7). The theoretical Eh of water containing dissolved oxygen can be expressed as:

$$Eh = E_o - \frac{RT}{F} \ln \frac{aOH^-}{\sqrt[4]{pO_2}} \quad (1)$$

where

E_o = standard oxidation potential voltage

F = Faraday constant in heat units

R = the gas constant

T = the absolute temperature

aOH^- = the activity of hydroxyl ions

pO_2 = the partial pressure of oxygen

At 1 atm, 18°C, Equation (1) may be rewritten as:

$$Eh = 1.234 - 0.058 \text{ pH} + 0.0145 \log pO_2 \quad (2)$$

With this equation, a redox potential of about 800 mV can be calculated for oxygen-saturated natural surface water. Observed potentials in oxygenated lake water are usually lower, approximately 400 to 600 mV, (Hutchinson 1957). In accordance with Equation (2), the redox potential of an aerated water system is relatively insensitive to oxygen concentration. Only a 30-mV decrease in Eh was observed when the oxygen

concentration decreased from 100 to 0.1 percent saturation in water. Thus, a shift from oxidizing to reducing conditions will not occur until the oxygen supply has been nearly exhausted (Greenwood 1962). The vertical distribution of Eh in lake waters has been monitored numerous times, with typical values of lake water surfaces ranging from 420 to 520 mV (Hutchinson 1957). In hypolimnetic waters of meromictic lakes, Eh can decline to approximately 80 mV. Much lower Eh values are expected within the sediments (i.e. -150 mV and lower). Under oxidative conditions, the Eh of the oxidized layer appearing at the water-sediment interface is about 100 mV or higher. Similar Eh distribution patterns have also been recorded in flooded soil systems such as rice paddy fields. Below the oxidized microzone, sediment Eh is invariably from 0 to about -200 mV, similar to the values recorded for flooded soils (Chen et al. 1979; Bell 1969; Turner and Patrick 1968). Flooded soils tend to reach a fairly stable pH in the range of 6.7 to 7.2 (Ponnamperuma et al. 1966). The pH of acid soil high in iron is controlled by the $\text{Fe}_2(\text{OH})_8\text{-H}_2\text{O-CO}_2$ system, while the pH of calcareous soils is defined by the partial pressure of CO_2 in the $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$ system.

Thermal stratification

9. Many CE reservoirs develop thermal stratification, resulting in density differences between water layers (Figure 1), which isolates the hypolimnion. This isolation, coupled with strong oxygen demand, usually produces a low dissolved oxygen concentration in hypolimnetic waters. Associated with the development of low dissolved oxygen concentration is the release from the sediments into the water of products of anaerobic processes, including reduced forms of iron, manganese, reduced organic compounds, nitrogen, and hydrogen sulfide. Many of these products adversely affect the quality of water destined for human consumption, recreation, and fishery uses. The hypolimnetic oxygen deficit in most lakes and reservoirs is usually due to the biological and chemical decomposition of organic matter; the clinograde oxygen distribution curve shown in Figure 1 commonly occurs in productive lakes during summer stratification. Under such conditions,

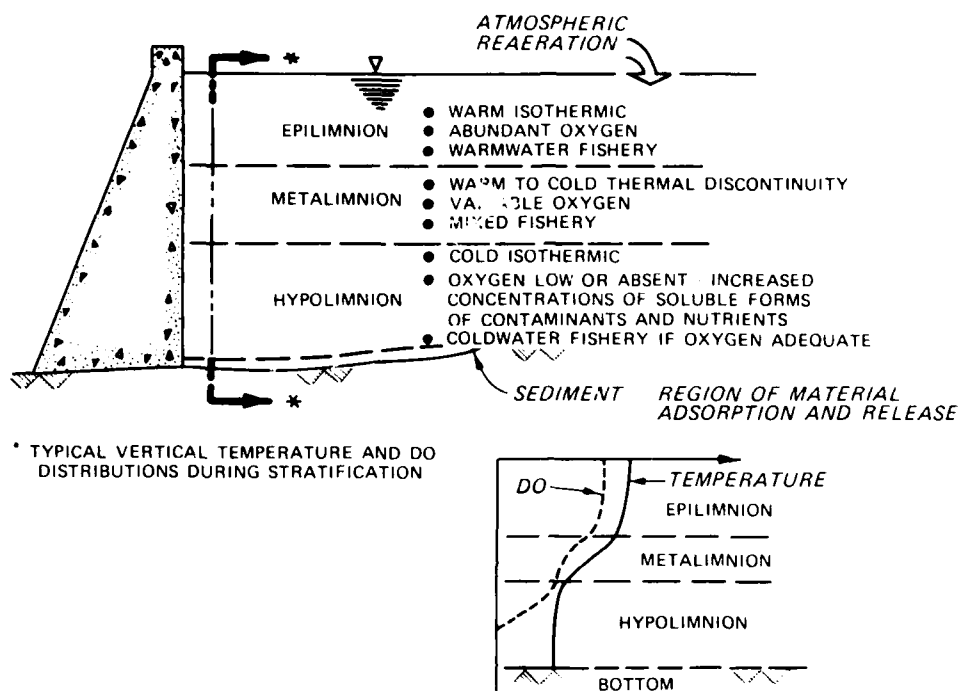


Figure 1. Thermally stratified reservoir and associated conditions of low dissolved oxygen (DO)

reaeration of anoxic hypolimnetic waters is minimal until destratification occurs.

10. Biogeochemical transformations of nutrients and metals under anaerobic conditions differ greatly from transformations in aerobic environments. Microbial and biochemical reactions in anaerobic environments commonly generate high concentrations of soluble forms of iron, manganese, ammonium, phosphorus, and sulfide that can yield undesirable tastes and odors or even toxic conditions. Release of nutrients from sediments to overlying water may also support undesirable algal blooms, although significant amounts of phosphorus may also be released in many types of lake sediments under aerobic conditions (Holdren and Armstrong 1980; Lee 1970).

11. Mechanical aeration methods have been used to improve water

quality and dissolved oxygen levels in anoxic hypolimnia of some stratified reservoir projects. Figure 2 illustrates one type of mechanical aerator along with several other methods for aerating reservoir releases. Large-scale mechanical aeration has been in service in CE reservoirs at Allatoona Lake and Clark Hill Lake for many years. Alternating aerobic and anaerobic conditions, however, by periodically introducing air into anoxic hypolimnetic waters, may reduce costs and maintain acceptable water quality. The success of periodic aeration will primarily depend on the kinetics of oxidation and reduction reactions that occur in the reservoir hypolimnion.

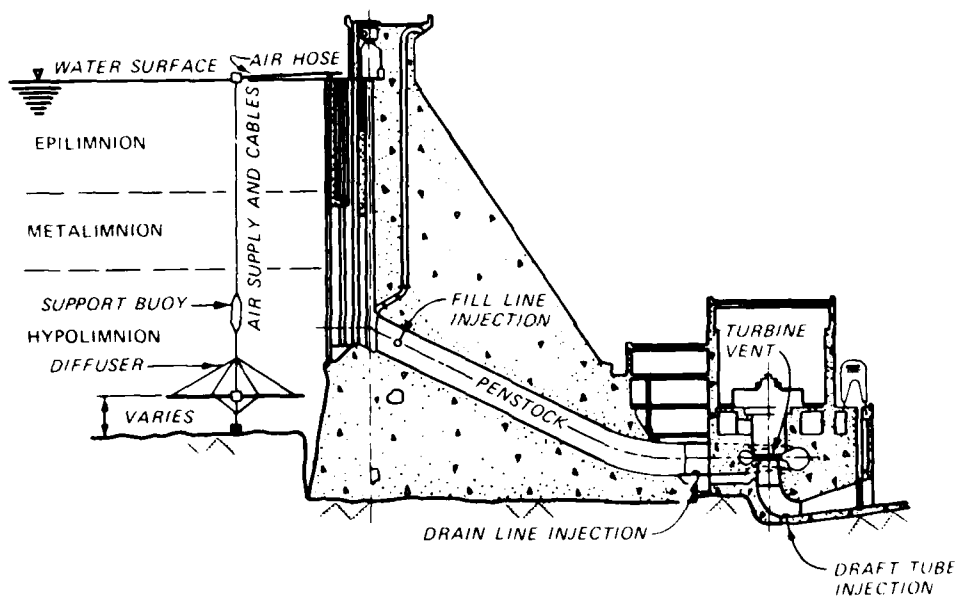


Figure 2. Alternatives for air or oxygen injection in hydropower projects

12. The current lack of knowledge about nutrient transformations under alternating aerobic-anaerobic conditions and of nutrient flux in water makes it impossible to predict precisely the nutrient, manganese, iron, and sulfide levels in reservoir water at a given time. Available technical information does not appear to be sufficient to forecast water quality in newly flooded or established CE reservoirs under reaerated or naturally destratified conditions. Therefore, most current mechanical

destratification approaches do not operate at maximum efficiency because the reservoir manager does not know when procedures should be initiated or terminated.

Types and sources of nutrients in CE reservoirs

13. Major aquatic plant nutrients in reservoirs, as in other natural water systems, are inorganic carbon, orthophosphate, nitrate, and ammonium. Organic forms of phosphorus and nitrogen may also be assimilated by organisms or converted to inorganic forms by biological or chemical reactions. Although carbon is essential for growth of aquatic plants, evidence to date indicates that carbon (in the form of CO_2) becomes limiting only under highly eutrophic conditions. Other essential nutrients for growth of aquatic plants include iron, sulfur, potassium, magnesium, calcium, boron, zinc, copper, molybdenum, manganese, cobalt, sodium, and chlorine. It is generally agreed, however, that nitrogen and phosphorus are the key elements in controlling the growth of aquatic plants in most freshwater ecosystems.

14. Nutrient sources include runoff from rural areas, agricultural drainage, atmospheric precipitation, urban runoff, nutrient release from reservoir sediments, and eutrophic inflow waters and sediment from upstream. Because of the nature and location of most CE reservoirs, the major source of nutrients entering the water is often runoff from cultivated agricultural lands. Excessive nutrients can also originate from poorly managed forest lands and mines. Nutrient-enriched runoff from feedlots and from cattle grazing near the reservoir are other important sources. Furthermore, reservoir sediment often contains high concentrations of nutrients which may be released to the overlying water through anaerobic nutrient cycles, even when external nutrient loadings are reduced. Consequently, for any given reservoir, all potential sources must be studied to predict the degree of eutrophication.

15. Problems with excessive nutrient loading and high dissolved oxygen demands in reservoirs frequently are most intensive during the first few years of impoundment. New reservoirs are not only subjected to external (allochthonous) loadings, but also contain a significant

internal (autochthonous) loading and oxygen demand resulting from the decomposition of inundated herbaceous plants, litter, leaves, and organically rich topsoil. In contrast, decomposition of woody plant material, such as trees, probably is not a significant cause of eutrophication and high dissolved oxygen demand because this material degrades slowly. Effective preimpoundment management and site preparation policies cannot be formulated until sufficient information is obtained on the relative importance of various materials as sinks for dissolved oxygen and sources of nutrients.

16. Most nutrients entering CE reservoirs are from nonpoint sources which cannot be controlled by the CE; however, the CE can limit internal nutrient regeneration through project design and operation (Keeley et al. 1978). Generally, any procedure that maintains dissolved oxygen concentrations of at least 2.0 mg/l in a reservoir hypolimnion will minimize the impact of anaerobic nutrient regeneration (Mortimer 1941, 1942; Fillos and Molof 1972). Alternatively, restoration techniques, such as dredging to remove nutrient-laden sediments from the reservoir or hypolimnetic aeration to increase dissolved oxygen levels, may limit oxygen depletion in hypolimnetic waters.

Changes of redox status in reservoirs

17. In an aqueous system, the degree of oxidation is limited by the electrochemical potential at which water becomes unstable and is oxidized to molecular oxygen (Baas Becking et al. 1960). Within the limits imposed by the stability of water, oxidation states of elements are affected by redox potential. The measured redox potential is largely determined by a few of the more abundant elements (Bohn 1971).

18. Stumm and Morgan (1981) and Bohn (1971) emphasized that natural waters are in a highly dynamic state. Measuring the redox potential in natural aquatic environments may lead to erroneous results because no single oxidation-reduction potential (Eh) electrode can reliably measure the redox potential. For example, Eh is inaccurately measured by a platinum electrode in oxygenated natural waters because the electrode is unstable in the presence of molecular oxygen.

19. Microbial activity can alter the oxidation-reduction status of reservoir waters. In the presence of oxygen, autotrophic microbes (including nitrifying bacteria, ferrous iron-oxidizing bacteria, sulfur-oxidizing bacteria, methane-oxidizing bacteria, and hydrogen-oxidizing bacteria) derive their energy from oxidizing reduced inorganic compounds. These microbes depend primarily on CO_2 fixation for their carbon. Principal components of a biochemical redox cycle in aquatic ecosystems are listed in the tabulation below.

Microbial Process	Principal Reaction	Energy Source (Electron Donor)	Electron Acceptor
Nitrification	$\text{NH}_4^+ \rightarrow \text{NO}_3^-$	NH_4^+	O_2
S oxidation	$\text{H}_2\text{S} \rightarrow \text{SO}_4^{2-}$	H_2S	O_2
Fe oxidation	$\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$	Fe^{+2}	O_2
Mn oxidation	$\text{Mn}^{+2} \rightarrow \text{Mn}^{+4}$	Mn^{+2}	O_2

Chemical transformations in aquatic environments during reaeration or destratification

20. In the presence of oxygen, biological decomposition of organic matter proceeds rapidly in a sediment-water ecosystem. Oxygen may be introduced into anoxic water by hypolimnetic aeration or natural destratification. Introduction of oxygen changes the redox status of anoxic waters and may reduce the solubility and/or concentrations of various nutrients and contaminants in the water column, thus eliminating certain adverse conditions associated with eutrophication (Martin and Meybeck 1979). A dissolved oxygen concentration of about 5 mg/L has been successfully maintained in the hypolimnia of small reservoirs by artificial oxygenation (Fast et al. 1975; Smith et al. 1975).

21. The following section briefly describes nutrient and contaminant cycles in aquatic ecosystems and the respective oxidation processes.

22. Carbon. A carbon (C) pathway in an aquatic environment is

outlined in Figure 3. Details of methane(CH_4)-production processes in reduced sediments have been clearly proposed and documented by Stadtman (1967). Stratified reservoirs normally do not produce large quantities

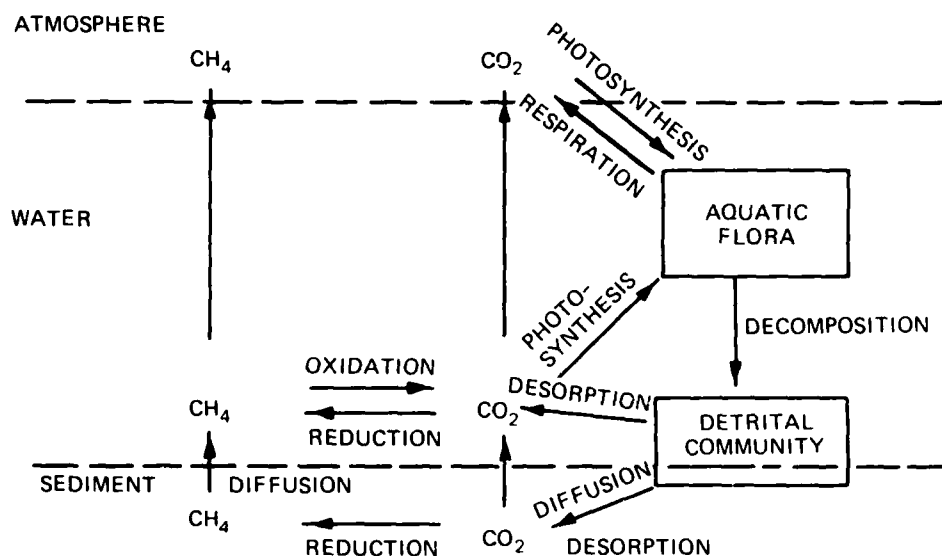


Figure 3. Outline of pathways of carbon in aquatic environments

of methane if the sediments contain dissolved sulfate. Theoretically, methanogenesis does not start until sulfate is completely depleted (Ponnamperuma 1972). Carbon dioxide (CO_2) is then utilized by microbes in the methane-forming process in a highly reduced aquatic environment. Increasing temperature enhances methane production (Mallard and Frey 1972). No significant methane evolution was detected at temperatures at or below 10°C during a reservoir simulation study in a WES laboratory (Chen, unpublished data).

23. Internal carbon cycling by methane oxidation in aerated aquatic environments occurs in a narrow band within the thermocline during summer stratification (Patt et al. 1974; Rudd and Hamilton 1975). Methane, which is biologically inert in the absence of oxygen, can be converted to carbon dioxide and cellular material in the presence of oxygen. Several field studies (Reeburgh 1969; Howard et al. 1971) have

confirmed that methane is always present in the anoxic bottom sediment and is released to the overlying water. Estimated methane cycling in Lake Mendota, Wisconsin, is summarized by Fallon et al. (1980) (see tabulation below*). High diffusion rates of methane through sediment seem to contribute to an increase in methane oxidation rates, and methane oxidation rates in aquatic environments increase as the concentration of oxidized inorganic nitrogen increases. In Lake Mendota during summer, for example, the methane oxidation rate was approximately $23.3 \text{ mmol/m}^2/\text{day}$ --a rate equivalent to 45 percent of the methane production rate in anoxic sediment (Fallon et al. 1980). During destratification in the fall overturn, the concentration of total methane in Lake Mendota waters decreased by 90 percent. Methane oxidation in Lake

Process	Methane Cycling	
	Carbon ₂ mmol/m ²	Percent Methane
Methane oxidized	999.5	45
Methane released to atmosphere	181.7	8
Hypolimnetic methane accumulation	1,028.8	47
Total methane produced	2,210	

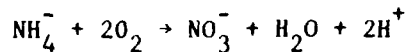
Process	Carbon Cycling	
	Carbon ₂ mmol/m ² /day	Percent Carbon Sedimented
Methane produced by deep sediments	35.8	54
Sedimentation of particulate organic carbon	67.5	

* Material reproduced by permission of American Society of Limnology and Oceanography, Inc., Grafton, Wis.

Tanganyika, East Africa, a deep meromictic lake, occurred mainly within a narrow zone at the boundary of the seasonally mixed layer and the permanently anoxic bottom waters; the methane oxidation rate there varied seasonally from 3.8 to 5.8 mmol/m²/day (Rudd 1980). Howard et al. (1971) noted that the methane oxidation rate may actually be much less than actually measured, since most of the studies were based on isolated systems in which the substrate was not continuously renewed.

24. Nitrogen. Lake sediment is generally considered to be a nitrogen (N) reserve in aquatic environments. Total N contained in surface sediment may range from 0.1 to 4 percent, depending on sediment characteristics and calcium carbonate (CaCO₃) content. The nitrogen cycle in an aquatic environment is strongly influenced by the dynamics of a particular lake. The nitrogen cycle in a sediment-water system as outlined by Chen (1971) is shown in Figure 4. The net concentration of various N species depends on the rates of N immobilization, mineralization, nitrification, and denitrification. In bottom waters of stratified eutrophic reservoirs, nitrate (NO₃⁻) declines to nil as oxygen is depleted and ammonium (NH₄⁺) begins to accumulate during summer stratification (Hutchinson 1957). High NH₄⁺-N levels in anoxic bottom waters are caused by release of NH₄⁺ from sediments and decomposition of settling sestonic material (Serruya and Berman 1969). Therefore, under anaerobic conditions, net N mineralization is characteristically greater than under aerobic conditions (Greenwood and Lees 1956).

25. Aeration of an ammonium-rich hypolimnion will lead to the disappearance of NH₄⁺ and the formation of oxidized forms of N. The net reactions are expressed as



The aerobic conversion of NH₄⁺ to NO₃⁻ is normally considered as a first order reaction (Endelmann et al. 1973; Misra et al. 1974; Selim and Iskandar 1981). Hall and Murphy (1980) demonstrated that nitrification is zero order for substrate and first order for microbial activity.

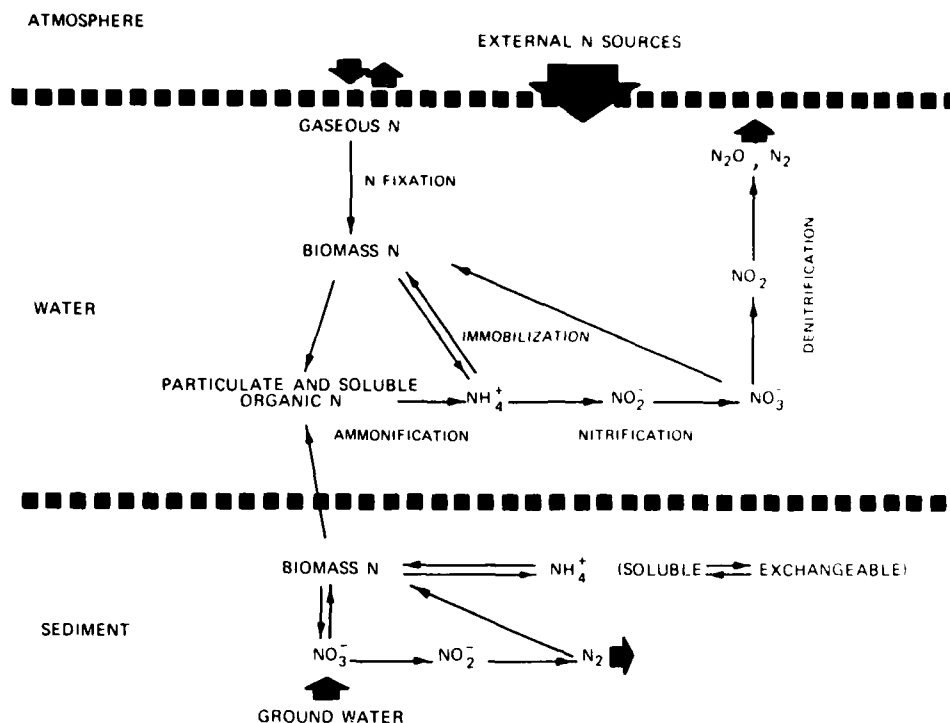


Figure 4. Outline of pathways of nitrogen in aquatic environments

However, nitrification reaction was proposed as a zero or a pseudozero order reaction by others* (Wong-Chong and Loehr 1975). Oxidized forms of N produced from NH_4^+ oxidation do not appear until about 1 week after aeration (Chen and Morris 1972) because biological reactions dominate the conversion of NH_4^+ to NO_3^- in aquatic environments. Nitrification has been shown to be carried out by both autotrophic and heterotrophic microbes. Conditions at the water-sediment interface have a major impact on the N balance of aquatic environments (Keeney 1972, 1973): if sediment or bottom water has a high oxygen demand, nitrate rapidly disappears once the supply of oxygen is discontinued. Unless the bottom

* Personal Communication, S. W. Johnson, 1978, Research Assistant, Keck Laboratory, California Institute of Technology, Pasadena, California.

waters are completely anoxic, nitrification should proceed just above the water-sediment interface (Lee 1970).

