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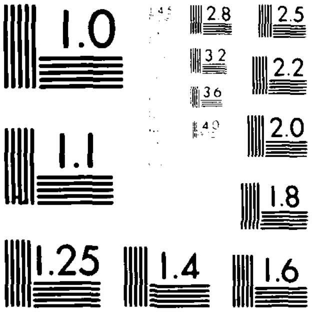
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The occurrence of dissolved oxygen depletion and anaerobic processes in the hypolimnion of Corps of Engineers (CE) reservoirs can adversely impact water quality and directly affect CE Civil Works activities. A literature review, a consultation with authorities on anaerobic systems, and a workshop indicated the feasibility of developing a conceptual model to depict major pathways for nutrient regeneration and metal mobilization under anaerobic conditions. The

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product of subsequent model development and experimental studies, Dissolved Oxygen Subroutine with Anaerobic Processes (DOSAP), is presented herein and its operation is described in detail. The DOSAP model is presented as a series of seven linked geochemical steps (phases) of increasingly anaerobic (reduced) conditions. Major factors influencing the rate and duration of each of the major pathways are discussed. The DOSAP model has subsequently been transformed into a mathematical subroutine for the CE one-dimensional reservoir water quality model, CE-QUAL-R1.

A literature search revealed a paucity of information on various physicochemical and biological rates affecting geochemical/water quality conditions in reservoirs, although abundant data for some parameters exist for other freshwater systems and marine environments. A series of investigations conducted in 250-ℓ laboratory reaction chambers provided an initial set of physicochemical rate data for DeGray Reservoir on the Caddo River in Arkansas. Use of large reactor systems appears to be a feasible approach for obtaining the physicochemical rate data required to use DOSAP on a site-specific basis, and this method is being used to develop a set of rate coefficients using sediments from CE reservoirs on a nationwide basis.

While detailed guidance on data requirements, sampling procedures, and rate coefficient selection for DOSAP will be presented in a later Engineering Technical Letter, this report summarizes procedures currently being used to obtain data for the subroutine.

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 work was conducted during the period September 1978-June 1979 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 Dr. R. L. Eley, 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 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 Dr. D. Gunnison and Mr. J. M. Brannon, ERSD. Mr. I. Smith, Jr., Ms. P. L. Butler, Mr. G. A. Burton, and Ms. K. M. Preston, ERSD, assisted with the laboratory experimentation. This report was written by Dr. Gunnison and Mr. Brannon and was reviewed by Dr. K. W. Thornton, and Dr. R. L. Chen, ERSD, and Dr. P. G. Malone, Environmental Engineering Division.

Directors of the WES during this study and the preparation and publication of this report were COL John L. Cannon, CE, and COL Nelson P. Conover, CE. Technical Director was Mr. F. R. Brown.

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CHARACTERIZATION OF ANAEROBIC CHEMICAL PROCESSES IN RESERVOIRS
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PART I: INTRODUCTION

Background

1. Many Corps of Engineers (CE) reservoirs experience low concentrations of dissolved oxygen and high concentrations of products of anaerobic transformation within the hypolimnion and, subsequently, 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, high 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. Existing modeling approaches do not adequately predict the many biological, chemical, and physical ramifications of anaerobic processes that occur in reservoirs, although several models of pertinent individual processes do exist: DOSAG of the Texas Water Development Board (1970) and the phosphorus models of Jørgensen et al. (1975) and Kamp-Nielson (1975, 1976). Moreover, present techniques give an ineffective characterization of the sources and extent of dissolved oxygen depletion, the development of anaerobic conditions in the hypolimnion, the mobilization of nutrients and contaminants, and sediment deposition and resuspension. Managers also lack the capability to evaluate various alternative methods for correcting such problems or to determine the subsequent effects of corrective measures on impoundment water quality.

Purpose

3. This study was undertaken to provide the information for the

development of an anaerobic model which could then be used as a tool to deal with water quality problems. This report presents the results of an investigation on processes associated with low dissolved oxygen and anaerobic conditions in reservoirs. This review has led to the formulation of a conceptual model of reservoir anaerobic processes and to the development of a descriptive subroutine: Dissolved Oxygen Subroutine with Anaerobic Processes (DOSAP). The anaerobic subroutine has subsequently been incorporated into the CE one-dimensional reservoir water quality model (CE-QUAL-R1) as a part of the Environmental and Water Quality Operational Studies (EWQOS) Task IC. After appropriate testing and evaluation, the subroutine will be documented in subsequent updates of the CE-QUAL-R1 user's manual. This report is confined to a technical description of basic changes in reservoir water quality created by low dissolved oxygen and anaerobic conditions and to the conceptual model that was formulated to describe these processes.

PART II: PROBLEMS WITH LOW DISSOLVED OXYGEN AND ANAEROBIC CONDITIONS IN CE RESERVOIRS

4. This portion of the report discusses problems associated with the development of low dissolved oxygen (DO) and anaerobic conditions in CE reservoirs. Consideration will be given to depletion of dissolved oxygen, to anaerobic nutrient regeneration and contaminant mobilization, and to the current strategies used by CE Field Offices to address these problems. Keeley et al. (1978) discussed these considerations in detail. Keeley et al. (1978) is summarized below to provide a background for the technical discussion presented in Part III of this report, beginning on page 13.

Dissolved Oxygen and Anaerobic Conditions

5. The impoundment of waters often results in the development of low dissolved oxygen concentrations within the impoundment and in reservoir releases. This situation may result in the accompanying release of undesirable products of anaerobic processes, including dissolved, reduced forms of nitrogen; iron and manganese; reduced organic compounds; and hydrogen sulfide. The problem is particularly relevant because of the adverse consequences of these conditions on recreational and fishery resources within and downstream of the impoundment and because of potential increases in water treatment costs incurred by users.

6. Many reservoirs, like natural lakes, develop thermal stratification (Figure 1). Reservoirs thus affected may subsequently develop low dissolved oxygen concentrations in hypolimnetic waters because the stratification serves as a barrier to vertical mixing with oxygenated surface waters. Natural reaeration of hypolimnetic waters is consequently minimal until destratification occurs. The low levels of dissolved oxygen and the anaerobic conditions that may ensue are the result of a complex, integrated series of physical and biogeochemical processes that use oxygen-demanding organic matter and various inorganic substances.

7. Biogeochemical processes occurring under anaerobic conditions differ greatly from those encountered in aerobic environments. Microbial

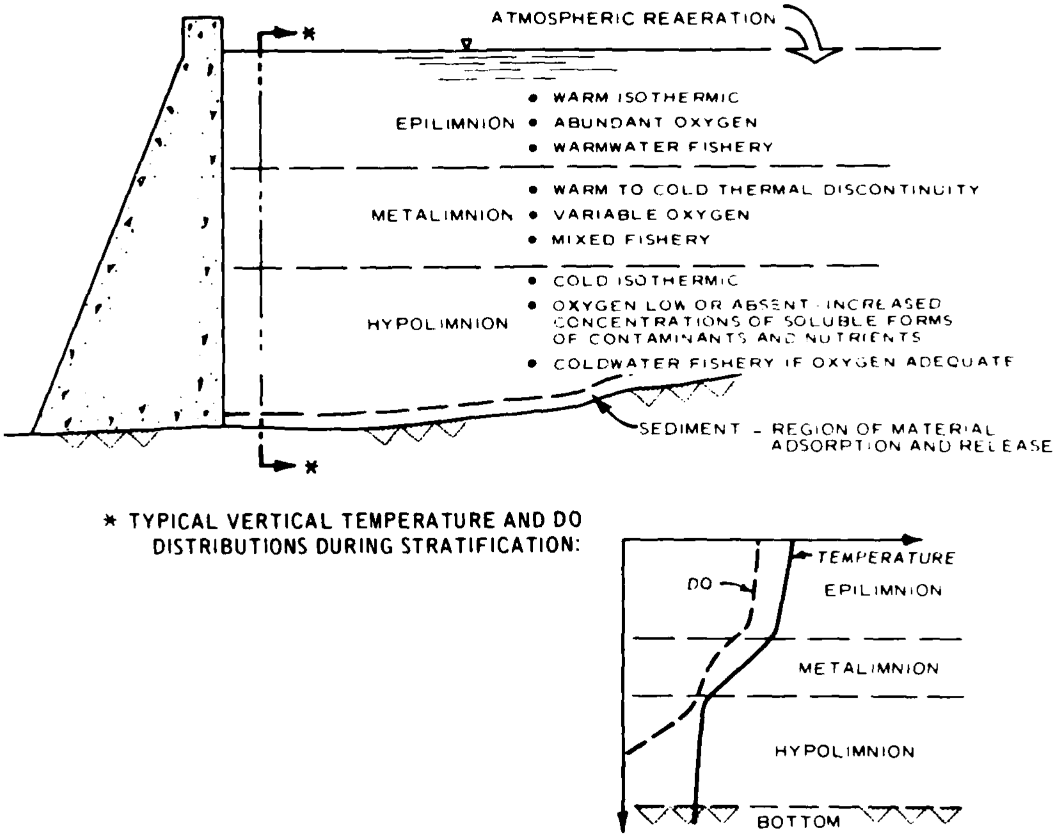


Figure 1. Thermally stratified reservoir and associated conditions of low dissolved oxygen

activities in anaerobic environments yield soluble, often highly concentrated, forms of nitrogen, iron, manganese, and sulfides that can produce toxicity, taste, odor, and staining problems. Moreover, anaerobic processes also release nutrients that may support undesirable algal blooms. Finally, extended evolution of hydrogen sulfide in reservoirs can result in severe problems with odors, corrosion of outlet structures, and toxicity to aquatic organisms.