26. A field study (Chen et al. 1979) demonstrated that nitrification begins soon after aeration of the ammonium-enriched hypolimnion. However, nitrate formation in a stratified reservoir is limited to a few weeks due to the depletion of ammonium (Wirth and Dunst 1967, Chen et al. 1979). Additional ammonium released from sediments during aeration would not be significant because N immobilization is enhanced in the presence of oxygen (O_2).

27. Nitrification, denitrification, and NO_3^- immobilization may proceed simultaneously in an aerated hypolimnion, but NH_4^+ immobilization probably is minimal (Keeney 1972). A nonquantitative conversion of NH_4^+ to NO_3^- indicates that denitrification mechanisms operate in aerated hypolimnetic environments. Accumulation of NO_2^- must also be considered in the overall N balance because the lack of microbial populations in the water column may result in NO_2^- accumulation. In an eutrophic impoundment, Brezonik and Lee (1968) estimated that the rate of nitrogen disappearance, presumably due to denitrification, was approximately 0.32 mg N/L/day.

28. Phosphorus. The rate at which sediment acts as a source or sink for phosphate-phosphorus largely depends on the redox status and pH of the aquatic environment. The most important forms of phosphorus in lake sediment are bound in amorphous iron hydroxy complexes (Syers et al. 1973). Rural runoff, wastewater discharge from municipal and industrial sources, and urban runoff are generally the major phosphate (PO_4^{3-}) sources for lakes and reservoirs (Lee 1966); precipitation and groundwater seepage furnish relatively little PO_4^{3-} in most aquatic ecosystems. Release of PO_4^{3-} from sediment to water is highly correlated with the iron content of surface sediment. Syers et al. (1973) reviewed the PO_4^{3-} cycle in a water-sediment system and outlined the phosphorous (P) cycle as depicted by the following schematic pathway (Figure 5).

29. In recent years, it has been generally concluded that sediments can act as a buffer to maintain a certain level of PO_4^{3-} in overlying water (Pomeroy et al. 1965; Stumm and Leckie 1971). Phosphate

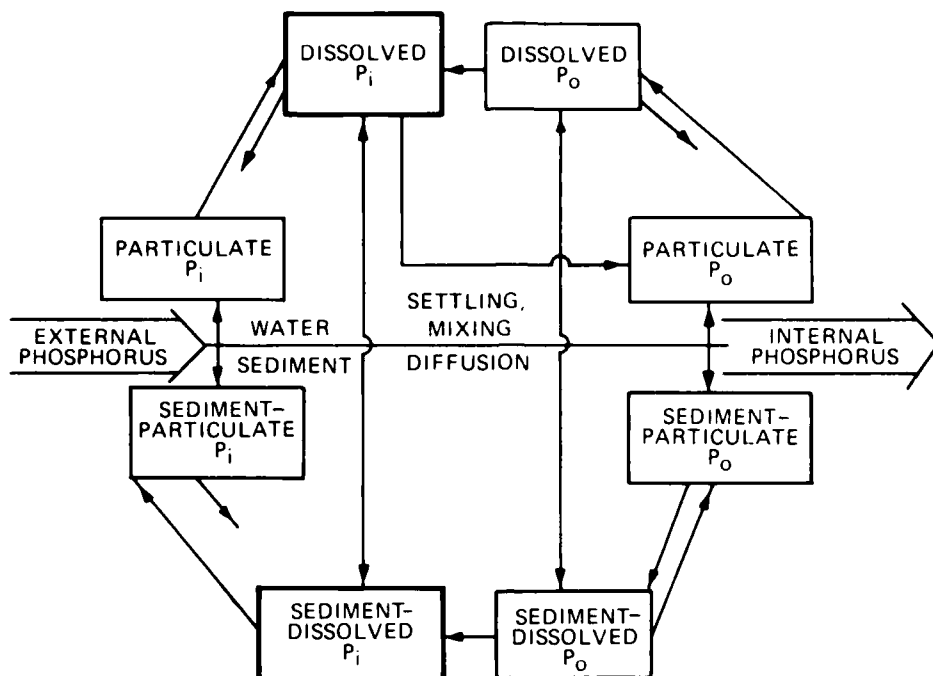


Figure 5. Interchange between water and sediment P compartments (P_i = inorganic P; P_o = organic P) (from Syers et al.¹ 1973, reprinted by permission of the American Society of Agronomy, Madison, Wis.)

transport across the sediment-water interface or "active sediment layer" plays an important role in the phosphorus status of lake waters (Armstrong 1980). The rate of transport is controlled by the physical, chemical, and biological characteristics of the aquatic system. The enhanced release of sediment P under anaerobic conditions is well documented (Golterman 1977); increasing temperature or lowering the O_2 concentration in the overlying water increases PO_4^{-3} release rates (Holdren and Armstrong 1980). Sediment resuspension removes dissolved PO_4^{-3} from the water column; however, a more dispersed state of the suspension may result in a higher level of particulate inorganic P in overlying water because of the presence of colloidal inorganic P. Release of inorganic

P from sediment to the overlying water is influenced by the forms of inorganic P present and by the rate and extent of the interaction of these forms with the aqueous phase (Syers et al. 1970, 1973; Ryden et al. 1973). The importance of the P contribution from sediment to the overlying water will decrease as lake depth increases and lake surface decreases.

30. Redox potential plays a major role in the chemical and physical mobility of PO_4^{-3} in water-sediment environments. Release of PO_4^{-3} from sediment to water is highly dependent on diffusion rate and turbulent mixing (Lee 1970). Iron in surface sediment and hypolimnetic water undergoes oxidation from ferrous (Fe^{+2}) to ferric (Fe^{+3}) as anoxic hypolimnetic waters pass through an oxygenation cycle. Adsorption of PO_4^{-3} on ferric oxides is particularly important in regulating inorganic PO_4^{-3} mobility in overlying water (Mortimer 1941, 1942; Williams et al. 1971; Shukla et al. 1971; Holford and Patrick 1981); in fact, radioactive tracer studies on the movement of inorganic PO_4^{-3} between sediment and water show that PO_4^{-3} concentrations in overlying waters are mainly regulated by sorption reactions (Mayer and Gloss 1980, Mortimer 1941, Lee 1970). Lake sediments can serve as a source of PO_4^{-3} to overlying waters under certain environmental conditions, even when oxygen is present in the overlying water. However, retention and release of PO_4^{-3} from sediment to overlying water under various Eh conditions are still unclear since PO_4^{-3} is not directly involved in redox reactions in aquatic environments. Release of PO_4^{-3} to water increases with temperature increase; temperature effects are most pronounced in calcareous eutrophic sediments (Holdren et al. 1977). Holdren et al. (1977) contend that the observed PO_4^{-3} release from sediment to the overlying water probably results from a decrease in the sediment redox potential instead of from increased dissolution or desorption of PO_4^{-3} from P-retaining components in noncalcareous sediments. The increase in temperature increases microbial activity in calcareous sediment, thus depleting O_2 in the interstitial water and reducing ferric iron to ferrous iron, with subsequent release of PO_4^{-3} . Vollenweider (1976) estimated that the phosphorus regeneration rate was $9.6 \text{ mg/m}^2/\text{day}$ from an anoxic sediment in a

eutrophic lake. A much higher regeneration rate (up to $18 \text{ mg/m}^2/\text{day}$ in Canadian lakes) was reported by Lean and Charlton (1976). The average release rate of PO_4^{3-} from sediment ranges from $0.62 \text{ mg/m}^2/\text{day}$ in northern oligotrophic soft water lakes to $51 \text{ mg/m}^2/\text{day}$ in calcareous eutrophic lakes in southern Wisconsin (Holdren and Armstrong 1980).

31. Iron. Although iron is abundant in natural water, most iron forms are poorly soluble. The available iron content of hardwater calcareous lakes is extremely low (Wetzel 1972). Sediment organic matter and chelating agents affect solubility and precipitation of iron in an aquatic environment. Redox pathways of iron and manganese in the aquatic environment are shown in Figure 6. The presence of sulfide in a natural water system indicates that Fe^{+3} has been completely reduced to Fe^{+2} , with some or all of the Fe^{+2} precipitated as FeS .

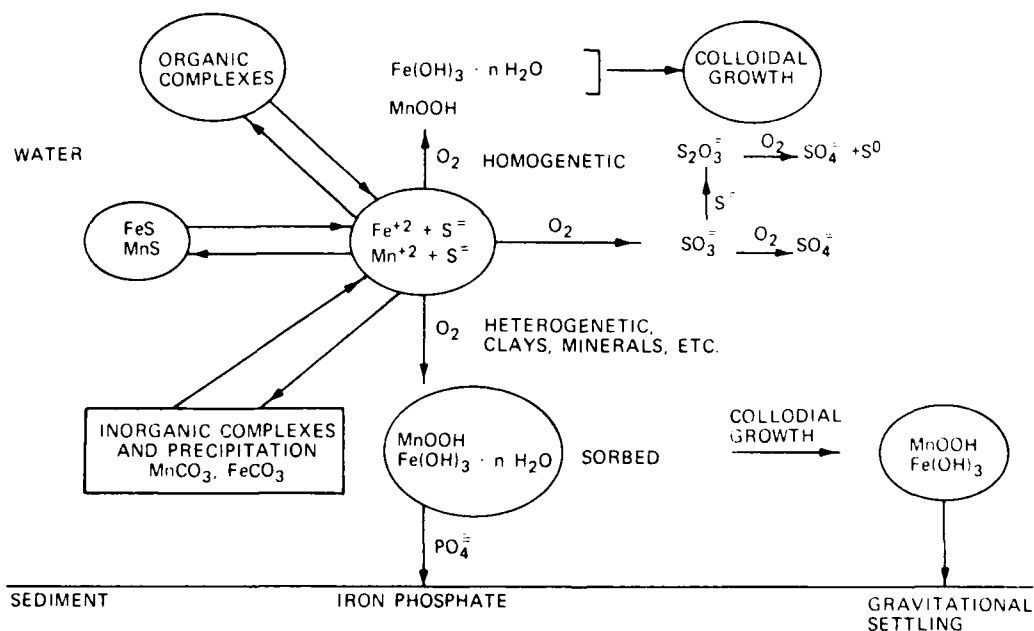
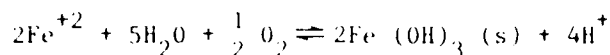


Figure 6. Outline of pathways of iron and manganese in aquatic environments

32. Introducing O_2 into an anoxic aquatic environment will result in the rapid oxidation of Fe^{+2} to its ferric form as outlined in the following expression:



This reaction is extremely sensitive to O_2 (Alexander 1961), and the stable metal bonding may be considered irreversible in an aerobic system. In an acid environment, where auto-oxidation of ferrous iron is not possible, the acidophilic microorganisms including Thiobacillus (Ferrobacillus) ferrooxydans can chemoautotrophically convert Fe^{+2} to Fe^{+3} . Many other heterotrophic iron- and manganese-oxidizing bacteria also contribute to the formation of iron and manganese oxides in lake sediments (Wetzel 1975). Under neutral conditions, the rate of ferrous iron oxidation is first order with respect to the concentrations of both ferrous iron and oxygen, and second order with respect to hydroxide (Ghosh 1974). Oxygenation kinetics of ferrous iron are reviewed and summarized by Sung and Morgan (1980) (see Table 1). The kinetic equation for ferrous iron oxidation is generally expressed (Stumm and Lee 1961, Morgan and Birkner 1966) as:

$$-\frac{d[\text{Fe(II)}]}{dt} = k [\text{Fe(II)}] [\text{O}_2] [\text{OH}^-]^2 \quad (3)$$

where

k = the oxidation rate constant

$[]$ = molar concentration or activity of substrate

t = time

Sung and Morgan (1980) proposed the following general rate law in carbonate buffered solutions when pH is less than 7:

$$-\frac{d[\text{Fe(II)}]}{dt} = k [\text{Fe(II)}] [\text{PO}_2] [\text{OH}^-]^2 \quad (4)$$

The variation of k with different alkalinities is due to differences in ionic strength and solution temperature.

33. The low solubility of iron oxides precludes high concentrations of iron in an aerated aqueous system. Thus, oxygenation of iron-enriched hypolimnetic water can significantly decrease solubility of ferrous iron (Symons et al. 1970).

34. The influence of pH and redox potential on the valence state and speciation of iron in a simple aqueous system is shown in Figure 7 (Krauskopf 1967). A marked interaction between redox potential and pH in controlling iron (Fe) solubility in soil solution systems was described by Patrick and Henderson (1981). High solubility of iron in an acidic aqueous system may have a great effect on Fe concentration in reservoir waters receiving acidic mine drainage. Ponnampetuma et al. (1967) confirmed ferric oxyhydroxide ($\text{Fe}(\text{OH})_3$) and ferrosferric hydroxide ($\text{Fe}_3(\text{OH})_8$) participation in redox equilibria in flooded soils. Van Breeman (1969) reported that the equilibrium between ferric and ferrous iron was largely governed by ill-defined ferric oxides which were intermediate in stability between amorphous $\text{Fe}(\text{OH})_3$ and lepidocrocite ($\gamma\text{-FeOOH}$).

35. At steady state in groundwater (Ghosh et al. 1966) or water with chemical additives, the Fe^{+2} oxidation rate k is estimated to be $2.01 \times 10^{10} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{day}^{-1}$ when the ionic strength was adjusted by NaClO_4 to 0.020 M (Sung and Morgan 1980) at 25°C . The mean residence time of Fe^{+2} varied from 4.3 to 54 minutes (Ghosh 1974) under aerobic conditions. Since most natural waters have alkalinities less than 300 mg/L as CaCO_3 , poor buffering capacity lowers the oxidation rate. Under acidic conditions ($\text{pH} = 3$), half-life time for ferrous iron oxidation is about 1000 days.

36. Surface ionization and complexation on ferrous hydroxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) (amorphous) and some hydrous oxides of metals at the oxide/water interface affect the absorption behavior of dilute heavy metal ions (Davis and Leckie 1978). This explains why the concentration of Fe^{+2} and Fe^{+3} must each exceed $10^{-15} \text{ M} \cdot \text{L}^{-1}/\text{L}$ (0.56 mg/L) to govern Eh (Coursier 1952). In a study of redox potential of the $\text{Fe}(\text{OH})_3 - \text{Fe}^{+2}$ system, Nhung and Ponnampetuma (1966) found that added $\text{Fe}(\text{OH})_3$ was stable in a flooded soil system when redox potential was above +200 mV.

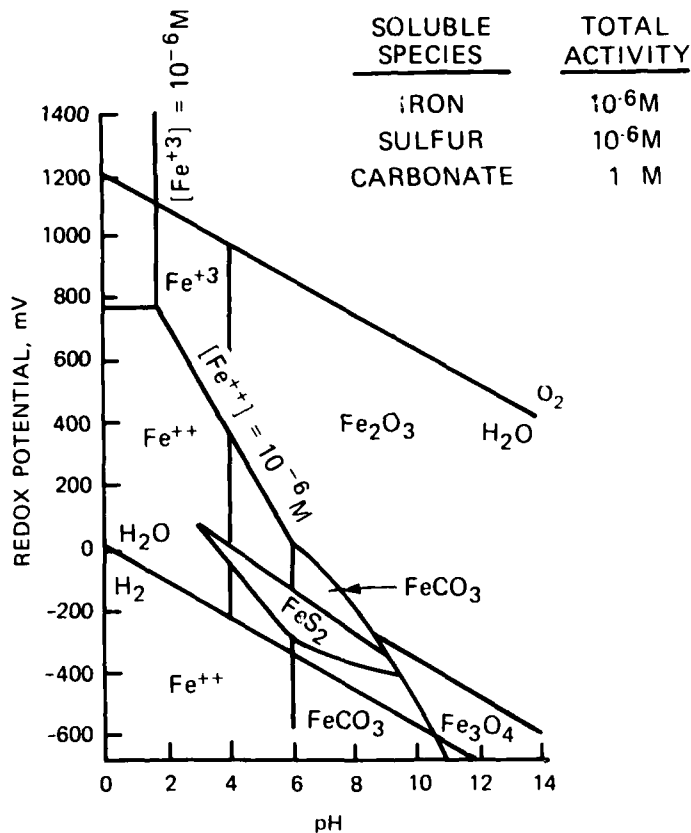
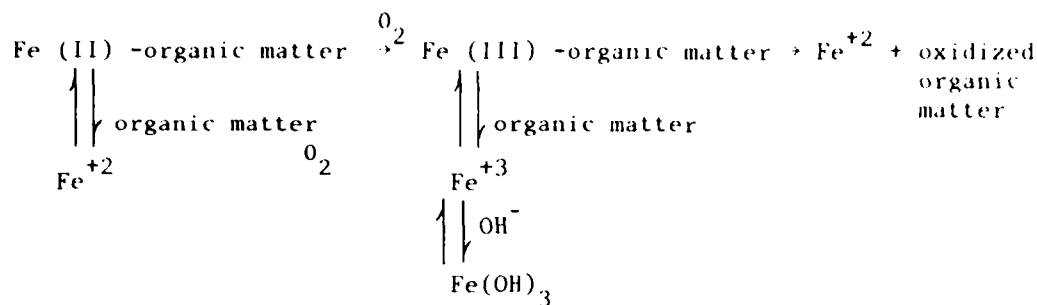
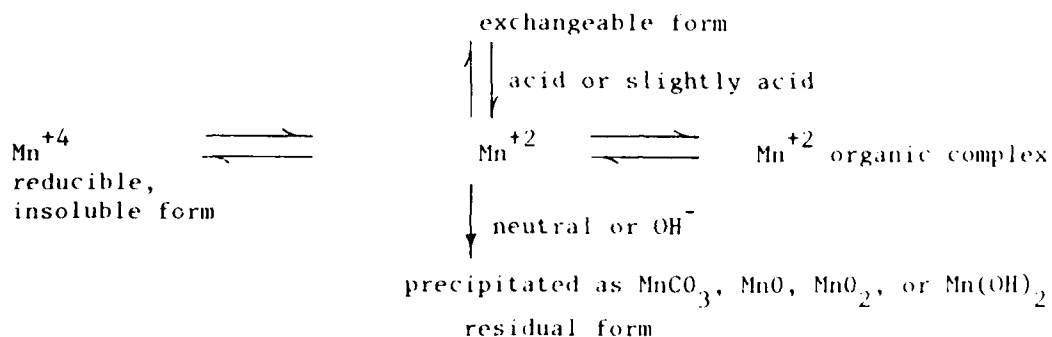


Figure 7. Redox potential-pH diagram indicating the stability field of common iron compounds (adapted from Krauskopf 1967, reprinted by permission of McGraw-Hill, Inc., N. Y.)

37. Organic matter and other decaying vegetation can retard oxidation of ferrous iron even when dissolved oxygen is present. In the presence of iron-organic matter complexation, the $Fe^{+2}-Fe^{+3}$ redox couple acts as an electron transfer catalyst for the oxidation of organic matter. Complexation of iron and organic matter increases as pH and the organic- Fe^{+2} ratio increase in aqueous systems (Theis and Singer 1974). The following diagram outlines the ferrous iron oxidation process in the presence of organic matter:



38. Manganese. Oxidation-reduction conditions and pH are two major factors that affect the distribution and solubility of manganese (Mn) in an aquatic environment. An outline of manganese redox pathways in an aqueous system can be expressed as



39. Under all pH conditions, water-soluble and exchangeable forms of Mn predominate in an anoxic aquatic environment. Compared with other metals, the organic-Mn complex is relatively unstable. Although Mn^{+2} , Mn^{+3} , and Mn^{+4} exist in natural environments, only Mn^{+2} and Mn^{+4} are important (Gotoh and Patrick 1972). Manganese is normally present in anoxic soil solutions as Mn^{+2} , MnHCO_3^+ and as organic complexes. The complex nature of chemical and microbial processes in natural aquatic environments makes it difficult to explain the behavior of manganese in terms of a simple chemical system.

40. Dissolved, reduced forms of Mn^{+2} accumulate in an anoxic hypolimnion, while very little soluble Mn is found in the oxidized surface water during summer stratification (Hutchinson 1957). Patrick and

Henderson (1981) concluded that soluble Mn is responsive to pH, but they showed no precipitation of Mn in a short-term oxidation study. The process of Mn^{+2} oxidation appears to be similar to that of iron, although occurring at a much slower rate. However, at low concentrations Mn^{+2} oxidation does not occur as readily as Fe^{+2} oxidation within the pH range of most natural waters. During or after destratification, soluble Mn^{+2} diffuses from reduced sediments to the oxygenated interface, is sorbed by Fe^{+3} and Mn^{+4} oxide hydrates, and is oxidized to produce Mn-enriched nodules (Ponnamperuma 1972). Since ferric oxides have a high sorption capacity for Mn^{+2} , it is likely that a considerable portion of the Mn can participate in the dissolved-particulate cycle without undergoing redox reactions.

41. Transformation of soluble Mn^{+2} in a CE reservoir (Eau Galle Reservoir, Wisconsin) were studied during 1980, and the results are presented in Figure 8. Manganese (II) was detected in Eau Galle Reservoir waters even when oxygen was present. Reduced manganese (II) was also observed in Lake Mendota, Wisconsin, waters concurrently with oxygen, by Delfino and Lee (1968). Destratification or aeration, which made more oxygen available, reoxidized most reduced Mn and Fe to insoluble oxides which were then deposited on the sediments. Oxidation of reduced manganese was also illustrated by the formation of black manganese dioxide (MnO_2) on rocks in the tailwaters of dams which release water from anoxic hypolimnia.

42. Products formed from the oxidation of Mn^{+2} under various pH conditions are nonstoichiometric and amorphous. Manganese (II) oxidation reaction rates are strongly pH-dependent. The average manganese oxidation state can be represented by $\text{MnO}_{1.90}$ (Morgan 1967) or by $\text{Mn}^{+2.3\sim 2.7}$ (Hem 1981; Emerson et al. 1982). The disappearance of reduced manganese in oxic conditions is an autocatalytic reaction in aqueous systems (Stumm and Morgan 1981). A solid phase able to absorb Mn^{+2} ions greatly accelerates the reaction by facilitating the surface electronic transfers from Mn^{+2} to Mn^{+4} . In the Cox Hollow Lake system, Wisconsin, about 40 to 50 percent of the hypolimnetic Mn^{+2} was associated with particulate matter in the entire anoxic water column.

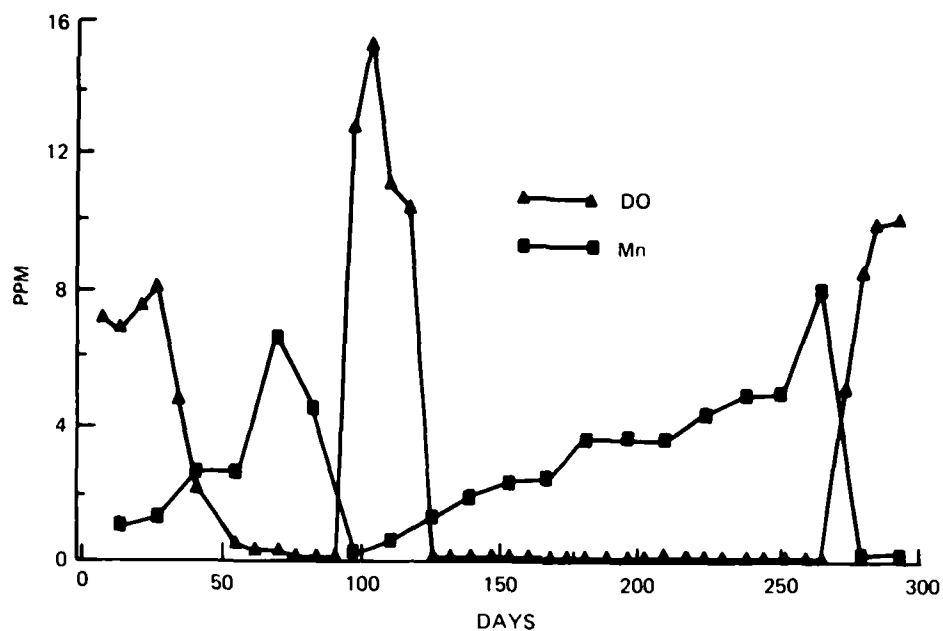


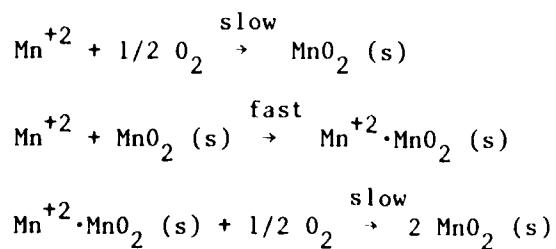
Figure 8. Changes in O_2 and soluble Mn concentrations with time in the overlying waters of a stratified CE reservoir

(Brezonik et al. 1969). In contrast to these findings, Delfino and Lee (1968) reported that the major portion of Mn in Lake Mendota was in the soluble form.

43. The kinetics of Mn^{+2} oxidation rate may be expressed as:

$$-\frac{d[Mn^{+2}]}{dt} = k_o [Mn^{+2}] + k [Mn^{+2}] [MnO_2] \quad (5)$$

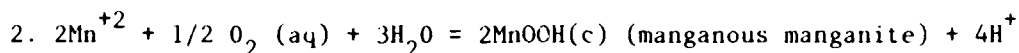
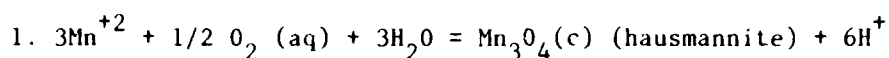
where k_o and k are rate constants. Stumm and Morgan (1981) summarized the rates of Mn^{+2} oxidation in an aqueous system as follows:



where s = solid. The relationship between Mn^{+2} oxidation rates and O_2 concentrations is the same as that of Fe^{+2} and O_2 concentrations, so k in Equation (5) can be formulated as:

$$k = k' [OH^-]^2 PO_2 \quad (6)$$

44. Oxidation pathways for reduced manganese in natural water was illustrated by Bricker (1965) and Hem (1981). The net process can be summarized as:



where c = precipitation. The reaction rate is then expressed as:

$$- \frac{d [Mn^{+2}]}{dt} = k_1 [Mn^{+2}] + k_2 A_{Mn \text{ ppt}} [Mn^{+2}] \quad (7)$$

where Mn^{+2} represents thermodynamic activity of dissolved unreacted manganese and $A_{Mn \text{ ppt}}$ represents the availability of reaction sites on the surface of the precipitated manganese oxide. Both hausmannite and manganous manganite further react to produce one of the forms of MnO_2 .

45. Formation of an organic-Mn complex can enhance colloid stability when hausmannite and manganous manganite settle from the oxic zone onto the surface of an anoxic sediment. Manganous manganese (Mn^{+2}) is removed from aerated water when it is oxidized to Mn oxides. Manganese (II) might also be adsorbed onto suspended particles such as particulate Mn or ferric oxides (Bewers and Yeats 1978), or incorporated into complex particulate matter matrices. Physical settling of these particulates would account for the observed loss of Mn from the water column and would slow oxidation rates. The main mechanisms for Mn^{+2} removal from aerated water are a combination of oxidative precipitation (Graham et al. 1976), sorption, and complexation reactions.

sulfide-sulfur-polysulfide cycle. Initial oxidation of sulfide to sulfur is a possible rate-determining step. Jørgensen et al. (1979) demonstrated that dissolved oxygen and H_2S could co-exist in the interface between oxygenated and sulfide-bearing waters.

48. Oxidation of sulfide in lake and reservoir environments is mainly biologically mediated, but chemical oxidation can occur (Engler and Patrick 1973). The reaction pathway shown previously is applicable only to chemical oxidation; biological sulfide oxidation to sulfur can eliminate the rate-determining step of initial sulfur formation. Both chemical and biological factors may subsequently play a significant role in further oxidation. Numerous attempts have been made in recent years to determine the kinetics of sulfide oxidation in freshwater systems. However, results of these investigations show considerable disagreement (Hoffmann and Lim 1979). Evidence indicates that sulfide oxidation rates are sensitive to trace metal catalysis by Mn^{+2} , Fe^{+2} , and other reduced metals (Chen and Morris 1972). Eventually the oxidation is also catalyzed by homogenous and heterogenous organo-metallic complexes in natural aquatic ecosystems (Hoffmann and Lim 1979). Oxidation of both sulfide and manganese can also be affected by the presence of kaolinite, montmorillonite, $\text{Fe}(\text{OH})_3 \cdot n \text{H}_2\text{O}$, and particulate organic matter.

49. An *in situ* study using a radioactive tracer technique indicates that sulfide is subject to rapid biological oxidation and has a half-life of 5-10 min, producing mainly sulfate and thiosulfate in the chemocline under both light and dark conditions (Jørgensen et al. 1979). The rate of oxidation to sulfate for intermediate compounds in sulfide oxidation is greater for $\text{S}_4\text{O}_6^{=}$, less for $\text{S}_2\text{O}_3^{=}$, and least for S^0 (Wainwright and Killham 1980). The kinetics of aqueous sulfide oxidation by O_2 is pH-dependent (Chen 1972), and oxidation is stimulated by the presence of NO_3^- (Wainwright and Killham 1980). The sulfide oxidation rate is slow under acidic conditions ($\text{pH} < 6$) where H_2S is the predominate species. The oxidation rate initially increases with pH and reaches a maximum at pH 8, then decreases to a minimum near pH 9; the rate increases again as pH increases to near 11, and decreases under more alkaline conditions.

Equilibrium Models Depicting Aerobic Processes

Water quality modeling

50. Use of the current version of the CE-QUAL-R1 water quality model indicated that its lack of generality and chemical orientation limited its use as a predictive tool for water quality in CE reservoirs. Other existing water quality models were reviewed and evaluated for their feasibility use as a subroutine for the CE-QUAL-R1 model to simulate the transformations of chemical constituents under various conditions normally found in CE reservoirs; the resulting single integrated model (CE-QUAL-R1 + aerobic subroutine) would be more useful than several overlapping models. As a consequence of a workshop on dissolved particulate interactions, the chemical equilibrium model MINEQL was initially selected as a basis for WES's aerobic chemical characterization. The REDEQL2-MINEQL-GEOCHEM series of related chemical equilibrium models can provide flexible and comprehensive approaches needed to study water quality in CE reservoir ecosystems, although a decision was made recently to develop a rate model for the aerobic subroutine in the CE-QUAL-R1 model (see paragraph 61). A brief discussion of these chemical equilibrium models is presented in the following section.

REDEQL2

51. REDEQL2 (McDuff and Morel 1975) is a computer program written in FORTRAN IV and is mainly used to calculate chemical equilibria in aqueous systems. The principal approach of the program is based on the Newton-Raphson method (Conte and deBoor 1972) for digital computation of chemical equilibrium. Chemical compounds or complexes in designated aqueous systems are expressed as functions of free metal and free ligand concentration. Equilibrium constants based on "critical stability constants" (Martell and Smith 1976-77) for each independent reaction are stored in the program to calculate rate-balance relationships. REDEQL2 (Ingle et al. 1978) has the data necessary to compute solubility and complexation reactions between 35 metals and 58 ligands. REDEQL2 can also calculate 24 standard couples of redox reactions; mixed solid reactions, such as chlorite, illite, microcline, and dolomite;

and adsorption and desorption of metal ions on metal oxides. A complete thermodynamic data deck includes a program of chemical equilibrium in aqueous systems incorporating a system of 788 soluble species, 83 possible solids, and a gas-phase component (Morel and Morgan 1972). REDEQL2 was applied by Hoffmann and Eisenreich (1976) to predict the relationship between Mn^{+2} and Fe^{+2} in the hypolimnion of a stratified southern Wisconsin lake and by Morel et al. (1975) to model the concentration of trace metals in wastewater discharge. REDEQL EPAK, a version of REDEQL2 including temperature correction for equilibrium constants, was developed recently by Ingle et al. (1980).

MINEQL

52. MINEQL was developed to provide a compact version of REDEQL2 for use with smaller computers; however, a full-size computer may be required to execute a larger scale program. MINEQL differs considerably from REDEQL2 in formatting, but applies much of the same information and definitions. Basically, the equilibrium constant method is used in MINEQL for chemical equilibrium problems of aqueous systems (Westall et al. 1976). Thermodynamic data stored in MINEQL's data file contain 35 metals and 58 ligands. Like REDEQL2, MINEQL can be used to study speciation of metals in algal culture media, solubility constants for metal chelates in complex media, degradation of nitrilotriacetic acid (NTA) in natural water, and chemical equilibria in aqueous solution (Westall et al. 1976, Morel et al. 1976).

GEOCHEM

53. GEOCHEM was initially developed to describe the soil solution system in its entirety. This computer program calculates the equilibrium speciation of the chemical elements in a soil solution based on chemical thermodynamics. GEOCHEM is a modified version of REDEQL2, containing more than twice as much thermodynamic data as REDEQL2; it utilizes thermodynamic data selected for soil systems and employs a different subroutine to correct thermodynamic equilibrium constants for the effect of nonzero ionic strength. Stored thermodynamic data include 36 metals and 69 ligands of interest in soil solutions.

54. Typical applications of GEOCHEM include: (a) predicting

the concentrations of inorganic and organic complexes of a metal cation in a soil solution, (b) calculating the concentration of a particular chemical form of a nutrient element in a solution bathing plant roots to correlate that form with nutrient uptake, (c) predicting the fate of a pollutant metal added to a soil solution of known characteristics, and (d) estimating the effect of changing pH, ionic strength, redox potential, water content, or the concentration of some element on the solubility of a chosen chemical element in a soil solution (Sposito and Mattigod 1979).

55. Although GEOCHEM identifies and quantifies many of the chemical species in a soil solution system, it is presently incapable of an all-inclusive definition of a particular soil solution because (a) information on the precise composition of soil solutions is lacking and (b) the GEOCHEM data base does not contain all the thermodynamic data needed to characterize the soil system.

Implication of chemical equilibrium models in aquatic environments

56. Although many computer models have been used to predict and manage water quality, lack of appropriate kinetic data limits the validation of ecological computer models. Development of chemical equilibrium models for water quality prediction appears to be relatively straightforward (Morel and Yeasted 1977); but construction of a complete kinetic model for a natural water system is exceedingly complex and is further complicated by the lack of kinetic information (Hoffmann 1981). Construction of comprehensive predictive models that describe natural water chemistry has to date proved impossible (Pankow and Morgan 1981) because of the complex and interdependent nature of the many processes occurring in natural waters. The complexity of natural ecosystems and their matter and energy inflows and outflows make closed-system equilibrium models only poor approximations of a natural aquatic environment (Morgan 1967).

57. Based on an updated compendium of stability constants (Martell and Smith 1976-77) and on the extensive experimental data from research studies on the changes in iron and manganese concentrations

during thermal stratification in a highly productive dimictic lake (Lake Mendota), Hoffmann and Eisenreich (1976) have successfully verified the capability of a chemical equilibrium model, a modified version of REDEQL2, to predict unusual seasonal transformations of these elements in the hypolimnetic water. Although application of the equilibrium model is limited by the reliability of available equilibrium constants, this revised model is capable of reproducing reasonably well the actual time-dependent concentrations of Fe and Mn in the hypolimnion of Lake Mendota during summer stratification (Hoffmann and Eisenreich 1981).

58. Application of equilibrium models such as REDEQL2 and GEOCHEM to analyses of biogeochemical interactions between nutrients and microorganisms in aquatic environments was demonstrated by Giammatteo et al. (1980). They showed that chemical equilibrium models can be used to isolate variables and reaction systems. Nevertheless, predictions of chemical equilibrium models are probably not sufficient to interpret biogeochemical processes in natural environments. Zimmerman (1980) examined the feasibility of using REDEQL2 to predict lead and phosphate transformations and the effect of pH on the availability of these elements in an aquatic environment. Zimmerman acknowledged that unknown reaction kinetics were the primary problem in applying equilibrium calculations; he noted, however, that reasonable agreement between equilibrium predictions and actual chemical speciations was indicated by solid formation when some of the initial assumptions were modified to account for slow reaction rates.

59. In spite of limited chemical and kinetic information, chemical equilibrium models still provide a useful technique to examine the effects of chemical interactions in aquatic environments (Freedman et al. 1980). Currently, chemical equilibrium models have been widely applied to evaluate the effect of toxicity assays (Jackson and Morgan 1978) and to analyze biogeochemical processes of trace metals in aquatic environments (Westall 1977, Sibley and Morgan 1977, Morel et al. 1975, Morgan and Sibley 1975). Potential utility of GEOCHEM in aquatic environments was also demonstrated by Sposito et al. (1980). Sposito (1981) used the program to calculate the equilibrium speciation in acid

precipitation and to predict the behavior of soluble metals in natural water contaminated by municipal wastes. Chemical equilibrium models can also be used to predict the interaction of heavy metals between solution and solid phase with changes in pH (Theis and Richter 1979). In general, these models are powerful tools for predicting chemical interactions of trace metals with liquids and particulate surfaces and competition among metals in natural waters (Vuceta and Morgan 1978).

60. The practicality of using chemical equilibrium models has been evaluated recently by Nordstrom et al. (1980). Their study indicated good agreement between model predictions and measured data for major chemical species in both freshwater and seawater systems. The poor agreement found for the minor species is probably due to differences in the thermodynamic data bases used by various equilibrium models. Nordstrom et al. (1980) reviewed over 30 chemical equilibrium models and concluded that a great deal of caution must be exercised when applying an equilibrium chemical approach to interpret aquatic chemistry. Research investigation must evaluate activity coefficient calculations, redox assumptions, temperature corrections, alkalinity corrections, and other environmental corrections required for thermodynamic considerations to provide a consistent set of values.

61. The chemical equilibrium models such as MINEQL and GEOCHEM, based on thermodynamics and used to calculate chemical equilibria in aqueous systems and soil solutions, have had rather limited success in predicting seasonal changes and chemical speciation of a few elements. In natural water systems, equilibrium models are generally unable to adequately predict biogeochemical processes. This is especially true during the transition from anaerobic to aerobic conditions in reservoirs when reaction kinetics become exceedingly important. In such a situation, rate models which rely on kinetic data are a better choice for accurately predicting water quality.

PART III: RE-AERS--REAERATION SUBROUTINE

62. Natural destratification or mechanical introduction of oxygen into anoxic aquatic environments rapidly reoxidizes some reduced chemicals such as sulfide and ferrous iron dissolved or suspended in the water column. Other oxidation processes such as nitrification or manganous manganese oxidation proceed slowly.

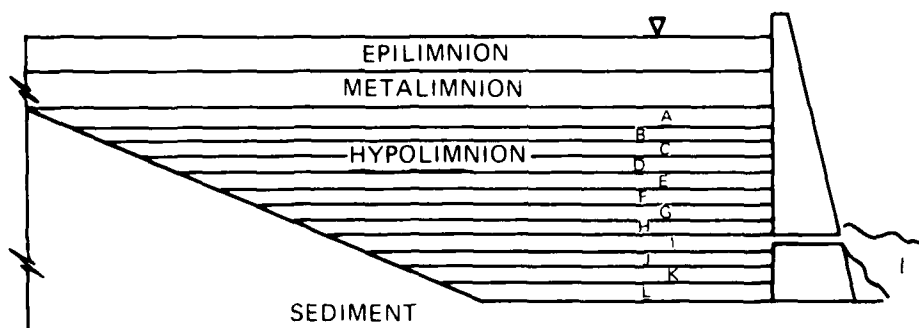
63. This section of the report describes the basic structure of the aerobic model RE-AERS, or REAERation Subroutine. The overall organization of the model, its various components, and integration of these components are discussed below.

Model Organization and Function

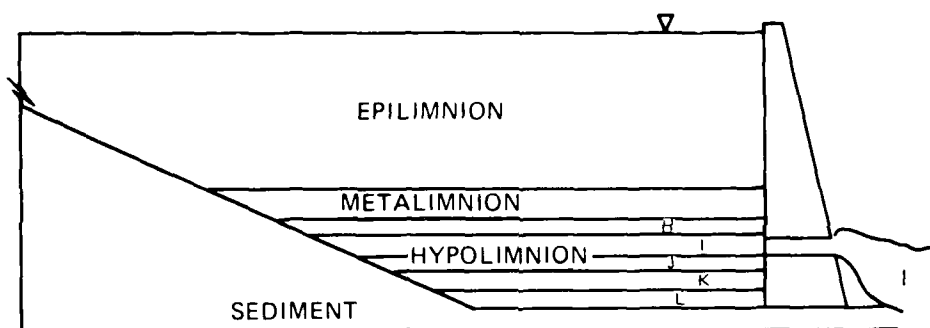
64. The manner in which RE-AERS functions is depicted in Figure 9. In many reservoirs, thermal stratification starts and continues from late spring, and anaerobic conditions develop in each water layer in the hypolimnion (Figure 9a) in the sequence proposed by Gunnison and Brannon (1981). Before destratification or artificial aeration, hypolimnetic discharges contain dissolved, reduced manganese and iron, ammonium, and trace amounts of other reduced chemical species. Due to prolonged oxygen depletion and the large requirement for oxidizable carbon sources, the topmost layer of the hypolimnion in most reservoirs probably will not proceed beyond accumulation of NH_4^+ or Mn (II) (Gunnison and Brannon 1981). Methanogenesis will probably never be found above the bottom sediment layers, except in water directly under the water-sediment interface (Figure 9a).

65. In the early stages of destratification, a decrease in surface temperature increases the density of surficial water which sinks and penetrates the metalimnion. Destratification occurs when the depth of the epilimnion increases as the depth of the hypolimnion decreases (Figure 9b). The metalimnion is lowered as a result.

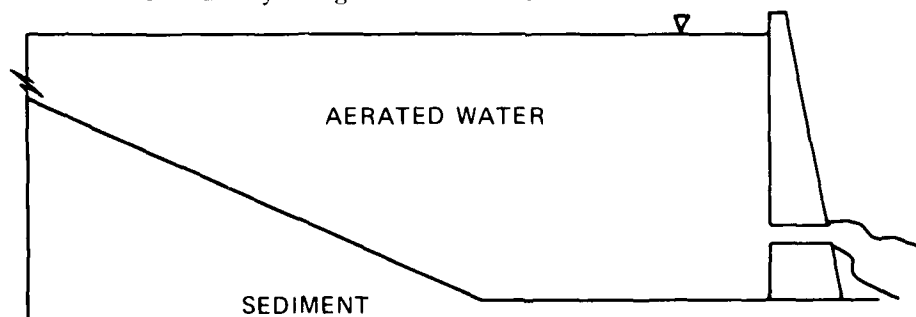
66. As the reservoir gradually cools, vertical water circulation increases until all lake waters are included in the circulation, and



- a. In the stage of stratification, DO is depleted and reduced forms of elements accumulate in the hypolimnion



- b. Early stage after destratification starts



- c. Completion of destratification: well-mixed overlying water column with adequate levels of DO

Figure 9. Thermal stratification cycle

fall turnover begins. During the initial stages of destratification, surface water that is close to oxygen-saturation circulates deeper into the hypolimnion. When circulation is complete, the water remains saturated with oxygen at temperature-dependent levels (Figure 9c). High concentrations of dissolved oxygen are observed in the entire water column (near 100 percent saturation or supersaturation) during cooler months.