8. Several approaches have been used to deal with problems associated with low DO and anaerobic conditions in reservoirs and their releases. The approaches have generally been very expensive and have often been effective only for small water bodies. In the case of release waters, existing approaches have only temporarily or partially achieved

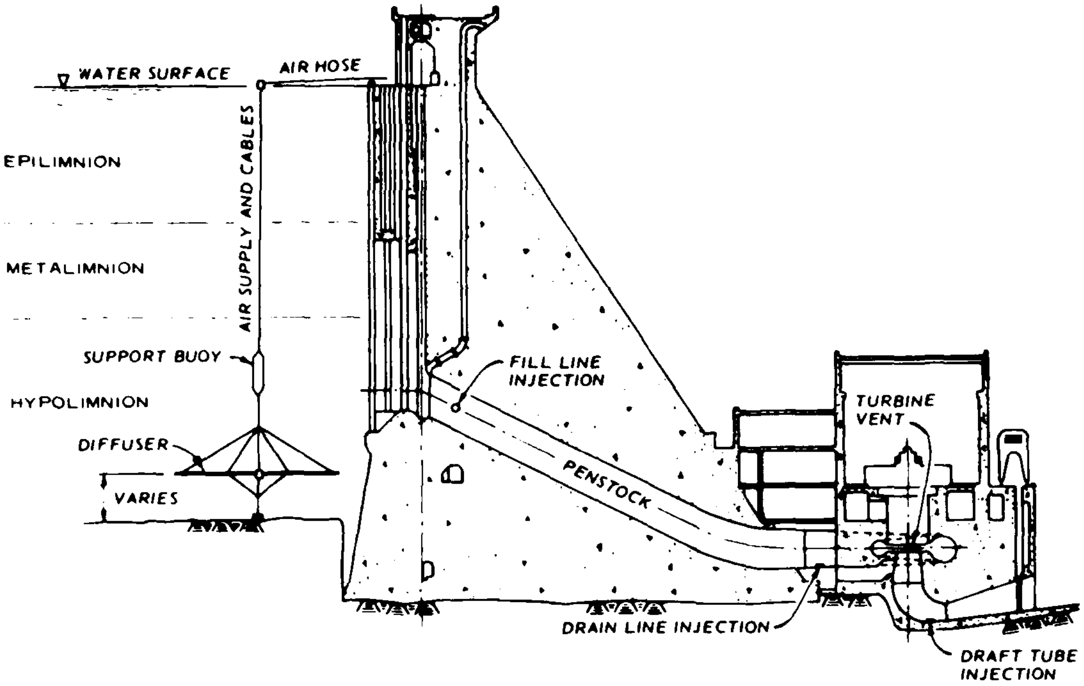
desired water quality conditions. Examples include injection of air or oxygen into the hypolimnion, mechanical destratification, penstock injection of oxygen or turbine venting, and selective withdrawal. Figure 2 illustrates several of these procedures. In most cases, inadequate guidance is available on the probable severity of anticipated problems or on when to initiate and when to terminate corrective procedures.

9. A final management strategy is the reduction of oxygen-demanding materials entering reservoirs. Reduction may be accomplished in several ways: diversion of waters containing oxygen-demanding substances (Edmondson 1970); appropriate clearing and site preparation prior to reservoir filling; or filling and flushing or incrementally filling the reservoir basin during initial stages of impoundment. Alternatively, selective withdrawal procedures may be used in reservoirs to avoid the release of low DO waters by removal from various levels in an impoundment (Bohan and Grace 1973) (Figure 2b).

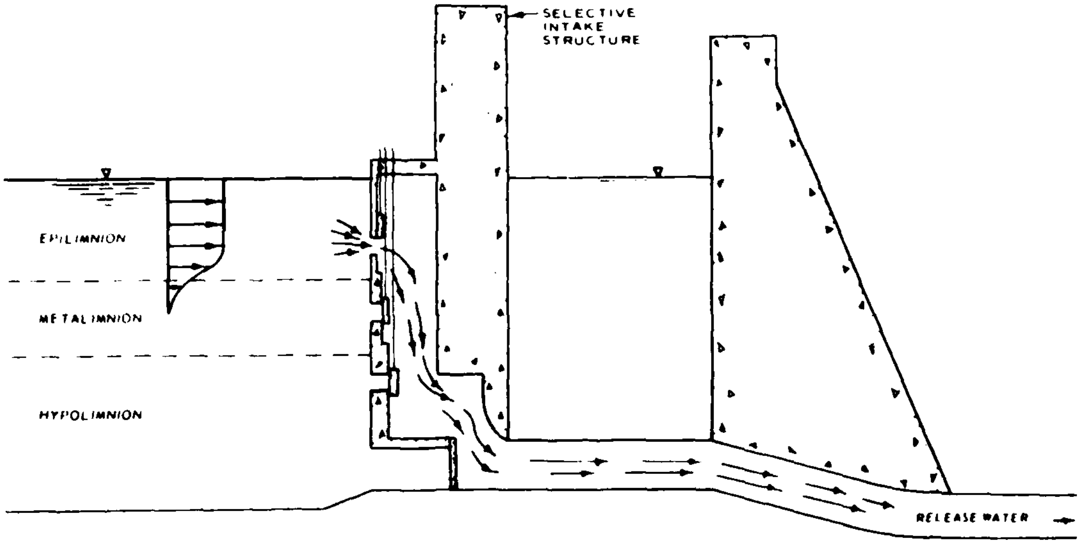
Nutrient Regeneration

10. Excessive nutrient enrichment of reservoirs can promote the development of nuisance algal blooms and the excessive growth of submerged plants. The decomposition of these plant materials may produce fish kills, taste and odor problems, and unaesthetic conditions (Keeley et al. 1978). Secondary effects that result from the presence of excessive algal growths include extreme fluctuations in diurnal oxygen concentrations and development of rough fish populations.

11. A major source of nutrient input into many reservoirs is runoff from agricultural lands. Excessive inputs of nutrients in some areas can also be attributed to poor management of forested lands and to mining activities in upstream portions of the watershed. Nitrate- and phosphate-rich runoff from feedlots and cattle grazing near the reservoir are other sources of enrichment. However, even if nutrient inputs are reduced, reservoir sediments under anaerobic conditions may serve as sources of nutrients, particularly nitrogen and phosphorus, through the process of anaerobic nutrient cycling.



a. Potential alternatives for air or oxygen injection in hydropower projects



b. Generalized schematic of a selective withdrawal structure for reservoir releases

Figure 2. Alternatives for problems associated with low DO and anaerobic conditions in reservoirs

12. Problems with excessive nutrient enrichment and DO demands in reservoirs frequently are most intense during the first few years of impoundment. New reservoirs not only are subjected to external (allochthonous) loadings, but also contain a significant internal loading and oxygen demand resulting from the decomposition of inundated herbaceous plants, litter, and organic rich topsoil. By contrast, the decomposition of woody plant material such as trees probably is not a significant cause of eutrophication and low DO because of the very slow rate of degradation. Effective preimpoundment clearing and site preparation policies cannot be formulated presently because of insufficient information on the relative importance of various materials as sinks for DO and sources of nutrients following initial reservoir filling and inundation.

13. Many of the watershed activities that contribute to the eutrophication of CE reservoirs cannot be controlled; however, the CE can influence the effects of nutrient regeneration through project design and operation (Keeley et al. 1978). Any procedure that maintains hypolimnetic DO will generally minimize the impact of anaerobic nutrient regeneration. Restoration techniques, such as dredging, that remove nutrient-laden sediments from the reservoir may be effective, but economically infeasible, as alternative operational strategies that prevent the initial stagnation of hypolimnetic waters. The need for these expensive corrective procedures might often be avoided if adequate techniques for predicting the nature and extent of anaerobic nutrient regeneration in reservoirs were available.

Mobilization of Contaminants

14. Contaminants have been defined as certain microorganisms or chemical substances that may have a deleterious effect on the environmental quality of a given aquatic resource, primarily through their adverse effects on man or on biological food chains (Keeley et al. 1978). From the standpoint of anaerobic conditions, only two types of contaminants are of major concern. The first type includes those

oxygen-demanding waste substances, particularly organic compounds, that deplete oxygen from water through autocatalytic processes or that are sufficiently abundant and biodegradable that their decomposition will remove oxygen from the water. The second class of contaminants includes those metals whose chemical or physical forms are altered under anaerobic conditions with the result that their solubility is modified and their concentration in the reservoir is increased.