67. Mechanically introducing and circulating oxygen usually improves dissolved oxygen levels in a stratified reservoir. For total circulation, the cold, anoxic hypolimnion is mixed with the warmer epilimnion to increase oxygen levels in bottom water; an entire water body can be circulated and aerated from a single site, and a lake will eventually attain a near-isothermal temperature regime. Total circulation may, however, completely eliminate the reservoir as a habitat for cold-water fish during the summertime as the bottom water temperature approaches the temperature of surface water. Hypolimnetic aeration, on the other hand, improves dissolved oxygen conditions in bottom water without disrupting thermal stratification (Figure 10); but because oxygen transfer is limited to the bottom water interface with most hypolimnetic aerators, oxygenation rate is slower and operation cost is higher than that of total circulation. Dissolved oxygen concentration in anoxic bottom water can usually be increased to approximately 5-6 mg/L by hypolimnetic aeration.

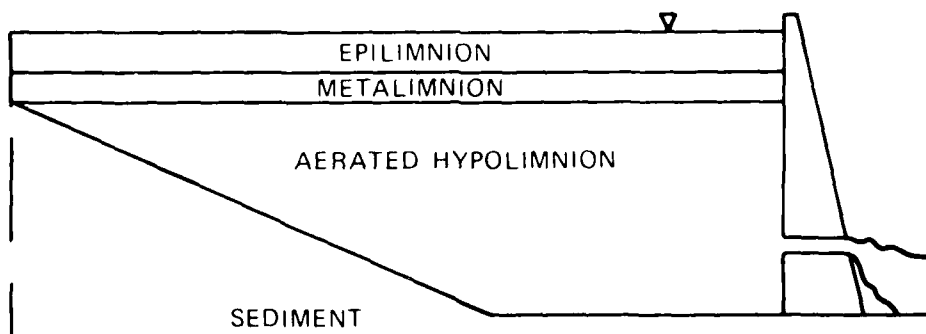


Figure 10. After hypolimnetic aeration: thermal stratification continues in the reservoir; hypolimnion DO level is maintained at approximately 5-6 mg/L.

68. RE-AERS consists of a limited number of phases that simulate the continuum of anoxic or oxic conditions in the hypolimnion. The model reflects aerobic stages that occur with aeration (e.g., natural destratification, hypolimnetic aeration, and total circulation).

Natural destratification

69. Beginning of loss of stratification. This phase begins at the onset of loss of stratification in late summer or fall when air temperatures begin to decline. During destratification, convection currents and epilimnetic circulation expand the thickness of the oxygen-bearing epilimnion. The decomposition rate of organic matter increases, and reduced chemical components originally in the top layer of the anoxic hypolimnion are oxidized. The water column above the metalimnion remains nearly saturated with oxygen.

70. Turnover. Turnover begins when the entire volume of lake water begins to circulate during the transition from summer stratification to circulation which can occur in a few hours, days, or weeks depending upon wind velocity, temperature gradient, reservoir depth, reservoir hydrodynamics, and other environmental factors.

Mechanical aeration

71. Destratification may begin when mechanical circulation is initiated. Mechanical destratification lifts cold, anoxic, hypolimnetic water to the surface, mixing it with the warmer, oxygenated, epilimnetic water. The new equilibrium depth for oxygen and the rate of oxygenation depends on the capacity of the mechanical circulator, oxygen supply rate, and rate of oxygen demand of the reservoir. Aerobic decomposition of organic matter and the chemical and/or biological oxidation of reduced constituents begin in the aerated water column. Having an isothermal re-aerated water column means that equilibrium constants and activity coefficients do not require temperature correction in an equilibrium model (Ingle et al. 1980).

Hypolimnetic aeration

72. Oxidation processes and aerobic decomposition of organic matter initially occur only in aerated hypolimnetic water. The temperature of the hypolimnion increases approximately to 0.6-1.1°C above

normal as it is partially mixed with the thermocline. Occasionally, metalimnetic oxygen levels are unstable during aeration. A zone of low dissolved oxygen or even anoxic conditions may occur near the metalimnion. The level of the metalimnion also drops as water is transferred from the hypolimnion to the metalimnion and epilimnion.

Interrelationships Among Reduced Chemicals as the Anoxic Water Column Is Aerated

73. Different phases in RE-AERS are based on (a) the pH range over which the phase is functional, (b) the DO concentration, (c) a summary of the sequences of major events, (d) diagrams (see Figures 11 and 12) which depict the major chemical components and interactions, (e) a tabulation of the processes represented by each of the arrows in the diagrams, and (f) a list of algorithms which summarize the various processes operative on each component shown in the diagrams. The boxes surrounding each component indicate whether that component is barely detectable (dashed line), increases in concentration (double lines), or is in relative equilibrium (single line).

Initial conditions: Anoxic
hypolimnion before aeration

74. The pH range over which the phase is functional is 6.6 to 7.4; the Eh is approximately +50 mV or below; the DO concentration in water is 0 mg/L.

75. Synopsis of initial conditions. In an anoxic hypolimnion, the redox potential has dropped to approximately +50 mV or lower during the course of stratification. Nitrate was totally exhausted followed by accumulation of dissolved ammonium and manganese (II) in hypolimnetic waters. Iron was then actively reduced and accumulated in hypolimnetic waters, as did inorganic phosphates that were released when ferrous iron was reduced. Sulfide can then be released from highly reduced sediments where it may react with ferrous iron in the water column and form highly insoluble ferrous sulfide. Sulfate can also be transported into the hypolimnion via inflowing water, or be produced by the decomposition of

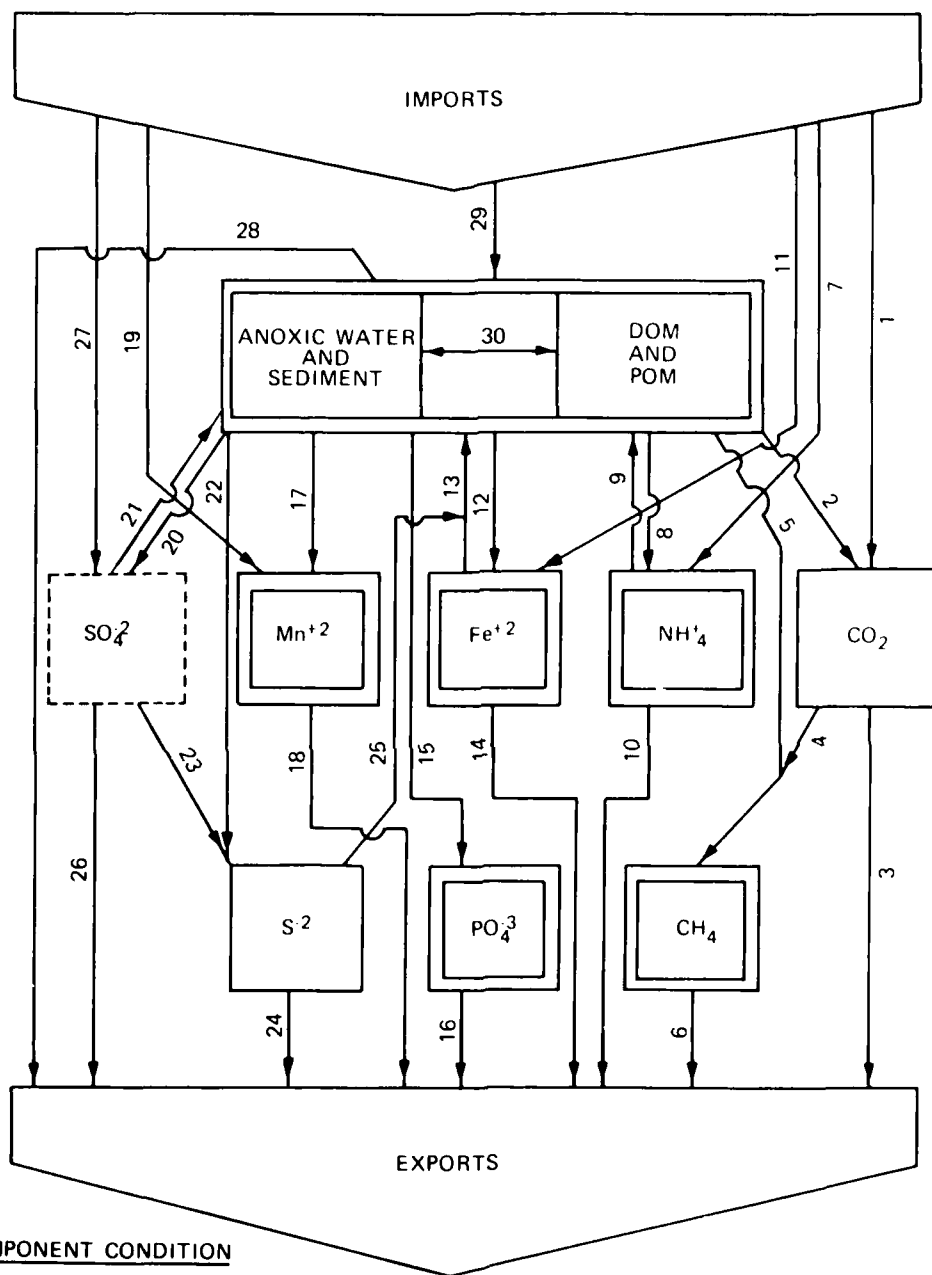


Figure 11. Major chemical changes and pathways associated with anaerobic conditions in the hypolimnion

sulfate associated with organic matter; this sulfate can then be reduced to sulfide which can also react with soluble ferrous iron to form insoluble ferrous sulfide. Anaerobic microorganisms then can use carbon dioxide to form methane. In hypolimnetic waters, ammonium, soluble reduced manganese, ferrous iron, and phosphate continue to be accumulated, as their presence in the tailwaters of projects with hypolimnetic withdrawals indicates. Suspended ferrous sulfide may also be present.

76. Summary of processes. Figure 11 presents the components and pathways of importance for anaerobic conditions in the hypolimnion. Arrows in Figure 11 are explained below:

Arrow No.	Processes Represented by Arrow
1	Import of dissolved carbon dioxide (as HCO_3^-)
2	Diffusion of dissolved CO_2 (HCO_3^-) from sediment
3	Export of dissolved CO_2 with outflows
4	Reduction of CO_2 to CH_4
5	Release of methane to the water layer from sediment in underlying anoxic water layer
6	Export of methane from system, primarily as rising bubbles of gas
7	Import of ammonium with inflow
8	Diffusion of ammonium from sediment, interstitial water or anoxic water layer beneath the water layer of concern into overlying water
9	Immobilization of ammonium
10	Export of ammonium in outflows
11	Import of reduced iron with inflow
12	Diffusion of dissolved reduced (mostly chelated) iron

(Continued)

Arrow

- | No. | Processes Represented by Arrow |
|-----|--|
| 13 | Precipitation of ferrous iron from water layer of concern to sediment |
| 14 | Export of dissolved reduced iron in outflows |
| 15 | Release of dissolved inorganic phosphate from sediment interstitial water into water layers of concern (two major mechanisms for producing dissolved inorganic PO_4^{-3} are desorption of occluded and nonoccluded inorganic PO_4^{-3} from sediment and mineralization of organic PO_4^{-3} to inorganic PO_4^{-3} in sediments) |
| 16 | Export of dissolved inorganic phosphate with outflows |
| 17 | Diffusion of reduced manganese from sediment into water layer of concern |
| 18 | Export of dissolved reduced manganese with outflows |
| 19 | Import of dissolved reduced manganese with inflows |
| 20 | Release of inorganic sulfate from anaerobically decomposing organic sulfate |
| 21 | Diffusion of dissolved inorganic sulfate into sediment or underlying anoxic water layers |
| 22 | Diffusion of dissolved inorganic sulfide from sediment or underlying anoxic water layer |
| 23 | Reduction of sulfate to sulfide |
| 24 | Export of dissolved sulfide with outflows and advection |
| 25 | Precipitation of dissolved sulfide to sediment or underlying anoxic water layer as a consequence of the formation of insoluble ferrous sulfide |
| 26 | Export of dissolved inorganic sulfate in outflows |
| 27 | Import of dissolved inorganic sulfate with inflows |
| 28 | Export of dissolved and particulate organic matter and sediment (suspended) with outflows |

(Continued)

Arrow No.	Processes Represented by Arrow
29	Import of dissolved and particulate organic matter and settling the suspended solid into the sediment-water system
30	Interchange of dissolved organic matter between sediment and interstitial water

77. Algorithms summarizing the various processes operative on each component in Figure 11 are given below:

Component	Factors Influencing Change of Concentration of Components
	<u>Dissolved</u>
dO_2/dt	= 0. DO concentration = 0 mg/L
dNH_4^+/dt	= Inflows + Release from Sediment or Underlying Water Layer + Ammonification - Outflows* - NH_4^+ (Biological Uptake + Diffusion into Overlying Layer)
dNO_2^-/dt	= 0. NO_2^- concentration = 0 mg/L
dNO_3^-/dt	= 0. NO_3^- concentration = 0 mg/L
$dDOM/dt$	= Inflows + Sediment Release + DOM (Particulate Organic Matter (POM) Decay) - Outflows - DOM (Dissolved Organic Matter Decay)
dCO_2/dt	= Inflows + CO_2 (Diffusion from Underlying Sediment or Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay) - Outflows - CO_2 (Carbonate Formation + Diffusion to Overlying Water Layer)
dPO_4^{3-}/dt	= Inflows + PO_4^{3-} (Dissolved Organic PO_4^{3-} Decay + Particulate Organic PO_4^{3-} Decay + Biological PO_4^{3-} Release) - Outflows - PO_4^{3-} (Formation of Particulates + Biological PO_4^{3-} Uptake) + Desorption of PO_4^{3-} from Particulate Matter

(Continued)

* Present in outflows.

Factors Influencing Change
of Concentration of Components

Dissolved (Continued)

$$\begin{aligned} dSO_4^{-2}/dt &= \text{Inflows} + SO_4^{-2} \text{ (Dissolved Organic Sulfate Decay +} \\ &\quad \text{Particulate Organic Sulfate Decay)} - \text{Outflows} - \\ &\quad SO_4^{-2} \text{ (Biological Uptake) - Sulfate Reduction} \\ dMn^{+2}/dt &= \text{Inflows} + Mn^{+2} \text{ (Diffusion from Sediments or Anoxic} \\ &\quad \text{Water Layers + Dissolved Organic Matter Decay +} \\ &\quad \text{Particulate Organic Matter Decay + Reduction of} \\ &\quad Mn^{+4} \text{ in Suspended Particulate Matter)} - \text{Outflows}^* - \\ &\quad Mn^{+2} \text{ (Biological Uptake + Diffusion to Overlying} \\ &\quad \text{Water + Formation of Insoluble Precipitates)} \\ dFe^{+2}/dt &= \text{Inflows} + Fe^{+2} \text{ (Diffusion from Sediment or Anoxic} \\ &\quad \text{Water Layers + Dissolved Organic Matter Decay +} \\ &\quad \text{Particulate Organic Matter Decay + Reduction of} \\ &\quad Fe^{+3} \text{ in Suspended Particulate/Colloidal Inorganic} \\ &\quad \text{Matter)} - \text{Outflows}^* - Fe^{+2} \text{ (Biological Uptake +} \\ &\quad \text{Diffusion to Overlying Water Layer + Formation of} \\ &\quad \text{Insoluble Precipitates (S}^{-2}\text{))} \\ dS^{-2}/dt &= S^{-2} \text{ (Diffusion from Sediment or Anoxic Water Layers +} \\ &\quad \text{Dissolved Organic Matter Decay}^{**} + SO_4^{-2} \text{ Reduction)} \\ &\quad - \text{Outflows}^* - S \text{ (Biological Uptake + Diffusion to} \\ &\quad \text{Overlying Water Layer + Formation of Insoluble} \\ &\quad \text{Precipitates)} \\ dCH_4/dt &= CH_4 \text{ (Diffusion from Sediment or Anoxic Water Layers} \\ &\quad + CH_4 \text{ (Methanogenesis) - Outflows}^* - CH_4 \text{ (Diffu-} \\ &\quad \text{sion to Overlying Water Layer)} \end{aligned}$$

Particulate

$$dPOM/dt = \text{Inflows} + POM \text{ (Settling from Overlying Water Layer)} \\ - \text{Outflows}^* - POM \text{ (Particulate Organic Matter Decay} \\ + \text{Settling to Underlying Water or Sediment Layer)}$$

(Continued)

* Present in outflows.

** Sulfhydryl groups that can be released as S^{-2} or SH^{-} , but cannot be oxidized due to lack of O_2 .

Factors Influencing Change
of Concentration of Components

Component

Particulate (Continued)

$$\begin{aligned} dPIM/dt = & \text{Inflows} + PIM (\text{Settling from Overlying Water Layer}) \\ & - \text{Outflows}^* - PIM (\text{Settling to Underlying Water} \\ & \text{or Sediment Layer} + \text{Particulate Inorganic Matter} \\ & (PIM) \text{ Decomposition}) \end{aligned}$$

* Present in outflows.

Aeration

78. Hypolimnetic water under initial conditions subjected to aeration should maintain a pH range of 6.3 to 7.5, an Eh above + 400 mV, and a DO concentration of approximately 5-6 mg/L or more. Formation of an oxidized layer on the sediment surface indicates the completion of aerobic mixing.

79. Synopsis of aeration. Mechanical circulation of the water column disturbs the reservoir and maintains a uniform dissolved oxygen content in the overlying water (approximately 5-6 mg/l) throughout the destratified reservoir. The upper sediment layer becomes oxidized when aerated water reaches the bottom layer of water. The sediment below the thin oxidized layer remains anoxic. Diffusion of reduced constituents from anoxic sediments to the overlying water through the oxidized surficial sediments is minimal.

80. Oxidation reactions of reduced chemicals begin soon after aeration of the hypolimnion. Formation of oxidized chemical forms is soon limited by depletion of the remaining reduced chemicals. Products of oxidation remaining in the water are subject to further reactions. Some soluble form of oxidized products, such as NO_3^- , will diffuse and interact with highly reduced sediment and undergo denitrification and/or reduction via microbial assimilation with a possible net loss of nitrogen.

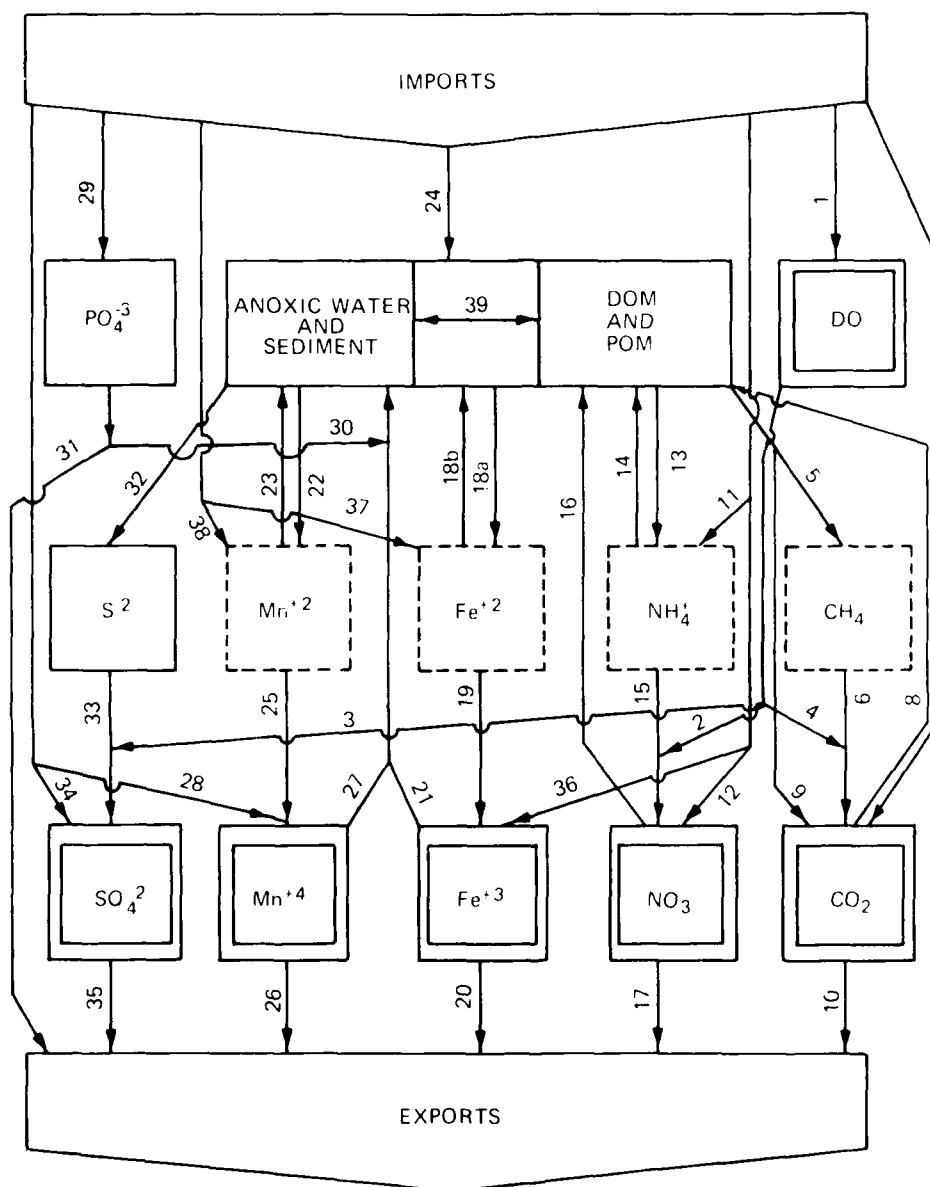
81. Simultaneous nitrification in the aerated hypolimnion rapidly replenishes any nitrate lost by diffusion or flushing. On the other hand, even when inorganic phosphate is added to a reservoir by inflows,

the concentration of phosphate in the water column is depleted by dilution because of precipitation or coprecipitation, mainly with Fe^{+3} . Sulfate accumulates as dissolved sulfate flows in, or as sulfide is released by organic matter, or as FeS on surface sediment is oxidized. Carbon dioxide accumulation results mainly from decomposition of organic matter and methane oxidation; however, respiration from aquatic plants may also contribute significant amounts of CO_2 to the system. Chemical oxidation of reduced iron in anoxic water normally yields poorly soluble ferric oxides and hydroxides or iron phosphates that precipitate onto the sediment; thus, concentrations of dissolved iron are relatively low in surface water. Reduced manganese undergoes an oxidation process similar to that of iron, but reaction rates are slower than those of iron in aerated water; reduced manganese may be chemically oxidized when the hypolimnion is oxygenated. Hydrolysis and/or organic complexation of oxidized manganese (IV) enhances colloidal stability as manganese settles onto and is incorporated into organic matrices. Oxidizing agents convert S^{-2} to elemental sulfur (S^0) which can be further oxidized to sulfate; oxidation of reduced sulfide to sulfate is mainly biologically mediated in aerated waters.