15. Contaminants are a source of problems in CE reservoirs primarily because certain chemical contaminants such as heavy metals (e.g. mercury) and certain pesticides (e.g. chlorinated hydrocarbons) are capable of undergoing biotransformation, and often bioaccumulation, in food chains. Reservoirs that presently do not have immediate contaminant problems may be subjected to continual low-level contaminant loadings, which have the potential for being accumulated and causing significant problems in later years of project life. This is particularly true if the loadings become deposited in the reservoir in locations where major biogeochemical activities may alter their solubility through anaerobic processes. Two fairly common metals, iron and manganese, may reach such high concentrations in anoxic hypolimnetic waters that reservoir discharges become discolored and cloudy when the reoxidation of these materials changes their properties from transparent dissolved to colored colloidal substances.

16. Three general approaches are currently used for the management of contaminants mobilized by processes active under anaerobic conditions. These include diversion of contaminant-laden inflows, removal of contaminant-laden sediments, and maintenance of aerobic conditions in the reservoir hypolimnion.

PART III: DEVELOPMENT OF LOW DISSOLVED OXYGEN AND ANAEROBIC CONDITIONS IN CE RESERVOIRS

17. The intensity of oxidative and reductive processes occurring in anaerobic sediments and natural water systems directly affects CE Civil Works activities. The environmental problems associated with releases of anaerobic waters from reservoir hypolimnions have been of special concern. The basic principles of DO depletion and subsequent anaerobic reactions and associated environmental controls must be understood before a predictive capability can be developed for anaerobic problems. The capacity to forecast the extent and intensity of anaerobic conditions achieved under various environmental constraints is important since the intensity of anaerobic conditions will determine the form and mobility of many chemical constituents. The form and mobility of a given chemical constituent will, in turn, determine the potential of a sediment or water system to exert an adverse environmental impact.

Literature Review

Reduction process in natural systems

18. Natural systems are considerably different from rigidly controlled laboratory systems having fixed characteristics (Clark 1972) since natural systems are constantly in a state of flux. In addition to changes in oxidation-reduction potential (Eh), natural systems also exhibit constant changes in chemical composition, hydrogen ion concentration, and diversities of microbial activities (Hewitt 1933). Oxidation-reduction potentials in natural systems, however, do vary between well-defined limits. The upper and lower limits, respectively, of Eh in natural systems are determined by the presence or absence of DO and by the point at which water becomes unstable and its components are oxidized to molecular oxygen and reduced to molecular hydrogen (Garrels and Christ 1956); the latter point is approached when anaerobic bacteria decompose organic matter and reduce molecular hydrogen. The oxidation

states of many organic and inorganic constituents are affected by the Eh of surrounding water and sediment.

Microbial effects and biodegradation of organic matter

19. When the oxygen supply to a flooded soil, sediment, or aquatic environment containing decomposable organic matter is curtailed, profound changes occur both in the composition of the indigenous microbial community and in the processes that these organisms carry out. The succession of microorganisms that follows includes strict aerobes first (that require oxygen) and then facultative anaerobes (that can exist with or without oxygen) where both populations achieve their maximum levels within the first 48 hr after flooding of a soil and curtailment of oxygen supply (Patrick and Mikkelsen 1971). These are subsequently replaced by populations of strict anaerobic bacteria, which cannot live in the presence of oxygen, once the supply of oxygen within the system has been totally exhausted (Takai and Kamura 1966; Takai, Koyama, and Kamura 1956).

20. The electrochemical transformations that occur in flooded soils and sediments have been well documented. The oxidation-reduction potential declines from highly positive preflood levels immediately after waterlogging as a consequence of the activities of aerobic and facultatively anaerobic bacteria. The drop in oxidation-reduction potential to negative values then permits the initiation of full activities by populations of anaerobic and sulfate-reducing bacteria (Takai and Kamura 1966). Most oxidation-reduction processes encountered in natural systems require biological mediation (Morris and Stumm 1967), which means that approaches to physicochemical equilibrium depend strongly on microbial activities.

21. Wetzel (1975) has described in considerable detail the many changes in organic matter that occur in association with the microbially mediated processes of anaerobic decomposition in sediments. In the sediments of freshwater systems such as streams, lakes, and ponds, methanogenesis is the major process by which the removal of large quantities of carbon occurs. The breakdown of organic matter to carbon dioxide and

methane occurs as a two-step process, although no distinction between the steps occurs in nature and the steps proceed simultaneously. The first step involves the hydrolysis and fermentation of carbohydrates, fats, and proteins to yield organic acids, alcohols, and a variety of inorganic products (Deyl 1961, McCarty 1964, Sokatch 1969, and Thimann 1963). The organic acids and alcohols are then subject to decomposition by the strictly anaerobic methanogenic bacteria to yield methane and/or carbon dioxide (Mah et al. 1977). The process is completed when gaseous methane bubbles up out of the sediments (ebullition) and rises through the water column, often creating "methane convection" currents that may carry sediment particles and dissolved materials of the hypolimnion with them into the trophogenic zone of a lake or pond (Wetzel 1975). Methane may also be oxidized by the activities of methane-oxidizing bacteria in portions of the water column having trace quantities of oxygen (Wetzel 1975; Reeburgh and Heggie 1977).

Chemical effects

22. Takai, Koyama, and Kamura (1956) incubated freshly flooded soils and found that NO_3-N disappeared at the beginning of incubation; this was followed by iron (Fe) reduction and then active sulfide formation. Takai and Kamura (1966) subsequently found that Fe reduction did not commence until manganese (Mn) reduction was essentially complete. Turner and Patrick (1968) found that reduction in soils was not strictly sequential because Mn reduction was not complete when Fe reduction began. However, little reduction of Mn and almost no reduction of Fe occurred until both oxygen and nitrate had disappeared. Ponnamperuma (1972), summarizing the results of many studies, reported that reduction of a submerged soil proceeds roughly in the sequence predicted by thermodynamics. Oxygen is first reduced, followed by nitrate reduction after oxygen concentration has dropped to levels below 0.2 mg/ℓ. Manganese dioxide is reduced next and followed by reduction of iron and sulfate. Ponnamperuma (1972) presented a table that stated the critical potentials for reduction of inorganic electron acceptors in stirred soil suspensions. These critical potentials, taken from the work of Patrick (1964), Connell and Patrick (1968), and Turner and Patrick (1968), are presented

in the following tabulation and provide a rough guide to the sequence of reduction steps in natural systems.

Observation*	Eh,^{7} mV**
Oxygen (undetectable)	330
Nitrate (undetectable)	220
Reduced manganese (detectable)	200
Reduced iron (detectable)	-120
Sulfate (undetectable)	-150

Note: Information modified from Ponnamperuma (1972).

* Comments in parentheses indicate major changes in the observations that become evident at the Eh^{7} indicated.

** Eh,^{7} mV = oxidation-reduction potential in millivolts at pH 7.

23. Other results indicate that, even in complex natural systems such as flooded soils, the thermodynamic properties of chemical constituents apparently influence the sequence of reduction. The sequence of reduction in any natural system should therefore be at least qualitatively predictable.

Measurement of oxidation-reduction potential

24. The measurement of oxidation-reduction potential in natural systems is replete with significant potential sources of error, and good technique is essential for obtaining reliable data. Morris and Stumm (1967) pointed out that microenvironments differing from the overall environment may be formed in natural systems. Stumm and Morgan (1970) emphasized that natural waters are in a highly dynamic state rather than in or near equilibrium. Consequently, no single oxidation-reduction electrochemical potential (Eh) representative of any one of the possible systems present can be expected to be reliably established with the measuring electrode (normally platinum). Furthermore, it is generally

recognized that Eh measurements in oxygenated natural waters are invalid because of the instability of the platinum electrode in the presence of molecular oxygen and the dominance of oxygen as an electron acceptor in oxidation-reduction reactions. Bohn (1971) felt that natural systems rarely achieve oxidation-reduction equilibrium because of the continual addition of electron donors (organic matter).

25. Despite the difficulties involved in the determination and interpretation of Eh readings in natural media, it is widely accepted that Eh readings in natural anaerobic systems can provide valuable environmental information relative to the dominant oxidation-reduction sequence in a qualitative sense. Breck (1974) considered that measurements of Eh with a platinum electrode might depict trends in a useful and quite reliable manner. Ponnamperuma (1972) considered Eh a useful environmental parameter in spite of its limitations and cited numerous studies in support of his contention. Whitfield (1969) found Eh useful as a semiquantitative indicator of the degree of stagnation of a particular aquatic environment as did Ponnamperuma (1972) for flooded soils and sediments.

Chemical oxidation-reduction sequences in natural aquatic environments

26. The following section examines the various oxidation-reduction chemical systems present in natural aquatic environments in sequence from most oxidized to most reduced.

27. Oxygen. The presence of O_2 in a system will maintain Eh at potentials in excess of +300 to +400 mV. Platinum electrodes do not, however, register steady or reproducible redox potentials in poorly poised (unstable) systems, such as aerated soils and natural waters (Ponnamperuma 1972). This problem in Eh measurements in aerobic systems has been attributed to the absence of electroactive systems in sufficiently high concentrations and to the presence of mixed systems that are not in equilibrium among themselves (Morris and Stumm 1967; Stumm and Morgan 1970). Patrick and Mikkelsen (1971) reported that aerated soils have characteristic redox potentials in the range of +400 to

+700 mV. Dissolved oxygen does not exert the potential that would be expected if it were functioning at equilibrium (Garrels and Christ 1956). Instead, it acts like a much weaker oxidizing agent, with an Eh of +650 to +700 mV at pH = 0 and about +300 to +350 mV at pH = 8 . Systems exposed to air show potentials (in volts at 25°C) according to the approximate relation (Garrels and Christ 1956) $Eh = 0.70 - 0.06\ pH$, in contrast to the expected theoretical relation $Eh = 1.23 - 0.06\ pH$.