82. Summary of processes. Figure 12 presents the components and pathways of importance for the oxidation phase. Arrows in Figure 12 are explained below.

Arrow No.	Processes Represented by Arrow
1	Import of DO with inflows, circulation, mechanical aeration
2	O_2 requirement for nitrification (NH_4^+ O_2 NO_2^- O_2 NO_3^-)
3	O_2 requirement for sulfide oxidation
4	O_2 requirement for methane oxidation
5	Release of methane from sediment to overlying water column
6	Methane oxidation
7	Import of dissolved carbon dioxide (predominantly as HCO_3^-) with inflows

(Continued)



COMPONENT CONDITION

- BARELY DETECTABLE
- === CONCENTRATION INCREASES
- IN RELATIVE EQUILIBRIUM

Figure 12. Major chemical changes and pathways associated with the destratification period in an anoxic hypolimnion

Arrow No.	Processes Represented by Arrow
8	Photosynthesis by algae in sediment
9	Diffusion of carbon dioxide from sediment into water layer of concern
10	Export of dissolved carbon dioxide (as HCO_3^-) with outflows
11	Import of ammonium with inflows
12	Import of nitrate and nitrite with inflows
13	Diffusion of mineralized ammonium from sediment to water layer of concern
14	N immobilization and fixation
15	Nitrification
16	Nitrate reduction
17	Export of nitrate and nitrite with outflows
18a	Release of reduced dissolved iron from anoxic sediment to overlying water column
18b	Precipitation of reduced iron to sediment as a consequence of organic and inorganic complexation
19	Homogenetic and heterogenetic oxidation of ferrous iron to ferric iron
20	Export of ferric iron with outflows
21	Colloidal growth of ferric iron followed by adsorption and/or settlement onto sediment as $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$
22	Release of dissolved reduced manganese from anoxic sediment to overlying water column
23	Precipitation of reduced manganese (Mn^{+2}) to sediment as a consequence of organic and inorganic complexation
24	Import of dissolved organic particulate matter and settling of the suspended solids into the sediment-water system

(Continued)

Arrow No.	Processes Represented by Arrow
25	Oxidation of manganous manganese
26	Export of manganese (Mn^{+4}) with outflows
27	Colloidal growth of manganese followed by adsorption and/or settlement onto sediment as $MnOOH$
28	Import of manganese with inflows
29	Import of dissolved phosphate with inflows
30	Formation of iron (ferric) phosphate (ppt)
31	Export of dissolved phosphate with outflows
32	Diffusion of dissolved inorganic sulfide out of sediment
33	Oxidation of sulfide to sulfate
34	Import of dissolved inorganic sulfate with inflows
35	Export of dissolved inorganic sulfate with outflows
36	Import of suspended inorganic and organic ferric compounds with inflows
37	Import of soluble reduced ferrous iron with inflows
38	Import of soluble reduced Mn^{+2} with inflows
39	Interchange of dissolved organic matter between sediment and interstitial water

83. Algorithms summarizing the various processes operative on each component in Figure 11 are given below.

Component	Factors Influencing Change of Concentration of Components
dDO/dt	= Inflows + Aeration rate - Outflow - DO (Nitrification + DOM Decay + Particulate OM decay + Sulfate Formation + Methane Oxidation + Fe^{+2} Oxidation + Mn^{+2} Oxidation + BOD + Sediment Organic Decay)

(Continued)

Component	Factors Influencing Change of Concentration of Components
$d\text{NH}_4^+/\text{dt}$	= Inflows + Diffusion from Sediment or Adjacent Water Layers + Ammonification - NH_4^+ (Conversion of NH_4^+ to Nitrite or Nitrate + Plant Uptake + Diffusion into Adjacent Water Layers + NH_4^+ Immobilization + NH_4^+ fixed on Clay Minerals)
$d(\text{NO}_3^- + \text{NO}_2^-)/\text{dt}$	= Inflows + Nitrification - Outflows - NO_3^- (Nitrate Reduction + Plant Uptake + Diffusion to Adjacent Water Layers or Sediments)
$d\text{DOM}/\text{dt}$	= Inflows + Sediment Release + DOM (Particulate Organic Matter Decay) - Outflows - DOM (DOM Decay + Precipitation and Complexation with Metals)
$d\text{CO}_2/\text{dt}$	= Inflows + CO_2 (Diffusion from Sediment or Adjacent Water Layers + Organic Matter Decay + Methane Oxidation) - Outflows - CO_2 (Diffusion into Adjacent Water Layers + Carbonate Formation + Biological Uptake)
$d\text{CH}_4/\text{dt}$	= CH_4 (Diffusion from Underlying Anoxic Sediment or Water) + Methanogenesis - Outflows - CH_4 (Oxidation + Diffusion to Adjacent Water Layers or Sediment)
	Dissolved
$d\text{Fe}^{+2}/\text{dt}$	= Inflows + Fe^{+2} (Diffusion from Adjacent Anoxic Water Layers and Sediment + Organic Matter Decay) - Fe^{+2} (Oxidation of Fe^{+2} + Formation of Insoluble Complex + Biological Uptake) - Outflows
$d\text{Fe}^{+3}/\text{dt}$	= Inflows + Fe^{+3} (Oxidation of Fe^{+2} + Diffusion from Adjacent Aerated Water Layers + Organic Matter Decay) - Outflows - Fe^{+3} (Formation of Insoluble Complexes + Settling to Underlying Water Layers or Sediment)
$d\text{Mn}^{+2}/\text{dt}$	= Inflows + Mn^{+2} (Diffusion from Adjacent Anoxic Water Layers or Sediment + Organic Matter Decay) - Outflows - Mn^{+2} (Biological Uptake + Diffusion to Adjacent Water Layers or Sediment + Oxidation to (Continued))

Component	Factors Influencing Change of Concentration of Components
Dissolved (Continued)	
dMn^{+2}/dt (Cont)	Mn^{+4} Formation of Insoluble $MnCO_3$ and other Organic Complexes)
dMn^{+4}/dt	= Inflows + Mn^{+4} (Oxidation of Mn^{+2} + Diffusion from Adjacent Aerated Water Layers) - Outflows - Mn^{+2} (Sorption on Clay Minerals + Settling onto Sedi- ment or Underlying Water Layers by Colloidal Growth)
dPO_4^{-3}/dt	= Inflows + PO_4^{-3} (Organic Matter Decay + Desorption from Sediment or Suspended Particle + Biological Release of PO_4^{-3}) - Outflows - PO_4^{-3} (Formation of Insoluble Precipitates with Fe^{+3} + Biological Uptake)
dS^{-2}/dt	= Inflows + S^{-2} (Diffusion from Adjacent Anoxic Sedi- ment or Water Layers + Anaerobic Organic Matter Decay) - Outflows - S^{-2} (Sulfide Oxidation + Biological Uptake + Diffusion to Adjacent Water Layers + Formation of Insoluble Precipitates with Metals)
dSO_4^{-2}/dt	= Inflows + SO_4^{-2} (Aerobic Organic Matter Decay + Oxidation of Sulfide + Diffusion from Adjacent Aerated Water Layers) - Outflows - SO_4^{-2} (Diffusion to Adjacent Water Layers) - SO_4^{-2} (Biological Up- take + Formation of Insoluble Precipitates)
Particulate	
$dPOM/dt$	= Inflows + POM (Settling from Overlying Water Layers + Immobilization) - Outflows - POM (Organic Matter Decay + Settling to Underlying Water Layer or Sediment)
$dPIM/dt$	= Inflows + PIM (Settling from Overlying Water Layer + Formation of Insoluble Complexes) - Outflows - PIM (Settling to Underlying Water Layer or Sediment + Decomposition of PIM)

PART IV: EVALUATION OF RELEVANT RATE DATA

84. There is only limited information available regarding aerobic processes in man-made impoundments. However, there is considerable information on natural destratification in freshwater lake systems. The range of data for various aerobic processes is shown in Table 2. These processes are site specific; values for nonreservoir systems are included only if data for particular processes in reservoirs are not available. All of the information shown in Table 2 is expressed in terms of grams or milligrams of the component being released or depleted per square meter of sediment surface per day.

85. Oxidation of reduced chemicals in reservoirs is highly temperature dependent. In reservoir hypolimnia in the United States, temperatures typically range from 5° to 15°C. Some laboratory studies cited in Table 2 tended to use large amounts of the particular substrate or were conducted at higher temperatures and may have yielded above-normal rates. Inflow and outflow rates depend primarily on a reservoir's hydraulic budget and are not considered in this study. Since almost all aerobic chemical transformation rates are site specific, the flux rates in Table 2 reflect the range of concentrations of aerobic products that may occur in aerated reservoirs. Estimated release rates are not shown. These rates must be furnished when using the RE-AERS aerobic conceptual subroutine based on this description, which simulates aerobic processes. RE-AERS is described in Part III of this report.

86. Sediment-water reaction chambers are currently being used in the WES laboratory to provide the rate data required by RE-AERS. Upon completion of the study of which this report is a part, data will be provided in an Engineering Technical letter (ETL), available from WES, in the form of fluxes (i.e., net rate and direct on of release) or first-order coefficients, or in other forms. The ETL will also provide information on user methods for obtaining data required for RE-AERS. Table 3 presents a preliminary guide to these methods.

PART V: LABORATORY AND FIELD STUDIES

Materials and Methods

Characteristics and sampling of sediment and soil

87. Sediments from existing CE reservoirs and soils from proposed CE reservoirs were sampled to determine the effects of oxygenation on nutrient and metal transformation rates and reaction processes. Soil and sediment samples from the following reservoirs were used:

<u>CE Reservoir</u>	<u>Location (CE District)</u>
Eau Galle Reservoir	St. Paul District, Minn.
Browns Lake	WES, Miss.
Beech Fork Reservoir	Huntington District, W. Va.
Eagle Lake	Vicksburg District, Miss.
Richard B. Russell Reservoir	Savannah District, Ga.
DeGray Reservoir	Vicksburg District, Ark.
Bloomington Reservoir	Baltimore District, Md.
Red Rock Reservoir	Rock Island District, Ill.
Greers Ferry Reservoir	Little Rock District, Ark.

88. Samples from proposed reservoir sites were collected and handled as described by Gunnison et al. (1979). Compositing sediment samples representing various soil types in each reservoir were mixed thoroughly. Laboratory and field experiments were carried out to evaluate the interaction of sediment or newly flooded soil with the overlying water during destratification or reaeration.

Laboratory Studies

89. Large-scale model. A reaction chamber was constructed of plexiglas in the form of a rectangular tank with dimensions of 46 cm long by 46 cm wide by 121 cm high (Figure 13). The chamber and laboratory experiments were based on the methods described by Gunnison and Brannon (1981). Several modifications described in the following

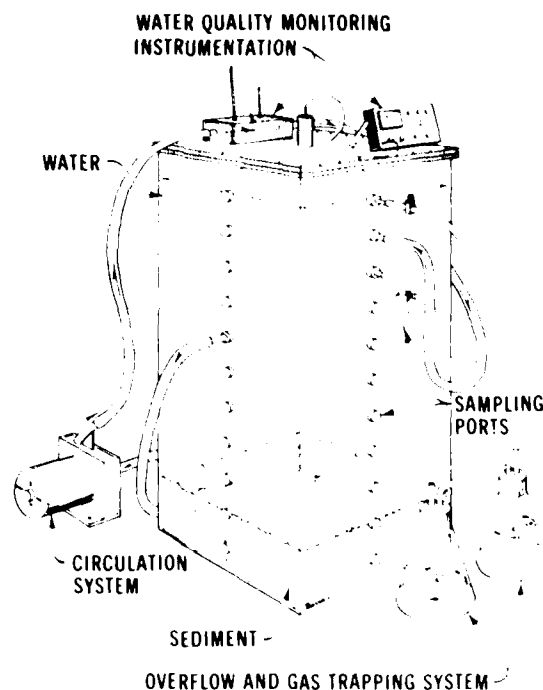


Figure 13. Sediment-water reactor for studying aerobic conditions in reservoirs

section were made to the reaction chamber to simulate destratification or reoxygenation conditions.

90. Small-scale model. This system used 17- by 92-cm polyethylene columns equipped with water sampling ports, platinum electrodes, and a gas diffuser system. Each column contained 4 L of sediment and 18 L of deionized water. Anoxic overlying water was reoxygenated by purging laboratory air into the system through an airstone diffuser approximately 10 cm above the sediment-water interface; aeration was conducted by bubbling air through the water-sediment system at an air flow rate of approximately 60 ml/min. Dissolved oxygen concentrations were maintained at around 7 ± 0.5 mg/L to simulate the average dissolved oxygen ranges of destratified bottom water in CE reservoirs.

91. Reaction chambers were sealed from the atmosphere and allowed to stand until the overlying water became anoxic. The overlying water was continuously circulated for mixing and equilibration.

92. Before aeration, waters overlying soil or sediment samples

were incubated for 4 to 6 months under anaerobic conditions. After the anoxic water was sampled, a gas exhaust port was opened on the top cover and aeration was begun. Incubation proceeded at a constant temperature of 20°C in the dark.

In Situ Study

93. An in situ incubation experiment was conducted in summer 1981 to determine the oxidation rate of ferrous iron (Fe (II)) and manganous manganese (Mn II) in the hypolimnion of Eau Galle Reservoir at depths of 0.5 and 9.5 m. Two-hundred-and-fifty ml of surface sediments, collected with an Eckman dredge, were mixed and added to 1-L wide-mouth plastic bottles which were then filled with bottom lake waters. Ten ml of solution containing reduced forms of iron and manganese were added to each bottle. Bottles were then returned to the bottom of the lake for a 24-hour incubation period. The temperature was 22.5 and 14.1°C, and dissolved oxygen was 4.3 and 0 mg/L in waters just above the sediments for the 0.5- and 9.5-m sites, respectively. The water samples were collected as described below.

Sample collection and preservation in laboratory

94. Anoxic water and sediment samples were initially sampled in a nitrogen atmosphere to maintain their anaerobic integrity. Particulate and dissolved forms of the chemicals were separated by filtering through a 0.45-µm membrane filter. Soluble, reduced metals (Fe and Mn) were filtered through a membrane filter of pore size 0.1 µm (Kennedy et al. 1974).

95. Samples for particulate and soluble nutrients were preserved immediately by freezing at -40°C. Metal samples were preserved by acidification to pH < 2 with concentrated HCl or HNO₃.

96. Interstitial water was separated from sediment by centrifuging a portion of the sediment at 10,000 rpm (16,300 x g) for 10 min. Sediment was then air dried and ground to pass an 80-mesh ASTM screen. The dried sediment samples were stored in tightly capped bottles at ambient temperature until chemical analysis.

Chemical Analyses

97. Water. Total kjeldahl nitrogen and total phosphorus were converted to ammonium and inorganic phosphate by digesting water samples on a semiautomatic digestion block (Ballinger 1979). Various forms of inorganic nitrogen and phosphate were determined with a Technicon Auto-analyzer II in accordance with procedures recommended by the U. S. Environmental Protection Agency (Ballinger 1979).

98. Total carbon and inorganic carbon, including soluble and particulate forms, were determined with a Beckman carbon analyzer (model 915 A) equipped with an infra-red detector. Sulfate concentrations were determined by the turbidimetric method (APHA 1980). Iron and manganese concentrations were determined with a Spectrometrics Spectraspan II Ecelle Grating Argon Plasma Emission spectrophotometer.

99. Soil and sediment. Exchangeable nutrients and metals were determined by extracting moist sediment samples (the residues following centrifugation to remove interstitial water) with a series of extracting solutions (Gunnison and Brannon 1981). Analytical methods for chemically extracted solutions were similar to those used for water samples (Table 3).

100. Total organic carbon in soil or sediment was determined directly by combusting air-dried samples at 550°C for 5 hours in a muffle furnace (Davis 1974). Carbon content was then calculated according to the equation of Allison and Moodie (1965). Inorganic carbon was determined by measuring the decrease in sediment weight resulting from CO₂ loss, by treating sediment with 3 M HCl (Allison and Moodie 1965).

Measurement of physical parameters

101. Dissolved oxygen was measured with the Azide modification of the Winkler method (APHA 1980), or was estimated by using an oxygen meter (Yellow Springs Instruments (YSI) model 54) equipped with an oxygen/temperature probe. Specific conductivity (corrected to 25°C) was measured with a mho meter using a YSI model 3403 conductivity cell. Water and sediment pH were measured by the glass combination electrode. Redox electrodes were constructed and calibrated following the procedures described by Graetz et al. (1973). A specific ion meter (Beckman

model S33) was used for Eh and pH measurements.

102. The temperature profile, dissolved oxygen, pH, and conductivity in Eau Galle Reservoir sediments used in the in situ study were measured with a Hydrolab Transmitter Probe (Hydrolab Corporation).

Results

Sediment and Soil Properties

103. Properties of the sediments and soils are shown in Table 4. Composited samples from the Richard B. Russell Reservoir site were collected from three representative areas of the proposed reservoir. Soil samples from the Richard B. Russell site were relatively high in metals and contained appreciable amounts of organic matter. Textural classification of the soils and sediments ranged from sandy loam (Eau Galle) to silty clay loam (Beech Fork). All sediment and soil samples except for the Eau Galle sediment (pH of 8.1) had a neutral pH and contained relatively little organic carbon and nitrogen.

Dissolved oxygen concentrations in the overlying waters

104. Concentrations of dissolved oxygen in the overlying water of the soil-water reactor chamber during an aeration period are shown in Table 5. Monitoring indicated that dissolved oxygen content of the overlying water increased from an average of 4.13 to 6.19 mg/L between the first and second day. These values were equivalent to an oxygen transfer capacity of 4.28 and 3.26 g O₂/m² of sediment surface area/day at 20°C. Dissolved oxygen content of the overlying water remained constant throughout the experiment after 1 week of aeration.

Water and sediment characteristics during aeration study

105. The pH of aerated water tended to increase during the aeration study, but changes in pH were minor and generally within 0.5 pH per unit. Before air was introduced into the reaction chamber, the redox potential (Eh) of anoxic water on the Beech Fork water-sediment system averaged +145 mV. Redox potential of the water increased promptly with

aeration to +350 mV after 5 hr and reached +570 mV by day 1. The Eh remained at +650 mV thereafter. Similar Eh changes in the overlying water were noted in the Eau Gallie water-sediment system at 20°C. Regardless of aeration treatment, sediment Eh registered between -200 to -230 mV and remained anoxic throughout the entire experiment. Chen et al. (1979) reported similar findings for other sediments and emphasized that destratification or other means of aeration in the overlying water did not affect sediment anoxic conditions anywhere but the thin oxidized zone of surficial sediment. There was no indication of redox electrode poisoning (Bailey and Beauchamp 1971) as the electrodes continually responded to the anaerobic-aerobic treatments. Water conductivity decreased once aeration began. In the Richard B. Russell water-sediment system, for example, conductivity declined from 23.6×10 to 18.3×10 $\mu\text{mho/cm}$ in 21 days.

Carbon content of the overlying water

106. Changes in organic and inorganic carbon contents of the overlying water in selected CE reservoirs during aeration are shown in Figures 14-20. In general, aerobic respiration of organic compounds is the most efficient metabolic process for carbon mineralization. Anoxic conditions in water-sediment systems generally favor high concentrations of inorganic and organic carbon, whereas oxic conditions tend to decrease inorganic carbon levels. Preliminary results indicate that initial concentrations of organic carbon were low in the anoxic water column, with very few changes observed during the aerobic treatment.

107. The disappearance rate of dissolved organic carbon was similar in most water-sediment systems over the initial 28 days of aerobic incubation. Total organic carbon concentrations remained constant or declined slightly during this incubation period.