28. Thus, it is apparent that Eh measurements in aerated systems are of little value. The oxidation state of aerobic systems is better characterized by measuring the DO concentration rather than by determining the Eh.

29. Nitrogen. It has been established that the Eh of anaerobic systems will be stabilized at potentials between +200 and +400 mV as long as NO_3^- is present (Turner and Patrick 1968, Ponnamperuma 1965, Ponnamperuma and Castro 1964, Yamane and Sato 1968, and Yamane 1969). The presence of NO_3^- prevents the production of other reduced forms (MN^{+2}, FE^{+2}, S^{-2}, CH_4, and H_2) in the sequence of oxidation-reduction events in lake waters and muds (Pearsall and Mortimer 1939; Mortimer 1941 and 1942) and in submerged soils (Turner and Patrick 1968; Ponnamperuma 1972). Consequently, the presence of NO_3^- will poise the system at a slightly reduced, but relatively oxygen-free level.

30. The NO_3^--NO_2^- couple has a calculated E_o of 430 mV at pH 7 (Whitfield 1972). Many workers (Bohn 1971, Stumm 1967, and Whitfield 1972), however, consider the NO_3^--NO_2^--NH_4^+ couples irreversible since the reduction of NO_3^- to NO_2^- to NH_4 and/or N_2O and N_2 (denitrification) is normally mediated by microorganisms. Evidence exists that although NO_3^- is subject to irreversible reactions such as denitrification, it will increase the Eh and retard a fall in Eh (Engler and Patrick 1974) when NO_3^- is added to anaerobic systems. Nitrate may affect the Eh by means of an electroactive mediator system. Elema (1932), cited by Thimann (1963),* found that a steady Eh was established when solutions of nitrate

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* Elema, B. 1932. De bepaling von oxydatie-reductie potentiaol in bacteriencultures en here beteekenis voor de stofivisseling, Ph. D. Dissertation, Delft, The Netherlands.

or a nitrite-containing hydrogen donor (usually ethanol) were inoculated with a culture of denitrifying microorganisms. Elema concluded that the reversible substance causing a steady Eh must have been released from the bacteria because the nitrite and alcohol alone were unable to register a steady potential. Moreover, enzymes (such as those in bacteria) are known to have the capacity to mediate the potentials of redox couples that do not exhibit activity by themselves (Clark 1972).

31. Manganese. Manganese is not as effective as nitrate in stabilizing or poising Eh. Once Mn^{+4} reduction had commenced, the influence of MnO_2 in stabilizing the Eh was found to be weak because of its relative insolubility and because of its use as an electron acceptor in respiration by only a limited number of bacteria (Ponnamperum 1972). Nhung and Ponnamperuma (1966) found, however, that added MnO_2 was much more effective than added $Fe(OH)_3$ in retarding the fall in Eh of a flooded acid sulfate soil. The effectiveness of the MnO_2 in retarding soil reduction was credited to the high standard oxidation-reduction potential ($E_o = 1.230$ mV) of the MnO_2 Mn^{+2} system. Native or added MnO_2, in addition to retarding the decrease in Eh or the onset of moderately anaerobic conditions in flooded soils, was also found to prevent the buildup of high concentrations of Fe^{+2} and other reduction products (Ponnamperuma and Castro 1964; Ponnamperuma, Yaun, and Nhung 1965).

32. Many studies have focused on the effect of the Mn^{+4} reduction process on Eh. Ponnamperuma, Loy, and Tianco (1969) found that the E_o's of Mn compounds in soils and sand plus MnO_2 were markedly lower than those of the ideal oxides and varied with the soil and the intensity of reduction. Experimentally derived E_o's deviated least from theory and were closest to those of the sand-MnO_2 medium for soils high in Mn and low in organic matter. Ponnamperuma, Loy, and Tianco (1969) used the constancy of E_o in a soil despite variations in Eh, pH, PCO_2, and Mn^{+2} activity, as the criterion for the presence of a particular Mn system. Olomu, Racy, and Cho (1973) found that E_o values calculated from experimentally measured Eh, pH, and Mn^{+2} concentrations appeared to indicate the presence of the Mn_2O_3-Mn^{+2} redox system.

33. Other workers have not found any relationship between Eh and

the Mn^{+4}/Mn^{+2} couple. Bohn (1968) found that the electrode potential of two soils was independent of the Mn^{+4}/Mn^{+2} couple. Gotoh and Patrick (1972) found marked deviation from the equations calculated for pure systems for the calculation of equations that relate experimentally obtained Mn^{+2} activity to pH and Eh in the pH range of 6 to 8. Bohn (1970) found that Mn^{+2} concentrations in control and autoclaved soil suspensions differed widely from the Mn^{+2} concentrations calculated from models; the latter require measurement of Eh or assume Eh to be fixed by another redox couple. However, the soil suspensions studied (Bohn 1970) were kept in loosely stoppered containers and were therefore subject to air oxidation.

34. Iron. Takai, Koyama, and Kamura (1963) found a close connection between Eh and pH of flooded soils and the amount of ferrous iron in the soil. Takai and Kamura (1966) considered oxidized iron in soils to be the most important factor retarding the onset of highly reducing conditions because of the high concentrations of reducible iron that normally occur in most soils. Ponnamperuma (1972) reported that the Eh, pH, and Fe^{+2} concentrations in reduced lake waters reported by various workers (Mortimer 1941 and 1942) conformed to the equilibrium values of the $Fe(OH)_3$ Fe^{+2} system. Hem (1960) found that the behavior of iron in natural systems was predicted to a large extent by fluctuations in the oxidation-reduction potential and pH environment. Ponnamperuma, Tianco, and Loy (1967) confirmed the participation of $Fe(OH)_3$ and $Fe_3(OH)_6$ in redox equilibria in flooded soils.

35. Ponnamperuma, Tianco, and Loy (1967) found that the Eh, pH, and Fe^{+2} activity of 32 flooded soil solutions sampled weekly for 17 weeks conformed closely to the equation

$$Eh = 1.058 - 0.059 \log Fe^{+2} - 0.177 \text{ pH} \qquad (1)$$

during the period of submergence, up to the point where water-soluble Fe^{+2} reached a peak when

$$Eh = 0.429 - 0.059 \log Fe^{+2} - 0.236 \text{ pH} \qquad (2)$$

and subsequently

$$Eh = 0.429 - 0.059 \text{ pH} \qquad (3)$$

better expressed the situation. This confirmed the participation of $Fe(OH)_3$ and $Fe_3(OH)_6$ in redox equilibria in flooded soils. The participation of iron in redox equilibria of flooded soils was also supported by the work of Gotoh and Patrick (1974), whose results suggested that Fe^{+2} activity in a flooded soil might be governed generally by the solubility of ferric oxyhydroxide. Van Breeman (1969) claimed that the equilibrium between ferric and ferrous iron was largely governed by ill-defined ferric oxides, which were intermediate in stability between amorphous $Fe(OH)_3$ and α - FeOOH .

36. Other workers have been unable to show the participation of iron in redox equilibria. Olomu, Racy, and Cho (1973) found that the calculated values of E_o , assuming an operative Fe_2O_3-Fe^{+2} redox system, were far greater than the theoretical value. However, they also found that almost all the Fe in soil solution was complexed with organic matter. The high degree of Fe complexing in soil solution was suggested as the reason for the failure to obtain the theoretical E_o value for the Fe_2O_3-Fe redox system from the experimental data. Bohn (1969) found that iron(II) sulfate added to aerobic soil suspensions did not govern Eh because of the immediate precipitation of the Fe^{+3} formed. Coursier (1952) found that the concentrations of iron(II) and (III) each must exceed 10^{-5} $\underline{M}$ (0.56 mg/ℓ) in order to govern Eh. In addition, Collins and Buol (1970) showed that some Mn and Fe precipitation reactions were not reversible over short periods of time.

37. The effect of the iron system is not as great as those of nitrate and magnanese on Eh. Ponnamperuma (1972) stated that because of the low standard potential of the $Fe(OH)_3$-Fe^{+2} system, its influence was not as obvious as that of NO_3^- or MnO_2. Nhung and Ponnamperuma (1966) found that added $Fe(OH)_3$ retarded to a limited extent the fall of Eh in a flooded acid sulfate soil. The effect of the added $Fe(OH)_3$ on Eh was not nearly as great as that of MnO_2. Ponnamperuma (1965) noted

that soils high in Fe^{+3} showed a slower rate of fall in Eh in the zone -50 to -200 mV than did soils low in Fe^{+3}.

38. Sulfur. The reduction of SO_4^{-2} to S^{-2} does not occur until an Eh of approximately -150 mV is reached within a pH range of 6.8 and 7.1 (Connell and Patrick 1968) and represents intense reducing conditions. Martens and Berner (1974) have recently shown that methane concentrations in the interstitial waters of Long Island Sound sediments did not reach appreciable concentrations until about 90 percent of seawater sulfate was removed by sulfate-reducing bacteria. Laboratory studies of anoxic marine sediments indicated that methane production does not occur until dissolved sulfate is totally exhausted (Martens and Berner 1974).