108. In the presence of oxygen, aerobic heterotrophs actively metabolize organic matter in water and surface sediments. Some methane was produced in the anoxic system, however, although the conversion rate of methane to CO_2 in the oxic water-sediment system has not yet been determined. Although a third of the carbon from oxidized methane was

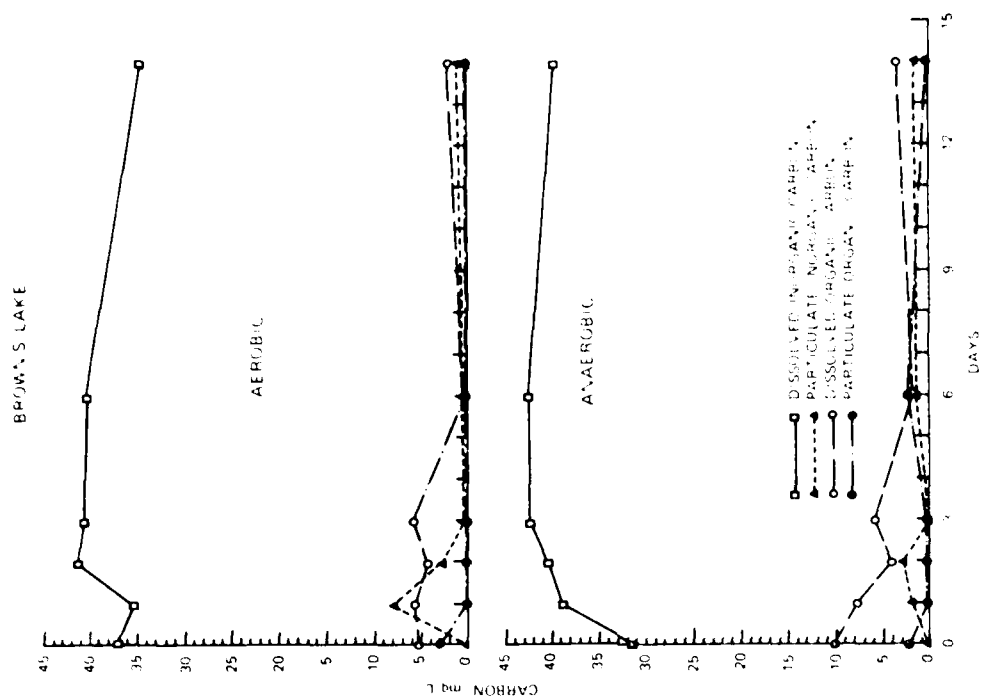


Figure 14. Changes in organic and inorganic carbon contents of the overlying water in Beech Fork Reservoir under aerobic and anaerobic conditions

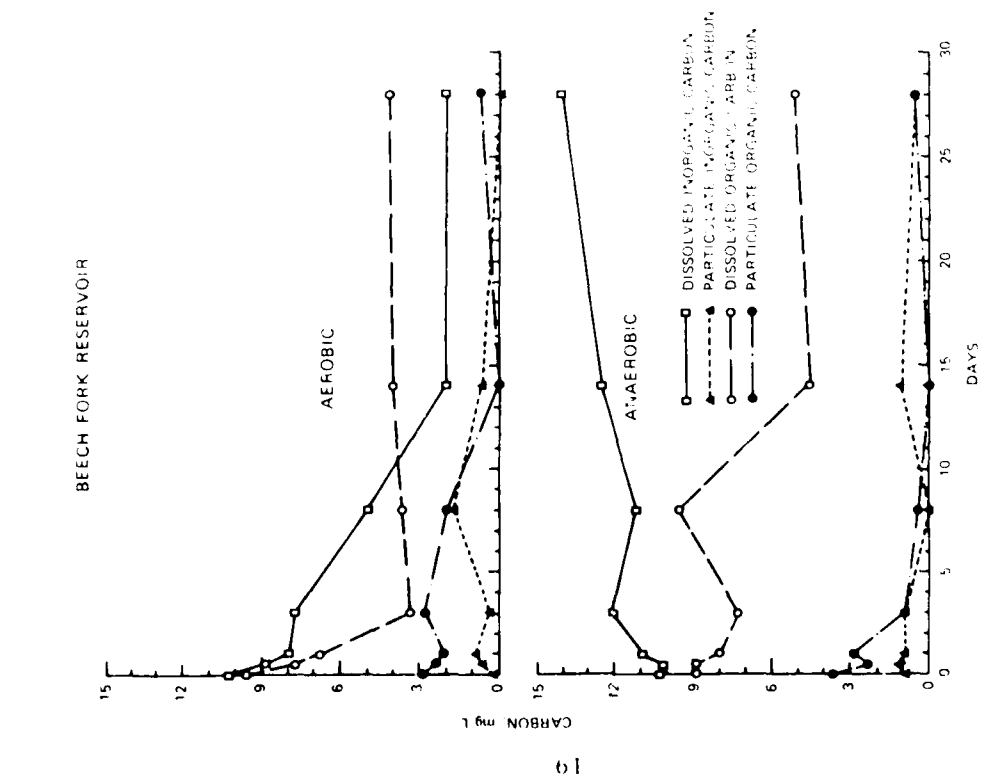


Figure 15. Changes in organic and inorganic carbon contents of the overlying water in Browns Lake under aerobic and anaerobic conditions

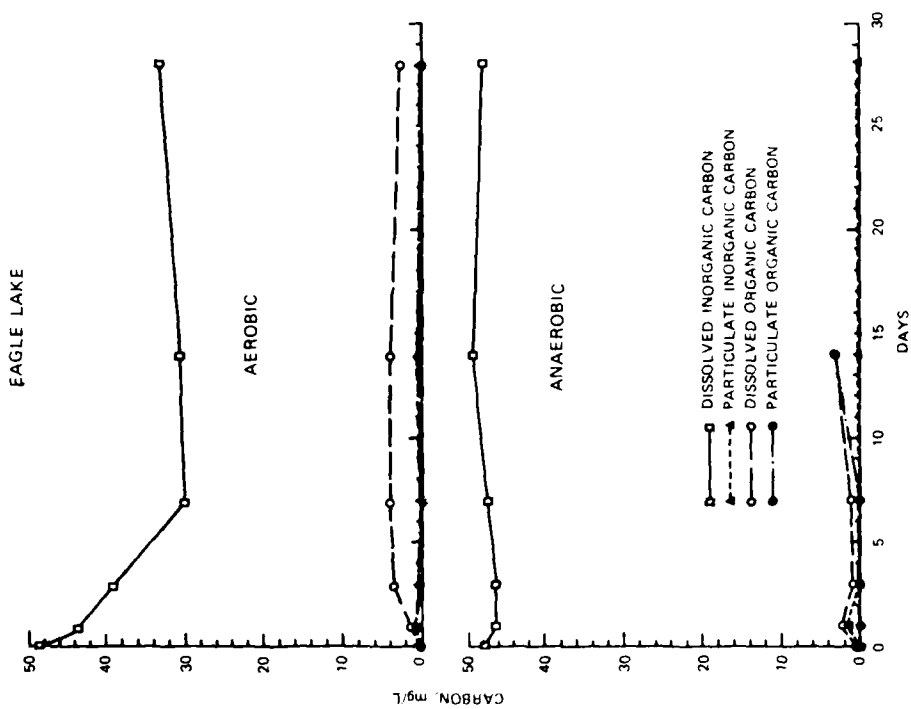


Figure 16. Changes in organic and inorganic carbon contents of the overlying water in Browns Lake (small column) under aerobic and anaerobic conditions

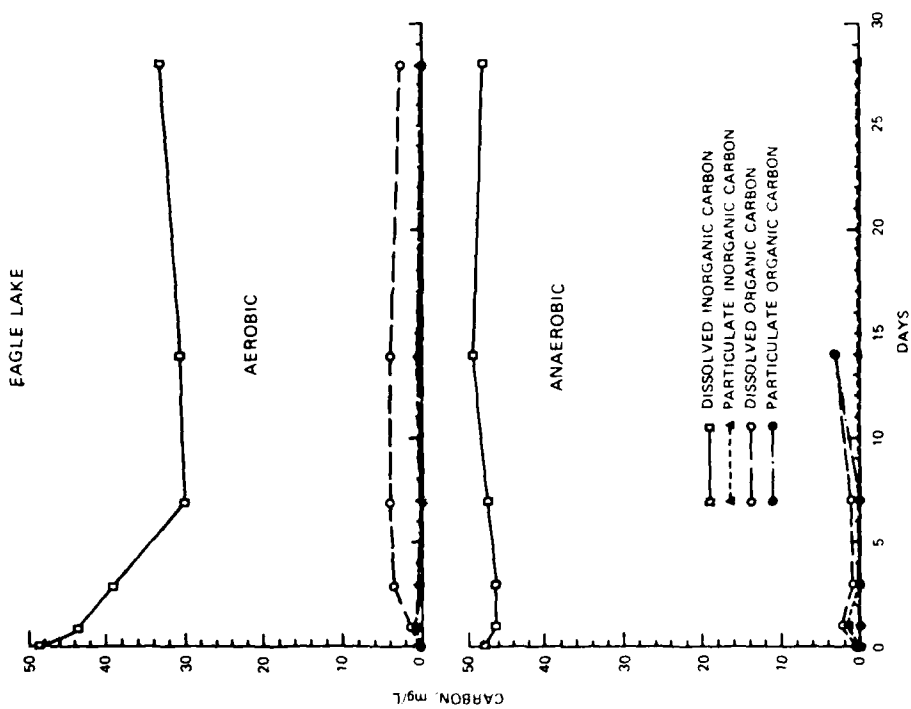


Figure 17. Changes in organic and inorganic carbon contents of the overlying water in Eagle Lake under aerobic and anaerobic conditions

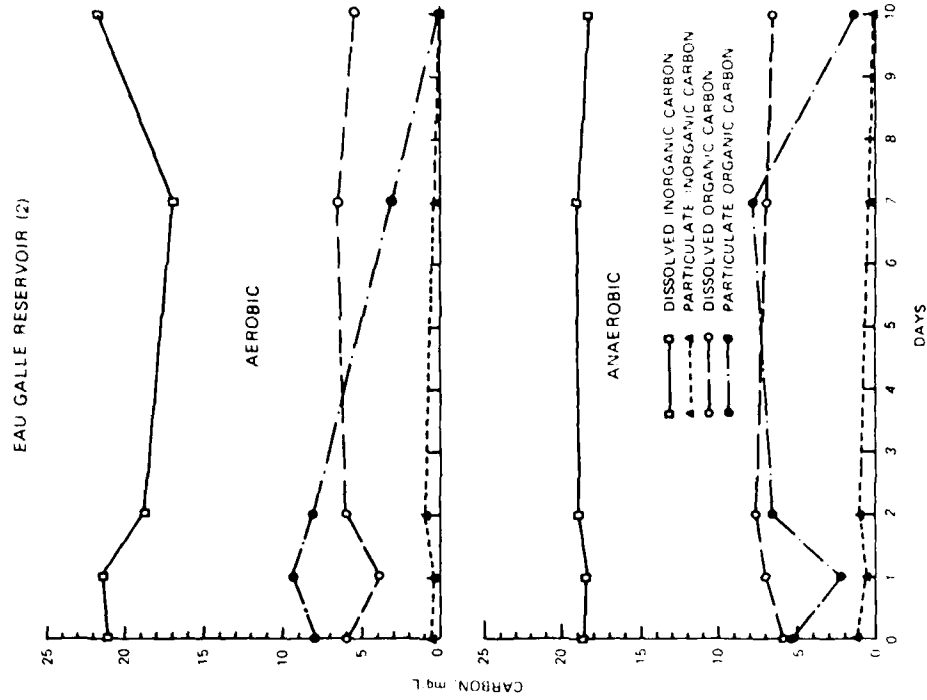


Figure 18. Changes in organic and inorganic carbon contents of the overlying water in Eau Galle Reservoir under aerobic and anaerobic conditions

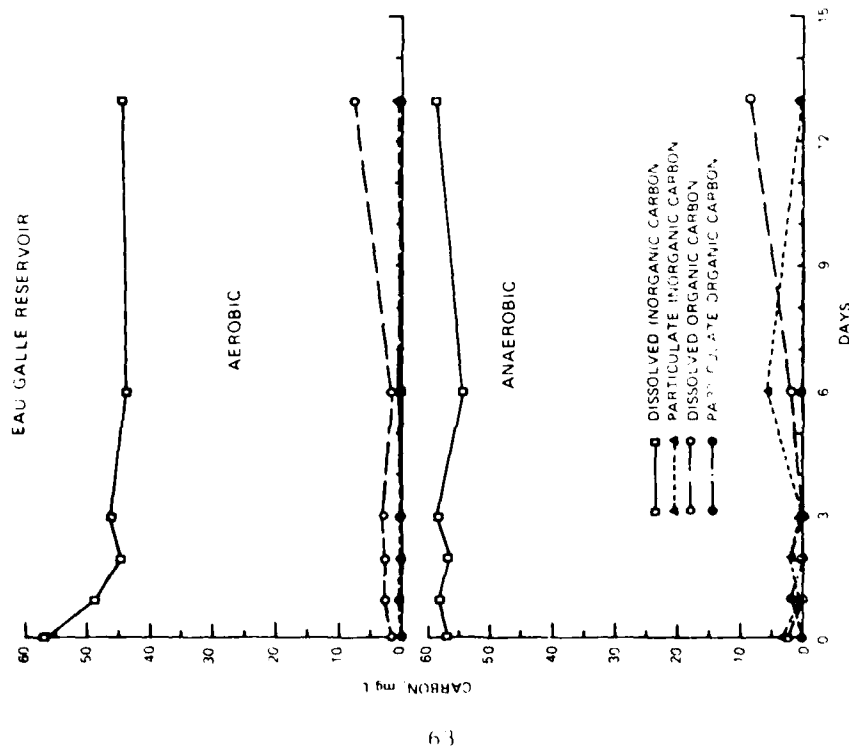


Figure 19. Changes in organic and inorganic carbon contents of the overlying water in Eau Galle Reservoir under aerobic and anaerobic conditions

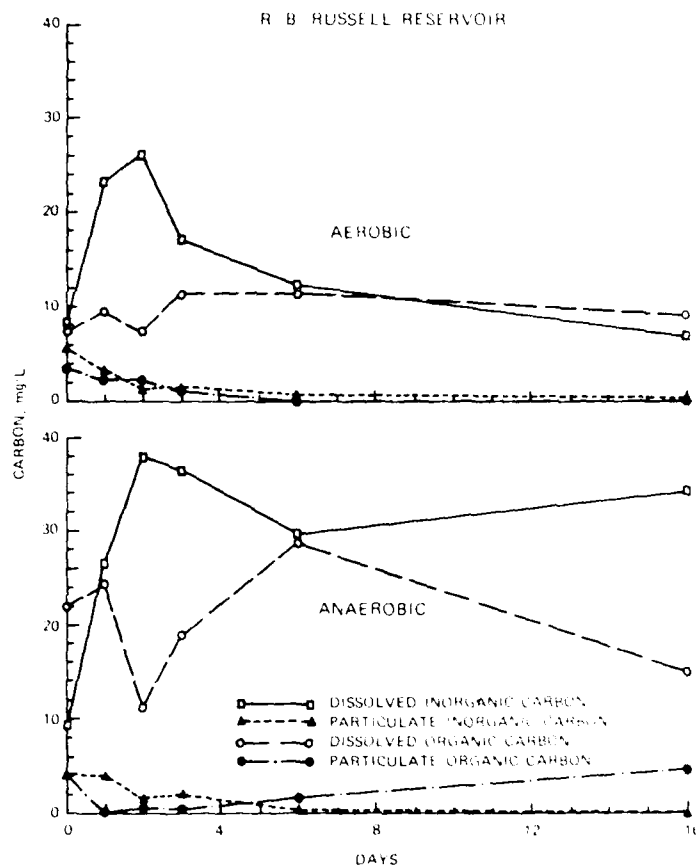


Figure 20. Changes in organic and inorganic carbon contents of the overlying water in Richard B. Russell Reservoir under aerobic and anaerobic conditions

found incorporated with organic carbon in lakes (Rudd et al. 1974), Zehnder and Brock (1980) reported a lower rate of methane oxidation in lake sediment.

109. The disappearance rates over 3 weeks of carbon in various water-sediment systems under aerobic conditions at 20°C are shown in the tabulation below. Carbon in the waters of Eagle Lake and Richard B. Russell Reservoir systems tended to accumulate, while that in Beech Fork Reservoir, Browns Lake, and Eau Galle Reservoir systems tended to decline.

CE Reservoirs	Carbon Disappearance Rate ($\text{g/m}^2/\text{day}$)	
	Aerobic	Anoxic
Beech Fork Reservoir	1.36	0.33
Browns Lake	0.54	0.14
Eagle Lake	2.23	-0.11
Eau Galle Reservoir	2.21	0.14
Richard B. Russell Reservoir	1.50	-0.19

Nitrogen concentrations in waters

110. Nitrification appeared to be slow in Browns Lake and Red Rock Lake sediment-water systems since substantial NO_3^- -N accumulation during aeration was not noted (Table 6). The low initial concentration (e.g. 0.11 $\mu\text{g/ml}$) of soluble NH_4^+ in the Browns Lake system did not change markedly in 14 days of aeration. Ammonium-N disappeared rapidly in the Red Rock system; however, conversion of NH_4^+ -N to NO_3^- -N only accounted for 10 percent of the total inorganic N during the 28-day aerobic incubation period.

111. In contrast, appreciable amounts of oxidized inorganic N accumulated, mainly as NO_3^- , in the waters under optimal aeration conditions at 20°C (Table 6). Chen et al. (1972) similarly found that there was a 1- to 3-day lag time before nitrification began. In most of the sediment-water systems, soluble NH_4^+ -N declined and approached undetectable levels under aerobic conditions. Approximately 0.5 mg/l. of nitrate-N accumulated in Red Rock water. An estimated 60 percent of the soluble NH_4^+ -N in the waters was converted to oxidized forms of N during 2 weeks of aerobic incubation. These results suggest that some of the NO_3^- -N formed during nitrification interacted with the diffused water-sediment interface. Further nitrate reduction reactions, including nitrate immobilization and denitrification, could account for the loss of N in the waters. The rates at which NH_4^+ is converted to NO_3^- in aerobic reservoir waters are summarized in Table 7.

Phosphorus concentrations in water

112. Inorganic phosphate concentrations in the overlying waters (Table 8) decreased under aerobic incubation in most of the CE reservoir systems shown. The ortho-phosphate concentration increased in the Browns Lake sediment-water system, which indicates that factors in this system other than redox potential may determine the release of inorganic phosphate from sediment to the overlying waters. Factors affecting the release of phosphorus from sediments to overlying waters were discussed in detail by Holdren and Armstrong (1980); these authors suggested that the increased concentrations of inorganic particulate phosphate in the overlying water immediately after aeration may have indicated physical suspension of sediment particles. Therefore, surface sediments can be a possible source of P to aerobic overlying water under favorable environmental conditions such as wave induction and mechanical circulation.

113. In laboratory anaerobic control systems, inorganic phosphate concentrations remained unchanged or increased with incubation time. An overall estimate of the disappearance rates of inorganic phosphorus under aerobic conditions is shown in the tabulation below:

Reservoir	Rate of Disappearance Dissolved Inorganic Phosphorus, g P/m ² /day
Beech Fork Reservoir	0.067
Browns Lake	-0.005
Eagle Lake	0.035
Eau Galle Reservoir	0.190
Richard B. Russell Reservoir	0.146
Red Rock Reservoir	0.020

Iron and manganese transformations in the waters

114. There was a noticeable release of ferrous iron and manganous manganese from reduced sediments to anoxic waters (Table 9). However,

oxidation of ferrous iron and reduced manganese in the overlying waters occurred rapidly once aeration began. Concentrations of reduced iron declined drastically to below the detection limit within 3 days of aerobic incubation (Table 9). A reddish-colored precipitate in the aerated overlying water indicated that ferric oxyhydroxides were formed during destratification in laboratory systems.

115. Simulated destratification also effectively removed manganese from the anoxic hypolimnion. In the Eagle Lake system, concentrations of reduced manganese decreased from about 2.3 to less than 0.05 $\mu\text{g/ml}$ after 3 days of aerobic incubation. Results indicated that more than 90 percent of reduced manganese initially released disappeared from aerated anoxic waters in 2 weeks. Precipitation during oxidation may be the most important way in which manganese is removed in reservoir ecosystems. The rates at which metals were removed from reaerated anoxic chambers are shown in the tabulation below:

Reservoir	Rates of Metal Precipitation	
	Iron (Fe II)	Manganese (Mn II)
	$\text{g/m}^2/\text{day}$	
Beech Fork Reservoir	2.656	0.166
Browns Lake	1.141	0.570
Eau Galle Reservoir	3.707	0.294
Eagle Lake	1.863	0.781
Richard B. Russell Reservoir	3.327	0.517
Red Rock Reservoir	0.357	0.046

In situ metal transformations

116. A preliminary in situ study evaluated the fate of reduced iron and manganese in CE reservoirs during destratification or summer aeration during August 1981. The study provided the oxidation rates of ferrous iron and reduced manganese at Eau Galle Reservoir. One hypolimnetic location was anoxic (site 1; station 20), and the other was oxic (site 2; station 50) (Figure 21). Concentrations of soluble metals recovered in Eau Galle waters after 24 hr of in situ incubation are

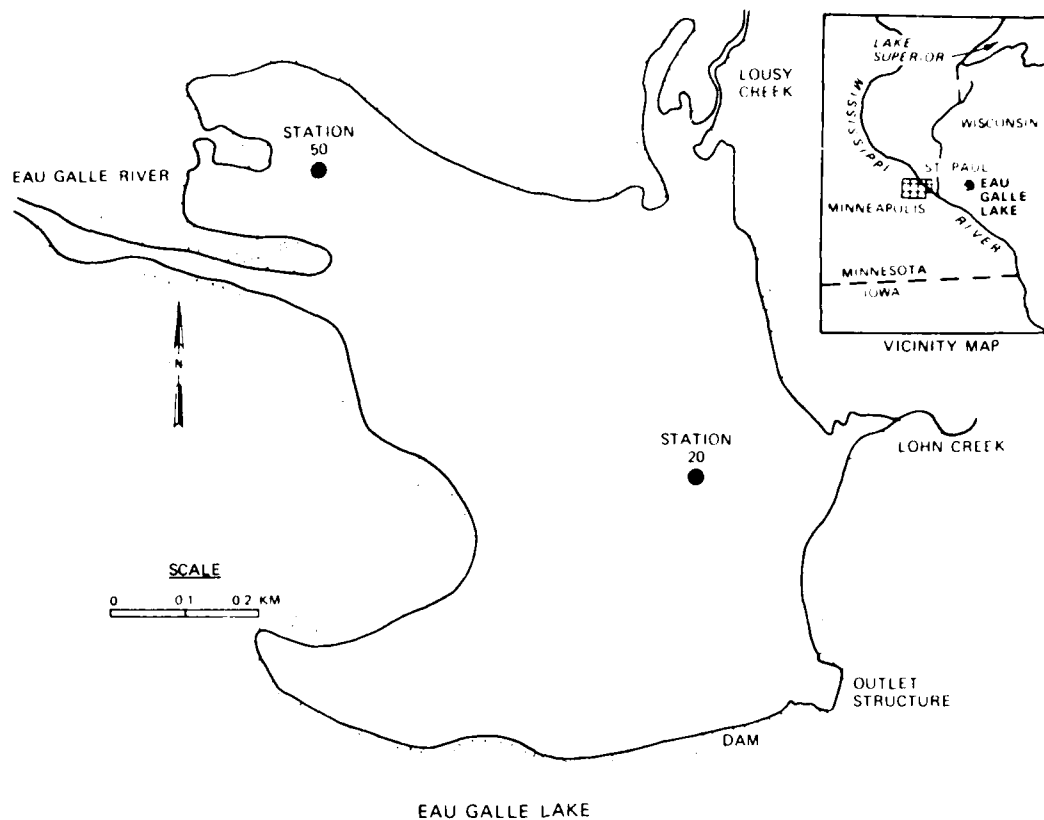


Figure 21. Map of Eau Galle Reservoir, Wisconsin

summarized in the following tabulation. Summer stratification developed at site 1, and soluble metals predominated in these anoxic waters during this investigation. In contrast, site 2 remained aerobic due to its shallow depth (0.5 m).