39. Berner (1963) demonstrated that the Eh of many sediments containing H_2S is controlled by the reversible half-cell

$$HS^-_{aq} \quad S^o_{rhmb} + H^+_{aq} + 2e^- \tag{4}$$

which is equivalent to the half-cell

$$S^{2-}_{aq} \quad S^o_{rhmb} + 2e^- \tag{5}$$

The controlling S^{2-}_{aq}/S^o_{rhmb} half-cell found by Berner (1963) was truly reversible (Voge 1939; Peschanski and Valenski 1949). Other workers (Whitfield 1969; Skopintsev, Romenskaya, and Smirnov 1966) have also demonstrated that the platinum electrode responds to the sulfide-sulfur half-cell in a wide variety of reduced systems containing sulfur.

40. The Eh of a natural H_2S containing sediment is controlled by the sulfide-sulfur half-cell only if an amount of oxidizing agent sufficient to bring about the oxidation of sulfide to elemental sulfur is present (Berner 1963). The presence of ferric hydroxide or geothite will oxidize H_2S to elemental sulfur; from there further oxidation to a saturated polysulfide solution can occur (Berner 1963).

41. Hydrogen. Reducing conditions become sufficiently strong in some anaerobic environments for the H^+-H_2 couple to affect the Eh. Yamane and Sato (1968) have found that the first minimum potential

following flooding can be as low as -420 mV and can be accompanied by the evolution of hydrogen. Baas-Becking, Kaplan, and Moore (1960) reported that the H^+-H_2 exchange current was great enough for its potential to be the major determinant of Eh in strongly reducing environments. The influence of the H^+-H_2 couple on Eh at 25°C may be described by the equation

$$Eh = -0.029 \; pH_2 - 0.059 \; pH \qquad (6)$$

42. The hydrogen ion concentration, in addition to the H^+-H_2 couple, may also influence Eh. Clark (1972) reported that the hydrogen ion concentration affects Eh by influencing the dissociation of oxidant or reductant. The effect of pH on Eh has been reviewed in detail by Laitinen (1960) and Ponnamperuma (1972).

Effect of organic matter on anaerobic processes

43. Organic matter, in addition to serving as an energy source for bacteria, is also a source of electrons (electron donor) for biological reduction processes (Ponnamperuma 1972). The organic matter that serves as a source of electrons becomes oxidized and can potentially form a couple with its reduced precursor. Thus, it is not surprising that the addition of decomposable organic matter will affect the rate and intensity of reduction in anaerobic systems. Addition of organic matter to anaerobic systems will generally increase the rate of reduction (Ponnamperuma 1972; Takai, Koyama, and Kamura 1963). A rapid decline in Eh was characteristic of soils with low contents of reducible Fe and Mn and a high organic matter content (Patrick and Mahapatra 1968). Ponnamperuma and Castro (1964) suggested that the potentials of reduced soils might be potentials of organic systems mediated by enzymes and bacteria.

44. Organic matter can exert a decided impact on the Eh of a system despite the electrochemical irreversibility of most organic couples (Clark 1972), since irreversible redox couples can exert an electrode potential via a mediator. Lehmann (1930), reviewed by Clark

(1972), demonstrated that the irreversible succinate/fumarate system could influence electrode potentials in the presence of a mediator. Electrode potentials at constant pH conformed to Eh's predicted from the ratio of [succinate]/[fumarate] and were independent of the nature or concentration of the mediator. Within a limited range of pH, the potentials were in conformity with the theoretical slope of 0.06.

45. When a soil is submerged, soil solution concentrations of volatile organic acids increase, reach a peak of value of 10 to 40 mmol/ℓ in 1 to 2 weeks, and then decline to less than 1 mmol/ℓ a few weeks later (Ponnamperuma 1972). Low temperatures lead to extensive accumulation of organic acids in the soil solution (International Rice Research Institute (IRRI) 1969). Motomura (1962), as cited by Ponnamperuma (1972), found that soils high in native or added organic matter have correspondingly high concentrations of organic acids. There is evidence that this buildup of organic acids may affect Eh. Clark (1972) summarized results of many studies that showed that addition of the alkali salts of acetic, citric, lactic, malonic, oxalic, salicyclic, or tartaric acid generally decreased the Eh of an Fe^{+3}/FE^{+2} system at constant pH. These observations, coupled with the buildup of organic acids in anaerobic systems, further demonstrate the potential effects that organics may exert on Eh.

Discussion

46. The survey of the literature, coupled with other studies (Brannon et al. 1978), suggests that the microorganisms and anaerobic processes involved in the decomposition of organic matter and in the reduction of nitrate, manganese, iron, and sulfate in organic-laden waters are very similar to those occurring in flooded soils and sediments. The sequence of reduction of these inorganic electron acceptors generally corresponded to results obtained by other workers (Morris and Stumm 1967; Takai and Kamura 1966; Takai, Koyama and Kamura 1956; Connell and Patrick 1968; Patrick 1964; Ponnamperuma 1972; Turner and Patrick 1968) wherein dissolved oxygen was rapidly depleted in the

culture medium with the rate of removal being proportional to the amount of organic matter present in the system.

47. Previous studies by the authors of this report (Brannon et al. 1978) have shown that the succession of microorganisms occurring in aquatic microcosms closely follows the successional pattern observed by other workers in flooded soils and sediments. The succession of microorganisms in flooded soils includes aerobes first and facultative anaerobes second, where both populations achieve their maximum levels within the first 48 hr after flooding (Ponnamperuma 1972). During this period, the supply of oxygen in the sediment is totally exhausted, and populations increase of strict anaerobic bacteria, to which O_2 is a lethal toxin (Takai and Kamura 1966; Takai, Koyama, and Kamura 1956).

48. Nitrate reduction commences when O_2 is either partially or totally consumed, with denitrification probably serving as the main removal mechanism for nitrate.

49. Brannon et al. (1978) has clearly demonstrated the similarity between reduction processes occurring in systems simulating reservoir waters and those occurring in soils and sediments, indicating that results of studies in flooded soils may well be applicable to other systems involving lake sediments. Indeed, Ponnamperuma (1972) has studied the movement of the boundary layer between the aerobic and anaerobic zones from within lake sediments to the water above the mud surface, and into the hypolimnion. By this process, the water of the hypolimnion may become an extension of the sediment interstitial water, although the intensity of reduction and the reduction products observed may not be identical. Mortimer (1941, 1942) has observed that, in thermally stratified eutrophic lakes, the Eh declines rapidly in the thermocline, and in the hypolimnion the Eh may acquire values as low as those in the underlying reduced sediments.

50. Results of the Brannon et al. (1978) studies indicate that the amount of organic matter present will be a major determinant of the rate of reduction of Fe^{+3} and Mn^{+4}. The concentrations that reduced components reach in the system depend not only on the amount of organic matter present, but also on the amount of reducible substrate initially

present. For accurate predictions of anaerobic processes in hypolimnions of CE reservoirs, the amount of decomposable organic matter and reducible Fe^{+3} and Mn^{+4} must be determined.

51. To illustrate the sequential nature of reductive processes as they occur in natural systems, a series of seven figures (Figures 3-9) is presented to illustrate aerobic/anaerobic processes observed in waters overlying the soil horizon taken from the area of the proposed Twin Valley Lake in western Minnesota (all figures are taken from Gunnison et al. (1979)). In each of the figures, depletion of DO and establishment of anaerobic conditions occur in the same order as indicated in Figure 3; the "Transition" section marked between 14 and 19 days of incubation in each of the figures denotes a changeover from aerobic to anaerobic conditions. Thus, as oxygen is depleted from the system and anaerobic conditions ensue, pH declines from 9.4 to 6.8 while conductivity increases (Figure 4); total dissolved organic carbon (TOC) accumulates in the water in an erratic manner while total inorganic carbon (TIC)

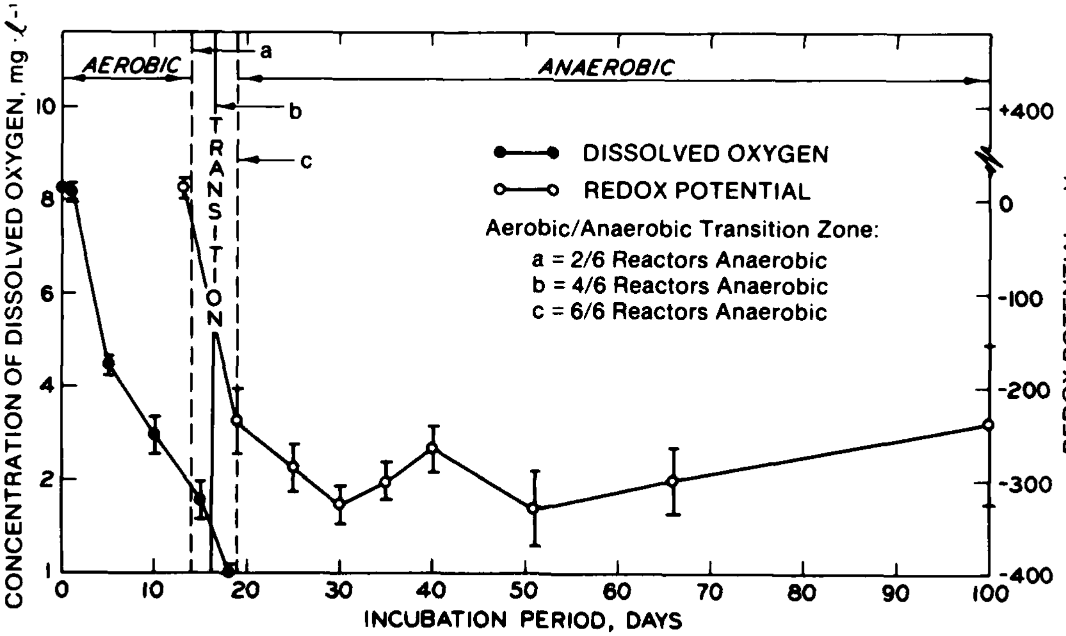


Figure 3. Changes in DO concentration and oxidation-reduction (redox) potential in water columns of the reactor units during 100-day incubation period. Bars around each mean value represent standard error of the mean

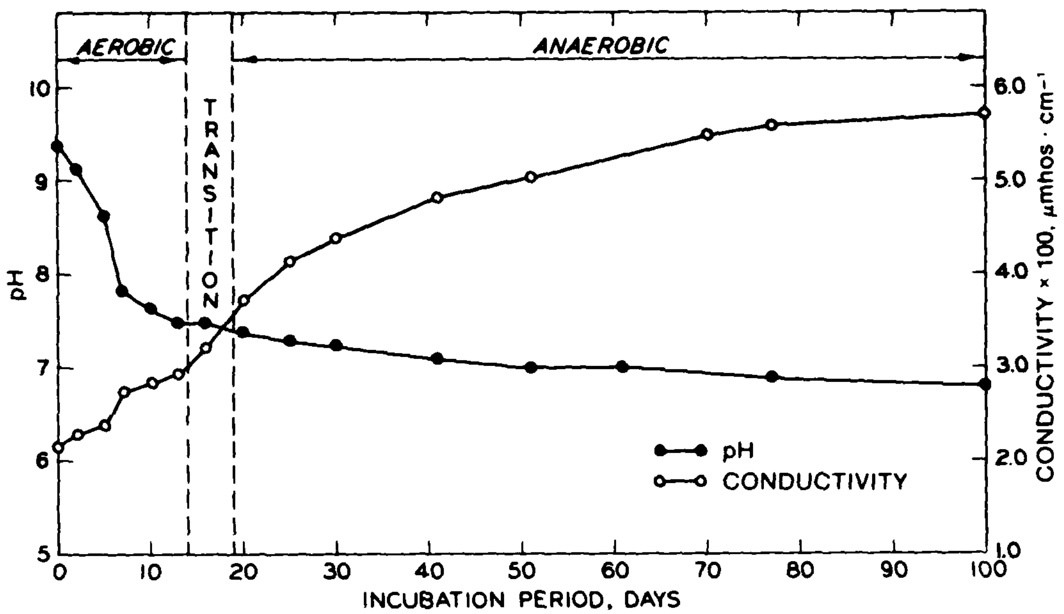


Figure 4. Changes in pH and conductivity in the water columns of the reactor units during 100-day incubation period. Deviations from mean values were insignificant and, therefore, are not presented here

increases nearly linearly (Figure 5); nitrate-nitrogen (NO_3-N) is depleted steadily as anaerobic conditions are developing; nitrite-nitrogen (NO_2-N) appears in a transitory fashion prior to the onset of anaerobic conditions, and ammonium nitrogen (NH_4-N) does not accumulate until after anaerobic conditions have been established (Figure 6); total phosphorus accumulates in the water column in an irregular manner, but orthophosphate phosphorus does not accumulate in significant concentrations until after the establishment of anaerobic conditions (Figure 7) and iron and manganese release from the soil to the water. Each of the latter constituents requires anaerobic conditions for accumulation (Figure 8), while sulfide production from sulfate does not ensue until anaerobic conditions have become well established (Figure 9).

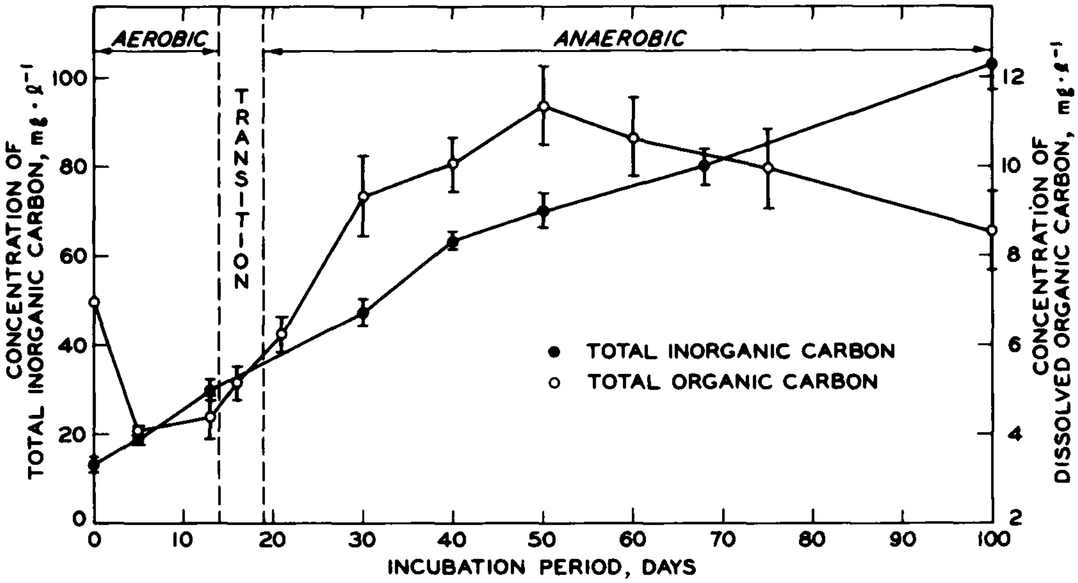


Figure 5. Changes in TIC and TOC in the water columns of the reactor units during 100-day incubation period. Bars around each mean value represent standard error of the mean

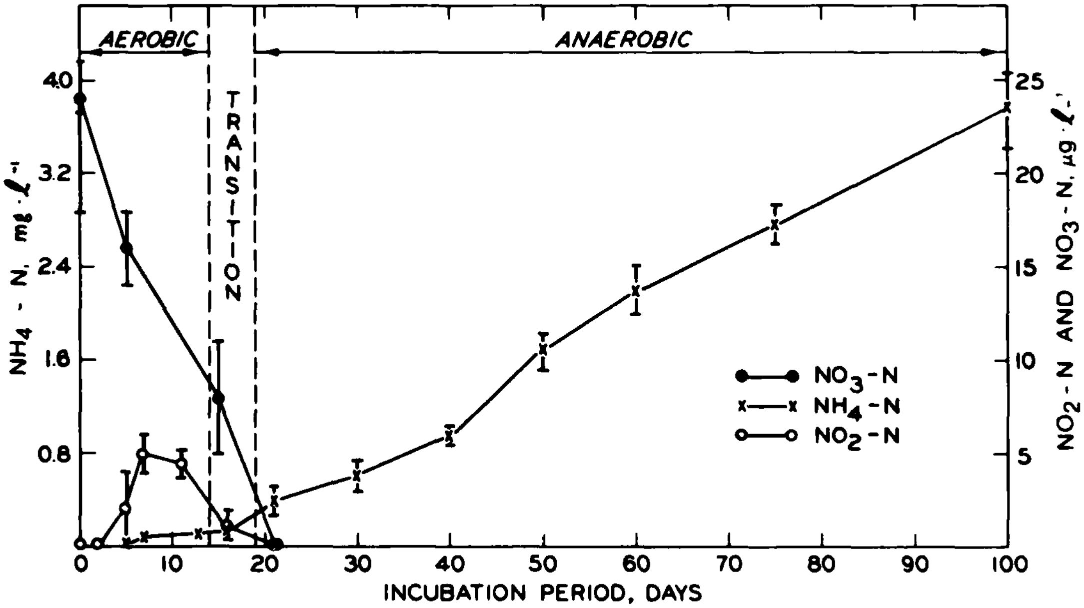


Figure 6. Changes in NH_4-N, NO_3-N, and NO_2-N in the water columns of the reactor units during 100-day incubation period. Bars around each mean value represent standard error of the mean