Incubation Time, hr	Concentrations of Metal* in the Waters mg/L			
	Iron		Manganese	
	Site 1	Site 2	Site 1	Site 2
0	5.93	0.49	7.13	5.98
24	9.73	0.17	3.19	2.54

* The initial metal concentration of 13.3 mg/L was based on the metal initially added to the incubation bottle.

117. The concentration of soluble metals decreased in anoxic and oxic waters after 24 hr of in situ incubation. In the oxic water, soluble iron disappeared at a much faster rate than soluble manganese; the anoxic hypolimnetic waters did not initially contain detectable quantities of soluble iron and manganese. After 24 hr of in situ incubation, soluble iron recovery accounted for 73.3 and 1.3 percent of the total iron in anoxic and oxic waters, respectively, while values for soluble Mn were 29.4 and 19.1 percent, respectively. Removal of the soluble metals from the waters may have been due to oxidation and precipitation or dispersal. Estimated oxidation rates of iron and manganese in the Eau Galle reservoir were 1.26 and 0.18 g/m²/day, respectively, at 22.5°C. These oxidation rates are similar to those obtained in the laboratory.

118. Rate coefficients developed in the laboratory such as have been presented in this section of the report will form the basic variables input to the reaeration subroutine RE-AERS. These laboratory-developed rate coefficients have agreed well with rate coefficients measured in the field at Eau Galle Reservoir.

PART VI: SUMMARY AND CONCLUSIONS

119. Through a review of the literature and discussions with authorities on aerobic nutrient and metal transformations, the effects of aeration and aerobic processes in lakes and reservoirs were compiled and organized. The most important of these processes were identified and used to formulate a realistic description of the processes occurring during the change from anaerobic to aerobic conditions. This description is presented in Part II of this report.

120. The description then formed the basis for the successful development of the aerobic subroutine RE-AERS, presented in Part III of this report. This subroutine is now available for incorporation into numerical reservoir water quality models.

121. Sediment water reaction chambers offer a viable way of obtaining a broad information base of input variables under a controlled environment. Data from these chambers are being obtained as part of the Corps' EWQOS Program for use in the RE-AERS.

122. Application of RE-AERS in a numerical water quality model to various CE reservoir projects using data obtained from the projects is a tool for examining the effectiveness of various management strategies upon problems associated with reoxygenation conditions. Under proper conditions and through the use of data obtained from neighboring bodies of water, a water quality model equipped with RE-AERS should also be applicable to preimpoundment investigations of the impact of stratification and destratification.

REFERENCES

- Alexander, M. 1961. Introduction to Soil Microbiology, Wiley and Sons, N. Y.
- Allison, L. E., and Moodie, C. D. 1965. "Carbonate," Method of Soil Analysis, Part 2, Chemical and Microbiological Properties, Amer. Soc. Agronomy, pp 1379-1396.
- American Public Health Association (APHA). 1980. "Standard Methods for the Examination of Water and Wastewater," 15th ed., 1134 p, American Public Health Association-AWWA-WPCF, Washington, D. C.
- Armstrong, D. E. 1980. "Phosphorus Transport Across the Sediment-Water Interface," Lake Restoration State of the Art Research, pp 169-175.
- Baas Becking, L. G. M., Kaplan, I. R., and Moore, D. 1960. "Limits of the Natural Environment in Terms of pH and Oxidation-Reduction Potentials," J. Geol., 68:243-284.
- Bailey, L. D., and Beauchamp, E. G. 1971. "Nitrate Reduction and Redox Potentials Measured with Permanently and Temporarily Placed Platinum Electrodes in Saturated Soils," Can. J. Soil Sci., 15:51-58.
- Ballinger, D. G. 1979. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, EPA, Cincinnati, Ohio.
- Bell, R. G. 1969. "Studies on the Decomposition of Organic Matter in Flooded Soils," Soil Biol. Biochem., 1:105-116.
- Berner, R. A. 1967. "Thermodynamic Stability of Sedimentary Iron Sulfide," Amer. J. Sci., 265:773-785.
- _____. 1963. "Electrode Studies of Hydrogen Sulphide in Marine Sediments," Geochim. Cosmochim. Acta, 27:563-575.
- Bernhardt, H. 1967. "Aeration of Wahnbach Reservoir Without Changing the Temperature Profile," J. Amer. Water Work Assoc., 59:943-964.
- Bewers, J. M., and Yeats, P. A. 1978. "Trace Metals in the Waters of a Partially Mixed Estuary," Estuar. Coastal Marine Sci., 7:147-162.
- Bohn, H. L. 1971. "Redox Potentials," Soil Sci., 112:39-45.
- Brezonik, P. L. 1968. "The Dynamics of the Nitrogen Cycle in Natural Water," Ph.D. Thesis, University of Wisconsin, Madison, Wis.
- Brezonik, P. L., and Lee, G. F. 1968. "Denitrification as a Nitrogen Sink in Lake Mendota, Wisconsin," Environ. Sci. Technol., 2:120-125.
- Brezonik, P. L., Delfino, J. J., and Lee, G. F. 1969. "Chemistry of N and Mn in Cox Hollow Lake, Wisconsin, Following Destratification," J. Sanit. Engrg. Div. ASCE Proc., 95(SA5):929-940.
- Bricker, O. P. 1965. "Some Stability Relations in the System Mn - O₂ - H₂O at 25°C and One Atmosphere Total Pressure," Amer. Mineral 50:1296-1354.

Chen, K. Y., and Morris, J. C. 1972. "Kinetics of Oxidation of Aqueous Sulfide by O_2 ," *Environ. Sci. Technol.*, 6:529-537.

Chen, R. L. 1971. Nitrate Formation and Transformations in Lake Sediments. M. S. Thesis, University of Wisconsin, Madison, Wis., 71 pp.

Chen, R. L., Keeney, D. R., and Konrad, J. G. 1972. "Nitrification in Sediments of Selected Wisconsin Lakes," *J. Environ. Qual.*, 1:151-154.

Chen, R. L., Keeney, D. R., and Sikora, L. J. 1979. "Effects of Hypolimnetic Aeration in Nitrogen Transformations in Simulated Lake Sediment-Water Systems," *J. Environ. Qual.*, 8:429-433.

Conte, S. D., and deBoor, C. 1972. *Newton Raphson Method*. McGraw-Hill, New York, pp 27-84.

Cooley, T. N., Dooris, P. M., and Martin, D. F. 1980. "Aeration as a Tool to Improve Water Quality and Reduce the Growth of Hydrilla," *Water Res.*, 14:485-489.

Coursier, J. 1952. "Interpretation des Mesures Potentiometriques au Moyen des Courbes de Polarisation (English Abst.)," *Anal. Chem. Acta*, 7:77-94.

Davis, B. E. 1974. "Loss-on-Ignition as an Estimate of Soil Organic Matter," *Proc. Soil Sci. Soc. Amer.*, 38:150-151.

Davis, J. A., and Leckie, J. O. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface. II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions," *J. Colloid Interface Sci.*, 67:90-107.

Davison, W., and Heaney, S. L. 1980. "Determination of the Solubility of Ferrous Sulfide in a Seasonally Anoxic Marine Basin," *Limnol. Oceanogr.*, 25:153-156.

Delfino, J. J., and Lee, G. F. 1968. "Chemistry of Manganese in Lake Mendota, Wisconsin," *Environ. Sci. Technol.*, 2:1094-1100.

Emerson, S., Kallhorn, S., Jacobs, L., Tebo, B. M., Nealson, K. H., and Rosson, R. A. 1982. "Environmental Oxidation Rate of Manganese (II): Bacterial Catalysis," *Geoch. Cosmoch. Acta*, 46:1073-1079.

Engler, R. M., and Patrick, W. H., Jr. 1973. "Sulfate Reduction and Sulfide Oxidation as Affected by Chemical Oxidants," *Soil Sci. Soc. Amer. Proc.*, 37:685-688.

Endelman, F. J., Northrup, M. L., Hughes, R. R., Keeney, D. R., and Boyle, J. R. 1973. "Mathematical Modeling of Soil Nitrogen Transformations I," *AIChE Symposium Series* 136:83-90.

Environmental Laboratory. 1982. "CE-QUAL-R1 = A Numerical One-Dimensional Model of Reservoir Water Quality," Instruction Report E-82-1, U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Fallon, R. D., Harrits, S., Hanson, R. S., and Brock, T. D. 1980. "The Role of Methane in Internal Carbon Cycling in Lake Mendota During Summer Stratification," *Limnol. Oceanogr.*, 25:357-360.

Fast, A. W., Overholtz, W. J., and Tubb, R. A. 1975. "Hypolimnetic Oxygenation Using Liquid Oxygen," *Water Res. Bull.*, 11:294-299.

Fillos, J., and Molof, A. H. 1972. "The Effect of Benthic Deposits on Oxygen and Nutrient Economy of Flowing Waters," *Journal of Water Pollution Control Federation*, Vol 44, pp 644-662.

Freedman, M. L., Cunningham, P. M., Schindler, J. E., and Zimmerman, M. J. 1980. "The Effect of Lead Speciation on Toxicity," *Bull. Environ. Contam. Toxicol.*, 25:389-393.

Ghosh, M. M. 1974. "Oxygenation of Ferrous Iron (II) in Highly Buffered Water," *Aqueous Environmental Chemistry of Metals*, A. J. Rubin, ed., Ann Arbor Sci. Publishers, Inc., Ann Arbor, Mich.

Ghosh, M. M., O'Connor, J. T., and Engelbrecht, R. S. 1966. "Precipitation of Iron Aerated Ground Waters," *J. Sanit. Div., Proc. ASCE*, (SA1):199-213.

Giammatteo, P. A., Schindler, J. E., Waldron, M. C., Freedman, M. L., Speziale, B. J., and Zimmerman, M. J. 1980. "Use of Equilibrium Programs in Predicting Phosphorus Availability," *Intl. Symp. Environ. Biogeochem.*, Stockholm, Sweden (In Press).

Golterman, H. L. (ed.). 1977. "Interactions Between Sediments and Fresh Waters," *Proc. Intl. Symp.*, Amsterdam, Holland.

Gotoh, S., and Patrick, W. H., Jr. 1972. "Transformation of Manganese in a Waterlogged Soil as Affected by Redox Potential and pH," *Soil Sci. Soc. Amer. Proc.*, 36:738-742.

Gordon, J. A. 1976. "Identification and Quantification of Water Quality Change Inducing Mechanisms in Stratified Reservoirs," Report 54, Tennessee Technological University, Cookeville, Tenn.

Graetz, D. A., Keeney, D. R., Aspiras, R. 1973. "Eh Status of Lake Sediment-Water Systems in Relation to Nitrogen Transformations," *Limnol. Oceanogr.*, 6:908-917.

Graham, W. F., Bender, M. L., and Klinkhammer, G. P. 1976. "Manganese in Narragansett Bay," *Limnol. Oceanogr.*, 21:665-673.

Greenwood, D. J. 1962. "Measurement of Microbial Metabolism in Soil," *The Ecology of Soil Bacteria*, Gray, I. R. G., and D. Parkinson, eds. Univ. Toronto Press, Canada, pp 138-157.

Greenwood, D. J., and Lees, H. 1956. "Studies on Decomposition of Amino acids in Soils. I. A Preliminary Survey of Techniques," *Plant Soil*, 7:253-268.

Gunnison, D., and Brannon, J. M. 1981. "Characterization of Anaerobic Chemical Processes in Reservoirs: Problem Description and Conceptual Model Formulation," Tech. Report E-81-6, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

Gunnison, D., Brannon, J. M., Smith, L., Jr., Burton, G. A., and Butler, P. L. 1979. "A Determination of Potential Water Quality Changes in

the Hypolimnion During the Initial Impoundment of the Proposed Twin Valley Lake, Appendix B," Tech. Report EL-79-5, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

Hall, E. R., and Murphy, K. L. 1980. "Estimation of Nitrifying Biomass and Kinetics in Wastewater," Water Res., 14:297-304.

Haynes, R. C. 1973. "Some Ecological Effects of Artificial Circulation on a Small Eutrophic Lake with Particular Emphasis on Phytoplankton. I. Kezar Lake Experiment, 1968," Hydrobiologia, 43:463-504.

Hem, J. D. 1981. "Rates of Manganese Oxidation in Aqueous Systems," Geochim. Cosmochim. Acta, 45:1369-1374.

Hoffman, M. R. 1981. "Thermodynamic, Kinetics and Extrathermodynamic Considerations in the Development of Equilibrium Models for Aquatic Systems," Environ. Sci. Technol., 15:345-353.

Hoffmann, M. R., and Eisenreich, S. J. 1976. "Development of a Computer-Generated Chemical Equilibrium Model for the Variation of Iron and Manganese in the Hypolimnion of Lake Mendota: Thermodynamic, Kinetic, and Extrathermodynamic Considerations," Mimeographed Paper, Environmental Engineering Program, University of Minnesota, Minneapolis, 45 pp.

_____. 1981. "Development of a Computer-Generated Equilibrium Model for the Variation of Iron and Manganese in the Hypolimnion of Lake Mendota," Environ. Sci. Technol., 15:339-344.

Hoffmann, M. R., and Lim, B. C. 1979. "Kinetics and Mechanism of the Oxidation of Sulfide by Oxygen: Catalysis by Homogeneous Metal-Phthalocyanine Complexes," Environ. Sci. Technol., 13:1406-1414.

Holdren, G. C., Jr., and Armstrong, D. E. 1980. "Factors Affecting Phosphorus Release from Intact Lake Sediment Cores," Environ. Sci. Technol., 14:79-87.

Holdren, G. C., Jr., Armstrong, D. E., and Harris, R. F. 1977. "Interstitial Inorganic Phosphorus Concentration in Lakes Mendota and Wingra," Water Res., 11:1041-1048.

Holford, I. C. R., and Patrick, W. H., Jr. 1981. "Effects of Duration of Anaerobiosis and Reoxidation on Phosphate Sorption Characteristics of an Acid Soil," Aust. J. Soil Res., 19:69-78.

Howard, D. L., Frea, J. I., and Pfister, R. M. 1971. "The Potential for Methane-Carbon Cycle in Lake Erie," Proc. 14th Cong. Great Lakes Res. Intl. Assoc. Great Lake Res., 236-240.

Hutchinson, G. E. 1957. Treatise on Limnology, Vol 1: Geography, Physics and Chemistry, Wiley and Sons, New York, 1015 pp.

Ingle, S. E., Keniston, J. A., and Schults, D. W. 1980. "REDEQL-EPAK, Aqueous Chemical Equilibrium Computer Program," EPA 600/3-80-049, Corvallis Environ. Res. Lab. EPA, Corvallis, Oreg.

Ingle, S. E., Schuldt, M. D., and Schults, D. W. 1978. "A User's Guide for REDEQL, EPA, A Computer Program for Chemical Equilibria in Aqueous

Systems," EPA-600/3-78-024, Corvallis Environmental Research Laboratory, USEPA, Corvallis, Oreg.

Jackson, G. A., and Morgan, J. J. 1978. "Trace Metal-Chelator Interactions and Phytoplankton Growth in Seawater Media: Theoretical Analysis and Comparison with Reported Observations," *Limnol. Oceanogr.*, 23:268-282.

Jørgensen, B. B. 1977. "The Sulfur Cycle of a Coastal Marine Sediment (Limfjorden, Denmark)," *Limnol. Oceanogr.*, 22:814-832.

Jørgensen, B. B., Kuenen, J. G., and Cohen, Y. 1979. "Microbial Transformations of Sulfur Compounds in Stratified Lake (Solar Lake, Sinai)," *Limnol. Oceanogr.*, 24:799-822.

Keeley, J. W., et al. 1978. "Reservoirs and Waterways. Identification and Assessment of Environmental Quality Problems and Research Program Development," Technical Report E-78-1. U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

Keeney, D. R. 1972. "The Fate of Nitrogen in Aquatic Ecosystems," Lit. Rev. No. 3, 59 pp. Eutrophication Inf. Program, WRC, Univ. of Wisconsin, Madison, Wis.

_____. 1973. "The Nitrogen Cycle in Sediment-Water Systems," *J. Environ. Qual.*, 2:15-28.

Kennedy, V. C., Zellweger, G. W., and Jones, B. B. 1974. "Filter Pore Size Effects on the Analysis of Al, Fe, Mn, and Fe in Water," *Water Resour. Res.*, 10:785-791.

Krauskopf, K. B. 1967. *Introduction to Geochemistry*, McGraw-Hill, New York, 721 pp.

Lean, D. R. S., and Charlton, M. N. 1976. "A Study of Phosphorus Kinetics in a Lake Ecosystem," *Environmental Biogeochemistry*, J. O. Nriagu, ed., Ann Arbor Sci. Publ., Inc., Ann Arbor, Mich.

Lee, G. F. (Chairman). 1966. "Report on Nutrient Sources of Lake Mendota," mimeo, Nutrient Sources Subcomm, Tech. Comm. of the Lake Mendota Problems Comm.

_____. 1970. "Factors Affecting the Transfer of Material Between Water and Sediments," Occasional Paper 1, Eutrophication Information Program, WRC, Univ. of Wisconsin, Madison, Wis., 50 pp.

Mallard, G. E., and Frea, J. I. 1972. "Methane Production in Lake Erie Sediments: Temperature and Substrate Effects," *Proc. 15th Conf. Great Lakes Res.* pp 87-93.

Martell, A. E., and Smith, R. M. 1976-77. *Critical Stability Constants*, 4 Volumes, Plenum Press, New York.

Martin, J. M., and Meybeck, M. 1979. "Element Mass-Balance of Material Carried by Major World Rivers," *Marine Chem.*, 7:173-206.

Mayer, L. M., and Gloss, S. P. 1980. "Buffering of Silica and Phosphate in a Turbid River," *Limnol. Oceanogr.*, 25:12-22.

- McDuff, R. E., and Morel, F. M. 1975. "Description and Use of the Chemical Equilibrium Program REDEQL 2," Tech. Report EQ-73-02, W. M. Keck Laboratory of Environmental Engineering Science, California Institute of Technology, Pasadena, Calif.
- Mirsa, C., Nielsen, D. R., and Biggar, J. W. 1974. "Nitrogen Transformations in Soil During Leaching; I. Theoretical Considerations," *Soil Sci. Soc. Amer. Proc.*, 38:289-293.
- Morel, F. M., McDuff, R. E., and Morgan, J. J. 1976. "Theory of Interaction Intensities, Buffer Capacities, and pH Stability in Aqueous Systems, with Application to the pH of Seawater and a Heterogeneous Model Ocean System," *Marine Chem.*, 4:1-28.
- Morel, F. M., and Morgan J. J. 1972. "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems," *Environ. Sci. Technol.*, 6:58-67.
- Morel, F. M., Westall, J. C., O'Melia, C. R., and Morgan, J. J. 1975. "Fate of Trace Metals in Los Angeles County Wastewater Discharge," *Environ. Sci. Technol.*, 9:756-761.
- Morel, F. M., and Yeasted, J. G. 1977. *Fate of Pollutants in the Air and Water Environments, Part I, Vol 8*, I. H. Suffet, ed., Wiley and Sons, New York.
- Morgan, J. J. 1967. "Chemical Equilibria and Kinetic Properties of Manganese in Natural Waters," *Principles and Applications of Water-Chemistry*, Faust, S. D., and J. V. Hunter, eds., Wiley and Sons, New York, pp 561-624.
- Morgan, J. J., and Birkner, F. B. 1966. "Precipitation of Iron in Aerated Ground Waters (Discussion)," *J. Sanit. Engr. Div., Proc ASCE*, 1b(SA6):137-143.
- Morgan, J. J., and Sibley, T. H. 1975. "Chemical Models for Metals in Coastal Environments," *Amer. Soc. Civil Engr. Conf. on Ocean Engr.*
- Mortimer, C. H. 1941. "The Exchange of Dissolved Substances Between Mud and Water in Lakes, I and II," *J. Ecol.*, 29:208-329.
- _____. 1942. "The Exchange of Dissolved Substances Between Mud and Water in Lakes, III and IV," *J. Ecol.*, 30:147-201.
- Murray, J. W., and Gill, G. 1978. "The Geochemistry of Iron in Puget Sound," *Geochim. Cosmochim. Acta.*, 42:9-19.
- Nhung, N. F. M., and Ponnampetuma, F. N. 1966. "Effects of Calcium Carbonate, Manganese Dioxide, Ferric Hydroxide, and Prolonged Flooding on Chemical and Electrochemical Changes and Growth of Rice in a Flooded Acid Sulfate Soil," *Soil Sci.*, 102:29-41.
- Nordstrom, D. K., et. al. 1980. "A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems," *Chemical Modeling in Aqueous Systems: Speciation, Sorption, Solubility and Kinetics*, E. A. Jenne, ed., Amer. Chem. Soc. Symp. Ser.