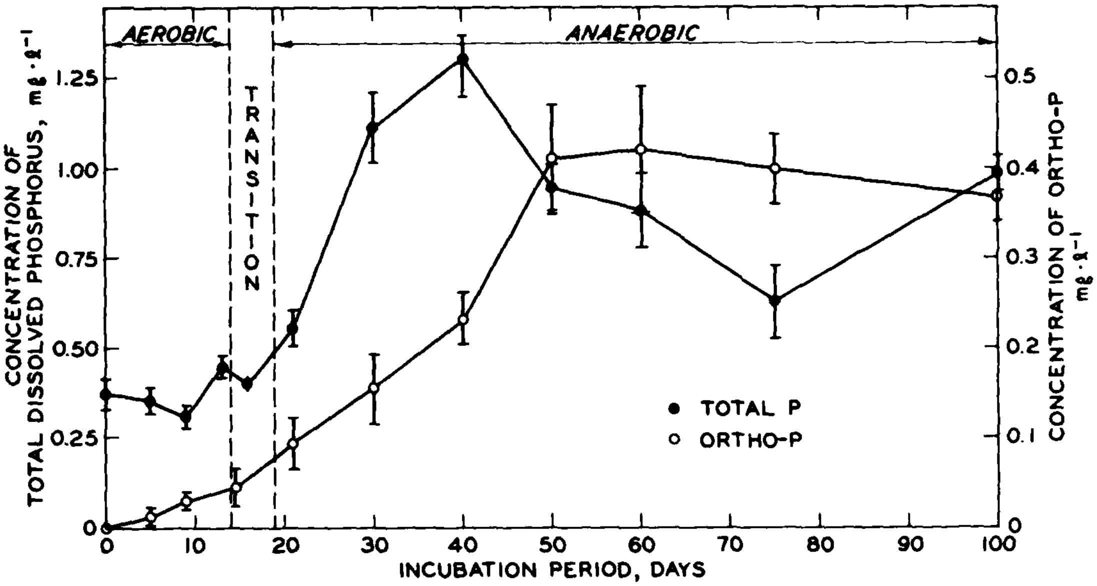


Figure 7. Changes in total P and ortho-P in the water columns of the reactor units during 100-day incubation period. Bars around each mean value represent standard error of the mean

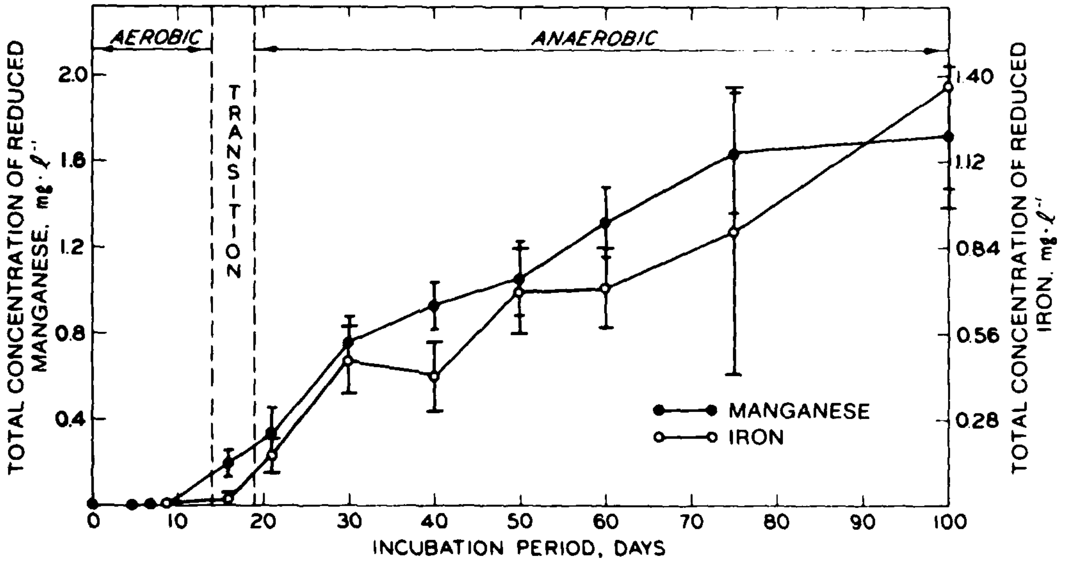


Figure 8. Changes in concentration of soluble reduced manganese (total Mn) and iron (total Fe) in the water columns of the reactor units during 100-day incubation period. Bars around each mean value represent standard error of the mean

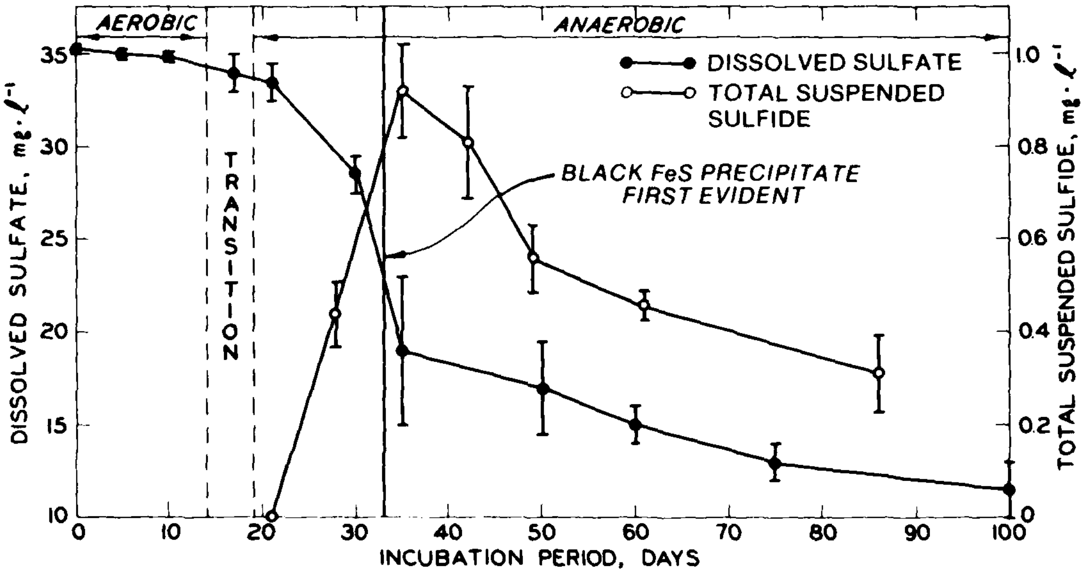


Figure 9. Changes in concentration of dissolved sulfate and total suspended sulfide in the water columns of the reactor units during 100-day incubation period. Bars around each mean value represent standard error of the mean

PART IV: DOSAP-DISSOLVED OXYGEN SUBROUTINE WITH ANAEROBIC PROCESSES

52. The DOSAP formulation described herein was developed as the conceptual basis for a mathematical subroutine for simulating anaerobic processes. Current mathematical water quality models lack the capability to track anaerobic processes. Although intended for use with the CE reservoir water quality model, CE-QUAL-R1, DOSAP can be interfaced with other numerical models.

53. This portion of the report describes in two sections the basic structure of the DOSAP formulation. The first section describes the overall organization of the subroutine, its various components, and then integrates these components into a functionally unified picture. The second section analyzes each component in detail and explains the various physical-chemical subsections of each component. A compilation of representative rate data for the subroutine, as obtained from the literature and the authors' studies, is presented and discussed in Part V.

Subroutine Organization and Function

54. The DOSAP subroutine consists of a series of seven steps or phases that gradually and continuously proceeds from aerobic (oxic) to anaerobic (anoxic) conditions and then proceeds through a limited succession of anerobic product-generating loops, each of which is more intensely anaerobic (reducing) than its predecessors.

Phases of DOSAP

55. Phase I: DO depletion. This phase is initiated at the onset of thermal stratification in the reservoir. During stratification, the diffusive exchange of DO between the epilimnion and the hypolimnion and advective transport of oxygen-bearing water into the hypolimnion are greatly diminished. Decomposition of organic matter proceeds together with the oxidation of reduced anaerobic constituents released from reservoir bottom sediments. Through these processes, water column DO may be depleted down to a level of 2 mg/ℓ, the initiation point for Phase II.

56. Phase II: DO exhaustion. Depletion of DO continues in this phase until all of the DO has been consumed; this is the signal to initiate Phase III. As a consequence of the decreasing concentration of DO, nitrate begins to replace oxygen as an inorganic electron acceptor for microbial respiration processes. As a result, the concentration of nitrate begins to decrease during Phase II.

57. Phase III: Ammonium accumulation. Nitrate is rapidly depleted and lost to the system. Ammonium begins to accumulate in the water column. This is a consequence of the nonavailability of oxygen to be used in the microbial oxidation of ammonium that is derived from decomposition of nitrogenous organic matter and from anaerobic reduction of nitrate to ammonium. Once all nitrate has been depleted, the system shifts to Phase IV.

58. Phase IV: Manganese accumulation. Soluble reduced manganese released from the sediments begins to accumulate in the hypolimnetic water column. The oxidation-reduction sequential process continues until reducing conditions become more intense, as indicated by maximum rates of manganese reduction and accumulation. A decrease in the rate of manganese reduction signals the start of Phase V.

59. Phase V: Iron accumulation. Reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) begins and the subsequent accumulation of soluble ferrous iron in the water column continues until the rate of iron accumulation begins to approach zero. Phase VI is then initiated.

60. Phase VI: Sulfate reduction. Reduction of sulfate present in the water and/or any sulfate entering the hypolimnion with inflows is initiated, and sulfide begins to appear in the water column. Sulfide released from the sediment to the hypolimnion is stable due to the intense anaerobic conditions. The rotten egg odor characteristic of hydrogen sulfide will be evident in any hypolimnetic waters that reach the surface, either upon destratification and mixing of the reservoir, or in samples of the hypolimnion that are brought up for examination. In addition, sulfide and its attendant odors will also occur in any releases made from the hypolimnion. Finally, the sulfide will easily combine with any reduced iron present in the water to form insoluble iron sulfide,

which is then precipitated. This phase is terminated when the supply of sulfate has been exhausted, and Phase VII is initiated.