- Pankow, J. F., and Morgan, J. J. 1981. "Kinetics for the Aquatic Environment," *Environ. Sci. Technol.*, 15:1155-1164.
- Patrick, W. H., Jr., and Henderson, R. E. 1981. "Reduction and Reoxidation Cycles of Manganese and Iron in Flooded Soil and in Water Solution," *Soil Sci. Soc. Amer. J.*, 45:855-859.
- Patt, T. E., Cole, G. C., Bland, J., and Hanson, R. S. 1974. "Isolation and Characterization of Bacteria that Grow on Methane and Organic Compounds as Site Sources of Carbon Energy," *J. Bacteriol.*, 120:955-964.
- Pomeroy, L. R., Smith, E. E., and Grant, C. M. 1965. "The Exchange of Phosphate Between Estuarine Water and Sediments," *Limnol. Oceanogr.* 10:167-172.
- Ponnamperuma, F. N. 1972. "The Chemistry of Submerged Soils," *Adv. Agron.*, 24:29-96.
- Ponnamperuma, F. N., Martinez, E., and Loy, T. 1966. "Influence of Redox Potential and Partial Pressure of Carbon Dioxide in pH Values and the Suspension Effect of Flooded Soils," *Soil Sci.*, 101:421-431.
- Ponnamperuma, F. N., Tianco, E. M., and Loy, T. A. 1967. "Redox Equilibria in Flooded Soils: I. The Iron Hydroxide Systems," *Soil Sci.*, 103:374-382.
- Reeburgh, W. S. 1969. "Observations of Gases in Chesapeake Bay Sediments," *Limnol. Oceanogr.*, 14:368-375.
- Rudd, J. W. M. 1980. "Methane Oxidation in Lake Tanganyika (East Africa)," *Limnol. Oceanogr.*, 25:958-963.
- Rudd, J. W. M., and Hamilton, R. D. 1975. "Factors Controlling Rates of Methane Oxidation and the Distribution of Methane Oxidizers in a Small Stratified Lake," *Arch. Hydrobiol.*, 75:522-538.
- Rudd, J. W. M., Hamilton, R. D., and Campbell, N. E. R. 1974. "Measurement of Microbial Oxidation of Methane in Lake Water," *Limnol. Oceanogr.* 19:519-524.
- Ryden, J. C., Syers, J. K., and Harris, R. F. 1973. "Phosphorus in Runoff and Streams," *Adv. Agronomy*, 25:1-45.
- Schenk, J. E., and Weber, W. J., Jr. 1968. "Chemical Interactions of Dissolved Silica with Iron (II) and (III)," *J. Amer. Water Works Assoc.*, 60:199-212.
- Selim, H. M., and Iskandar, I. K. 1981. "Modeling Nitrogen Transport and Transformation in Soils: I. Theoretical considerations," *Soil Science* 131:233-241.
- Serruya, C., and Berman, I. 1966. "The Evolution of Nitrogen Compounds in Lake Kinneret," *Developments in water quality research*, pp. 7-18.
- Shukla, S. S., Syers, J. K., Warram, J. L. B., Armstrong, D. E., and Harris, R. F. 1971. "Sorption of inorganic phosphate by lake sediments," *Soil Sci. Soc. Amer. J.*, 35:441-447.

- Sibley, T. H., and Morgan, J. J. 1977. "Equilibrium Speciation of Trace Metals in Freshwater Seawater Mixtures," Proc. Intl. Conf. Heavy Metals in the Environ., Vol 1, pp 319-338.
- Smith, S. A., Knauer, D. R., and Wirth, T. L. 1975. "Aeration as a Lake Management Technique," Wisconsin Dep. of Natl. Resour. Tech. Bull. No. 87, Madison, Wis., 39 pp.
- Sposito, G., and Mattigod, S. V. 1979. "GEOCHEM: A Computer Program for the Calculation of Chemical Equilibria in Soil Solutions and Other Natural Water Systems," mimeo, Dept. Soil and Environ. Sci., Univ. of California, Riverside.
- Sposito, G., Page, A. L., and Frink, M. E. 1980. "Effects of Acid Precipitation on Soil Leachate Quality: Computer Calculations," EPA-600/3-80-015, Environmental Protection Agency, Corvallis, Oreg.
- Sposito, G. 1981. "Trace Metals in Contaminated Waters," Environ. Sci. Technol., 15:396-403.
- Stadtman, T. 1967. "Methane Fermentation," Ann. Rev. Microbiol., 21:121-142.
- Strecker, R. G., Steichen, J. M., Garton, J. E., and Rice, C. E. 1977. "Improving Lake Water Quality by Destratification," Transactions ASAE., 20:713-720.
- Stumm, W., and Leckie, J. O. 1971. "Phosphate Exchange with Sediments: Its Role in Productivity of Surface Waters," Water Resources Res., 26:1-16.
- Stumm, W., and Lee, G. F. 1961. "Oxygenation of Ferrous Iron," Ind. Engr. Chem., 53:143-146.
- Stumm, W., and Morgan, J. J. 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, Wiley-Interscience, New York, 780 pp.
- Sung, W., and Morgan, J. J. 1980. "Kinetics and Products of Ferrous Iron Oxygenation in Aqueous Systems," Environ. Sci. Technol., 14:561-568.
- Syers, J. K., Harris, R. F., and Armstrong, D. E. 1975. "Phosphate Chemistry in Lake Sediments," J. Environ. Qual., 2:1-14.
- Syers, J. K., Murdock, J. T., and Williams, J. D. H. 1970. "Adsorption and Desorption of Phosphate by Soils," Soil Sci. Plant Anal., 1:57-62.
- Symons, J. M., Carswell, J. K., and Robeck, G. G. 1970. "Mixing of Water Supply Reservoirs for Quality Control," J. Amer. Water Works Assoc., 62:322-334.
- Tamura, H., Goto, K., and Nagayama, M. 1976. "Effect of Anions on the Oxygenation of Ferrous Ion in Neutral Solutions," J. Inorg. Nucl. Chem., 38:113-117.

- Theis, T. L., and Richter, R. O. 1979. "Chemical Speciation of Heavy Metals in Power Plant Ash Pond Leachate," *Environ. Sci. Technol.*, 13:219-224.
- Theis, T. L., and Singer, P. C. 1974. "Complexation of Iron (III) by Organic Matter and Its Effect on Iron (III) Oxygenation," *Environ. Sci. Technol.*, 8:569-573.
- Turner, F. T., and Patrick, W. H., Jr. 1968. "Chemical Changes in Water-logged Soils as a Result of Oxygen Depletion," *Trans. 9th Intern. Congr. Soil Sci.*, Adelaide, Australia, 4:53-65.
- Van Breeman, N. 1969. "The Effect of III-Defined Ferric Oxides on the Redox Characteristics of Flooded Soils," *Neth. J. Agr. Sci.*, 17:256-260.
- Vollenweider, R. A. 1976. "Advances in Defining Critical Loading Levels for Phosphorus in Lake Eutrophication," *Mem. Inst. Ital. Idrobiol.*, 33: 53-83.
- Vuceta, J., and Morgan, J. J. 1978. "Chemical Modelling of Trace Metals in Freshwaters: Role of Complexation and Adsorption," *Environ. Sci. Technol.*, 12:1302-1309.
- Wainwright, M., and Killham, K. 1980. "Sulphur Oxidation by *Thiobacillus Solani*," *Soil Biol. Biochem.*, 12:555-558.
- Westall, J. C. 1977. "Chemical Methods for the Study of Metal-Ligand Interactions in Aquatic Environments," Ph.D. Thesis, Massachusetts Inst. of Technol., Cambridge, Mass.
- Westall, J. C., Zachary, J. E., and Morel, F. M. 1976. "MINTEQA: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems," Tech. Report 18, Dept. Civil Engr., Massachusetts Inst. of Technol., Cambridge, Mass.
- Wetzel, R. G. 1975. "Biogeochemical Cycling of Essential Micro-nutrients," *Limnology*, Wetzel, R. G., ed., pp 258-261.
- Wetzel, R. G. 1972. "The Role of Carbon in Hard-water Marl Lakes," *Nutrients and Eutrophication: The Limiting Nutrient Controversy*, G. E. Likens, ed., Special Symp., Amer. Soc. Limnol. Oceanogr., 1:84-91.
- Williams, J. D. H., Syers, J. K., Shukla, S. S., Harris, R. F., and Armstrong, D. E. 1971. "Levels of Inorganic and Total Phosphorus in Lake Sediments as Related to Other Sediment Parameters," *Environ. Sci. Technol.*, 5:1113-1120.
- Wirth, T. L., and Dunst, R. C. 1967. "Limnological Changes Resulting from Artificial Destratification and Aeration of an Impoundment," Wisconsin Conserv. Dept., Fish. Res. Report No. 22, Madison, Wis.
- Wong-Chong, G. M., and Loehr, R. C. 1975. "The Kinetics of Microbial Nitrification," *Water Res.*, 9:1009-1106.
- Zehnder, A. J. B., and Brock, T. D. 1980. "Anaerobic Methane Oxidation: Occurrence and Ecology," *Appl. Environ. Microb.*, 39:194-204.
- Zimmerman, M. J. 1980. "Aquatic Chemistry: A Chemical Equilibrium Approach," Ph.D. Thesis, The University of Georgia, Athens.

Table 1
Summary of Previous Results on Oxygenation Kinetics of Ferrous Iron*

Investigators	Solution Composition	Reported Rate Information	Remarks
Stumm and Lee (1961)	29 to 39 meq/L of alk as NaHCO_3 , P_2 varies, $T = 20.5^\circ\text{C}$	$k^{**} = 8.0 \pm 2.5 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$	Assume ionic strength $\approx 34 \times 10^{-3} \text{ M}$ $\gamma_{\text{OH}}^{\dagger\dagger} \approx 0.84$ $k_{\text{H}}^{\ddagger}$ oxygen at $20.5^\circ\text{C} = 0.00118 \text{ M}$ atm^{-1}
Morgan and Birkner (1966)	$\text{P}_2 = 0.6 \text{ atm}$, $T = 25^\circ\text{C}$, alk = 32 meq/L	$t_{1/2}^{\ddagger\ddagger} \approx 16 \text{ min}$ at pH 6.70 + $k = 2.0 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$ $t_{1/2} \approx 47 \text{ min}$ at pH 6.52 + $k = 1.7 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$	
Schenk and Weber (1968)	$\text{P}_2 = 0.21 \text{ atm}$, $T = 25^\circ\text{C}$, alk = 30-50 meq/L	$k = 2.1/0.5 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$	Assume ionic strength $\approx 40 \times 10^{-3} \text{ M}$
Theis and Sing, r (1974)	$\text{P}_2 = 0.5 \text{ atm}$, $T = 25^\circ\text{C}$, alk = 0.0158 M as NaOH initially	$t_{1/2} = 25.4 \text{ min}$ at pH 6.3 + $k = 1.36 \times 10^{14} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$	
Tamura et al. (1976)	$T = 25^\circ\text{C}$, P_2 varies, alk $= 10^{-2} \text{ M NaHCO}_3$, total ionic strength = 0.11 M	0.1 M ClO_4^- : $k = 2.38 \times 10^{14} \text{ M}^{-3} \cdot \text{s}^{-1}$ $= 1.8 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$ 0.1 M NO_3^- : $k = 2.04 \times 10^{14} \text{ M}^{-3} \cdot \text{s}^{-1}$ $= 1.6 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$ 0.1 M Cl^- : $k = 1.63 \times 10^{14} \text{ M}^{-3} \cdot \text{s}^{-1}$ $= 2 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$ 0.1 M Br^- , 0.1 M I^- , 0.033 M SO_4^{2-} : $k = 1.36 \times 10^{14} \text{ M}^{-3} \cdot \text{s}^{-1}$ $= 1.0 \times 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$	
Murray and Gill (1978)	$T = ?$, Puget Sound seawater	$t_{1/2} = 3.9 \text{ min}$ at pH 8.0 + $k = 8.9 \times 10^{11} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$	First 5 min linear on first order plot

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** k = oxidation rate constant.

† M = mole/L.

†† $\gamma_{\text{OH}} = (\text{OH}^- \text{ ion activity}) \times 10^7$ for a given pH.

‡ k_{H} oxygen = constant partial pressure of oxygen at various pH values.

‡‡ $t_{1/2}$ = half-life of ferrous iron.

Table 2

Oxidation and Transformation of Various Reduced Components in Aerated
Reservoirs and Other Freshwater Environments

Reaction	Environmental Conditions	Flux Rate	Reference
N immobilization	Aerated reservoir hypolimnion, in situ, 23°C	0.008 - 0.062 g N m ⁻² day ⁻¹	Haynes (1973)
NH ₄ disappearance	Aerated Tim's Ford Reservoir, 12.5°C	0.0258 g N m ⁻² day ⁻¹	Gordon (1976)
	Aeration of simulated hypolimnion, 10°C	0.118 - 0.124 g N m ⁻² day ⁻¹	Chen et al. (1979)
	Aerated reservoir hypolimnion, 23°C	0.017 g N m ⁻² day ⁻¹	Haynes (1973)
	Aerated Cox Hollow Reservoir hypolimnion, 12°C	0.002 - 0.022 g N m ⁻² day ⁻¹	Brezonik et al. (1969)
Nitrification	Aeration of simulated hypolimnion, 10°C	0.101 - 0.106 g N m ⁻² day ⁻¹	Chen et al. (1979)
	Aerated Lake Mendota hypolimnion, 10°C	0.058 - 1.44 g N m ⁻² day ⁻¹	Brezonik (1968)
Fe (II) oxidation	Aerated reservoir hypolimnion, 10°C	0.1 mg Fe m ⁻² day ⁻¹	Cooley et al. (1980)
	Aerated reservoir hypolimnion, 23°C	0.043 - 0.049 g Fe m ⁻² day ⁻¹	Haynes (1973)
Mn (II) oxidation	Aerated Lake Mendota hypolimnion, 10°C	0.08 g Mn m ⁻² day ⁻¹	Brezonik et al. (1969)
	Aerated reservoir hypolimnion, 15°C	0.967 mg Mn liter ⁻¹ day ⁻¹	Bernhardt (1967)
	Aerated reservoir hypolimnion, 23°C	0.017 - 0.02 g Mn m ⁻² day ⁻¹	Haynes (1973)
Sulfide oxidation	Aerated aqueous solution with initial conc of O ₂ = 1.6 to 8.0 × 10 ⁻⁴ M S = 0.5 to 2.0 × 10 ⁻⁴ M	10 ⁻¹⁰ S min ⁻¹	Chen and Morris (1972)
Ortho-P disappearance	Aerated reservoir hypolimnion, 15°C	1.2 mg P liter ⁻¹ day ⁻¹	Bernhardt (1967)
	Aerated reservoir hypolimnion, 23°C	0.001 to - 0.0015 g P m ⁻² day ⁻¹	Haynes (1973)
Total P disappearance	Aerated reservoir hypolimnion, 23°C	0.01 to - 0.008 g P m ⁻² day ⁻¹	Haynes (1973)
	Aerated Tim's Ford reservoir hypolimnion, 12°C	0 - 0.01 g P m ⁻² day ⁻¹	Gordon (1976)
Oxygen uptake	Aerated Tim's Ford reservoir hypolimnion, 12°C	0.571 - 0.835 g O ₂ m ⁻² day ⁻¹	Gordon (1976)

* Conc of element increase in overlying water after aeration.

Table 3

Summary of Methods Used to Obtain Data for RE-AERS*

Component	Method	Reference
Dissolved oxygen	Use BOD probe with associated dissolved oxygen meter; calibrate by iodometric method for dissolved oxygen measurement	APHA (1980)
Oxidation-reduction potential	Use platinum electrode and calomel reference electrode with $\pm$ millivolt scale of a standard millivolt-pH meter	Graetz et al. (1973)
Soluble nutrients	Filter sample through 0.45- μ m membrane filter (NOTE: If sample is taken from anoxic waters, all sample collection and filtration must be conducted in a nitrogen atmosphere); preserve by immediate freezing to -40°C	
a. Total kjeldahl nitrogen	Kjeldahl digestion followed by semiautomated block digestion method, Storet #00625	Ballinger (1979)
b. Ammonia nitrogen	Automated phenate method	Ballinger (1979)
c. Nitrite-nitrate nitrogen	Cadmium reduction method	APHA (1980)
d. Total phosphorus	Semiautomated block digestion method	Ballinger (1979)
e. Orthophosphate phosphorus	Ascorbic acid method	APHA (1980)
f. Dissolved organic carbon	Combustion-infrared method	APHA (1980)
g. Sulfate	Turbidimetric method	APHA (1980)
Total nutrients (dissolved plus particulate)	Use same methods as for dissolved nutrients, except do not filter sample	
Soluble metals: iron and manganese	Filter through 0.10- μ m membrane filter; preserve with 11.6 M HCl (0.2 ml acid/15 ml of sample); analyze by flame photometry	APHA (1980)
Total inorganic carbon	Combustion method	APHA (1980)
Total sulfide	Collect and preserve using zinc acetate; analyze within 24 hr using titrimetric method	APHA (1980)

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Table 4

Characteristics of Selected Sediments and Soils Used in the Laboratory Studies

Sediment	Particle Size Distribution				pH	Total Carbon percent	Total Kjeldahl Nitrogen percent	Exchangeable NH ₄ ⁺ , ppm	Total Phosphorus ppm	Interstitial Water	
	percent			Fe						Mn	
	Sand	Silt	Clay								
Beech Fork Reservoir	10.0	51.3	38.7	6.3	1.36	1.74	171.1	567.5	18.57	4.93	
Browns Lake	13.8	57.5	28.7	7.0	2.77	2.22	46.6	748.1	11.12	5.32	
Eagle Lake	17.5	27.5	55.0	7.3	1.94	2.25	178.7	782.9	1.85	8.57	
Eau Galle Reservoir	70.0	16.3	13.7	8.1	3.87	1.81	72.1	480.2	21.94	8.48	
Red Rock Reservoir	37.5	45.0	17.5	6.7	1.45	1.12	71.4	423.3	40.37	24.28	
R. B. Russell Reservoir	64.0	22.5	13.5	6.2	1.46	1.65	68.0	480.5	--	--	

Table 5
Changes in Concentrations of DO in the Overlying
Waters During Aeration Study

Time (day)	CE Reservoirs, ppm						Average
	Beech Fork	Browns	Eau Galle	Eagle	R. B. Russell	Red Rock	
0	0.0	0.3	0.0	0.0	0.0	0.0	0
1	5.2	6.5	3.6	1.0	3.9	3.4	4.1 ± 1.8
2	6.9	7.0	6.3	4.6	6.6	--	6.2 ± 0.9
4	7.1	7.0	6.5	6.2	6.8	4.8	6.6 ± 0.5
7	7.6	6.9	6.4	6.3	6.8	5.1	6.7 ± 0.6
14	7.5	7.0	7.3	7.0	7.3	7.4	7.3 ± 0.3

Table 6

Concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in Waters Overlying Sediments from SelectedCE Reservoir Systems Incubated Under Aerobic Conditions at 20°C, $\mu\text{g N/ml}$

Aeration time days	Beech Fork		Browns L.		Eagle L.		Eau Galle		Red Rock		Richard B.	
	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3
0	1.29	0.05	0.11	0.04	1.73	0.07	3.69	0.06	5.42	0.01	2.98	0.09
1	1.17	0.07	0.06	0.11	--	--	3.33	0.07	5.07	0.01	2.62	0.05
3	1.02	0.08	0.07	0.15	1.10	0.15	2.41	0.34	3.94	0.03	2.22	0.09
7	0.53	0.69	0.05	0.18	0.06	1.35	0.31	1.51	3.82	0.06	0.47	1.19
14	0.08	1.29	0.05	0.23	0.08	1.37	0.00	1.69	1.89	0.48	0.09	1.06

Table 7
The Rate of N Transformations in CE Reservoir Systems Incubated
Under Aerobic Conditions at 20°C for 3 Weeks in the Dark

Reservoirs	Nitrification Rate	Rate of N Disappearance in the Waters
	g N/m ² /day	g N/m ² /day
Beech Fork Reservoir	0.092	0.011
Browns Lake	0.014	-0.013
Eagle Lake	0.189	0.058
Eau Galle Reservoir	0.252	0.163
Richard B. Russell Reservoir	0.189	0.244
Red Rock Reservoir	0.015	0.171

Table 8
Changes of Inorganic Phosphate (Ortho-P) Concentration in the
Overlying Waters of Selected CE Reservoir Systems
Under Aerobic Conditions at 25°C in the Laboratory

Reservoirs	Change of Inorganic Phosphate Concentration at Particular Hours, µg/m				
	0	1	3	6	14
Beech Fork Reservoir	0.106	0.104	0.077	0.062	0.025
Browns Lake	0.026	0.027	0.048	0.032	0.035
Eagle Lake	0.100	0.005	0.005	0.051	0.034
Eau Galle Reservoir	0.367	0.020	0.005	0.010	0.005
Richard B. Russell Reservoir	0.020	0.005	0.030	0.030	0.032
Red Rock Reservoir	0.120	0.130	0.105	0.065	0.060

Table 9
Concentration of Reduced Fe and Mn in Waters Overlying Sediments from Selected CE
Reservoir Systems Incubated Under Aerobic Conditions at 20°C, µg/ml

Incubation Time	Beech Fork Reservoir		Browns L. Reservoir		Eagle L. Reservoir		Eau Galle Reservoir		Red Rock Reservoir		Richard B. Russell Reservoir	
	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0	8.59	2.22	0.14	0.68	5.44	2.31	7.32	1.37	1.03	1.07	17.30	8.73
1	1.43	1.98	0.08	0.13	<0.05	0.05	2.27	1.21	0.25	1.10	1.23	7.26
3	0.82	1.65	0.09	<0.05	<0.05	<0.05	<0.05	0.52	<0.05	1.01	0.46	6.84
7	--	--	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.54	<0.05	4.43
14	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.10	<0.05	0.72

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8