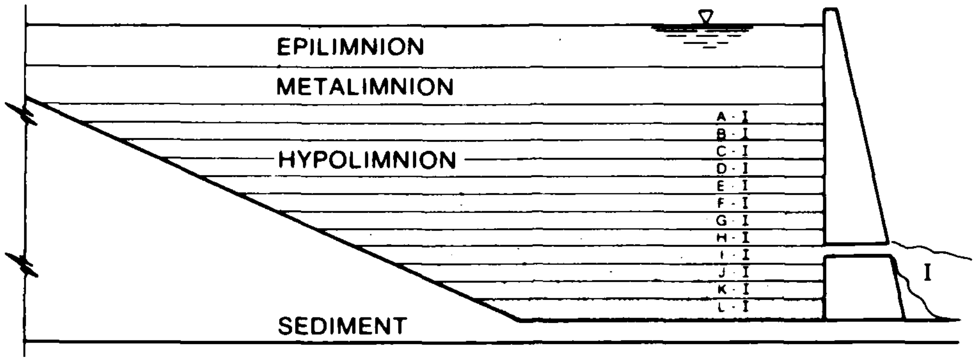
61. Phase VII: Methanogenesis. Methane formation is initiated and continues until the system is perturbed or the reservoir destratifies.

62. Destratification. As an interim measure, the destratification process automatically reoxidizes all reduced chemical entities dissolved or suspended in the layer. While this simplified approach does not prevent the useful application of the subroutine, certain inconsistencies, such as the instantaneous oxidation of manganese, result because of the automatic reoxidation process. However, the presence of such inconsistencies is minimal relative to the error introduced by omitting the reoxidation step. A more realistic formulation for processes whereby reduced substances accumulated under anaerobic conditions are chemically and biologically oxidized after destratification is presently being developed and tested as part of this work unit. Once this has been completed, various interactions between dissolved and particulate matter will also be added to the subroutine.

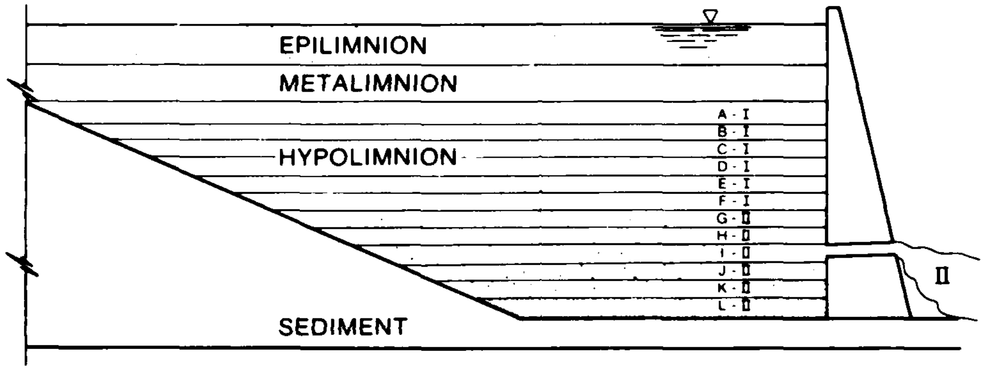
DOSAP function in relation to CE-QUAL-R1

63. An example of the manner in which DOSAP might function as an algorithm in CE-QUAL-R1 or an equivalent water quality model is depicted in Figure 10. The hypolimnion of the reservoir may be modeled as a series of horizontal slices of variable thickness (user selected) stacked from the bottom of the water column. The DOSAP algorithm would be initiated following the onset of thermal stratification. According to this example, all slices of the hypolimnion would be in Phase I of the DOSAP algorithm at this time (Figure 10a).

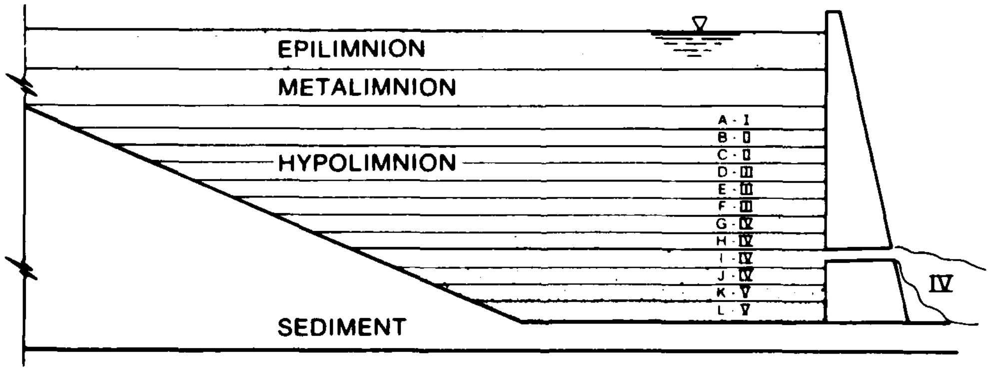
64. After a period of thermal stratification, the oxygen demand of the bottom sediments and bottom layers of water may become large enough to deplete these layers of DO, thereby pushing these sediments and layers into Phase II. With continued oxygen depletion, resulting from oxygen depletion exceeding oxygen gains, the upper layers of the hypolimnion could also become depleted and these layers would enter Phase II as shown in Figure 10b.



a. Early stratification. All layers in Phase I



b. Several weeks after onset of stratification. DO is running out in the hypolimnion



c. Late after onset of stratification. DO is gone and ammonium, manganese, and iron are being accumulated in the hypolimnion

Figure 10. Diagram depicting hypothetical operations of DOSAP in simulating conditions in the hypolimnion of a reservoir being modeled as a series of horizontal layers. Stippled areas in layers E through L represent suspended sediments. For details, see text

65. Continued thermal stratification and development of anaerobic conditions would gradually result in each of the layers in the hypolimnion progressing through the seven DOSAP phases with eventual development of an anaerobic hypolimnion (Figure 10c). Hypolimnetic discharges would contain dissolved manganese, ammonium, and traces of iron. Because of the prolonged period of oxygen depletion and the large requirement for oxidizable carbon sources, it is doubtful that, in most reservoirs, the topmost layer of the hypolimnion would procede much beyond Phase III or IV. In addition, it is doubtful also that Phase VII would ever be found above the bottommost layers.

66. The DOSAP algorithm can also be used to simulate the effects of a metalimnetic oxygen demand where high oxygen demand associated with interflows of decomposition of settling organic particulates causes depletion of oxygen in a layer of the metalimnion; therefore, this layer(s) enters Phase II.

Phase Components and Interrelationships

67. Detailed descriptions of each DOSAP phase are presented below. The description for each phase contains: (1) the pH range over which the phase is functional; (2) the oxidation-reduction (redox) potential range for the phase; (3) the DO concentration, if any; (4) a synopsis or scenario that summarizes the sequence of major events that occur during the phase; and (5) a diagram that depicts the major chemical components and interactions present during the phase along with a tabulation of the processes represented by each of the arrows in the diagram and a list of algorithms summarizing the various processes operative on each component in the diagram. The boxes surrounding each component indicate whether that component is barely detectable (dashed line), is increasing in concentration (double lines), is becoming depleted (dotted line), or is in relative equilibrium (single line).

Phase I: DO Depletion (DO DEPLETE)

68. The pH range over which the phase is functional is 6.3 to 7.5.

69. The Eh range for the phase is +400 to +600 mV.

70. The DO concentration is saturated or supersaturated (at given temperatures) to equal approximately 2 mg/ℓ in the water column.

71. Synopsis of phase. Stratification has partially isolated the hypolimnion from diffusive exchange of gases with surface layers, thus decreasing reaeration. The topmost layer of the sediment is oxidized. Reduced dissolved organic materials and ammonium diffuse from the underlying layers of sediment to the top layer; however, sufficient oxygen remains in this layer to oxidize or promote microbial oxidation of these substances as they are released. Nitrate diffuses into the sediments from the overlaying water layer and is denitrified or assimilated. However, the nitrification process in the hypolimnion is rapid enough to replenish any nitrate lost by diffusion or flushing of the system. Depletion of DO exceeds any amount that might be brought in by inflows. Inorganic phosphate is continually being brought in by inflows and is also being regenerated from organic phosphate within the system. However, phosphate is also lost from the system through formation and precipitation of ferric phosphates. Sulfate may be accumulated by the system, either directly through inflows bearing high levels of dissolved sulfate, or indirectly via oxidation of sulfides released by decomposition of organic matter. Carbon dioxide accumulation results from respiration both in the water column and in the underlying sediments.

72. Summary of processes. The components and pathways for Phase I are presented in Figure 11. Arrows in Figure 11 are explained below:

Arrow No.	Processes Represented by Arrows
1	Import of dissolved inorganic phosphate with inflows.*
2	Import of dissolved inorganic sulfate with inflows.
3	Import of dissolved inorganic nitrate with inflows.
4	Import of dissolved inorganic nitrite with inflows.

(Continued)

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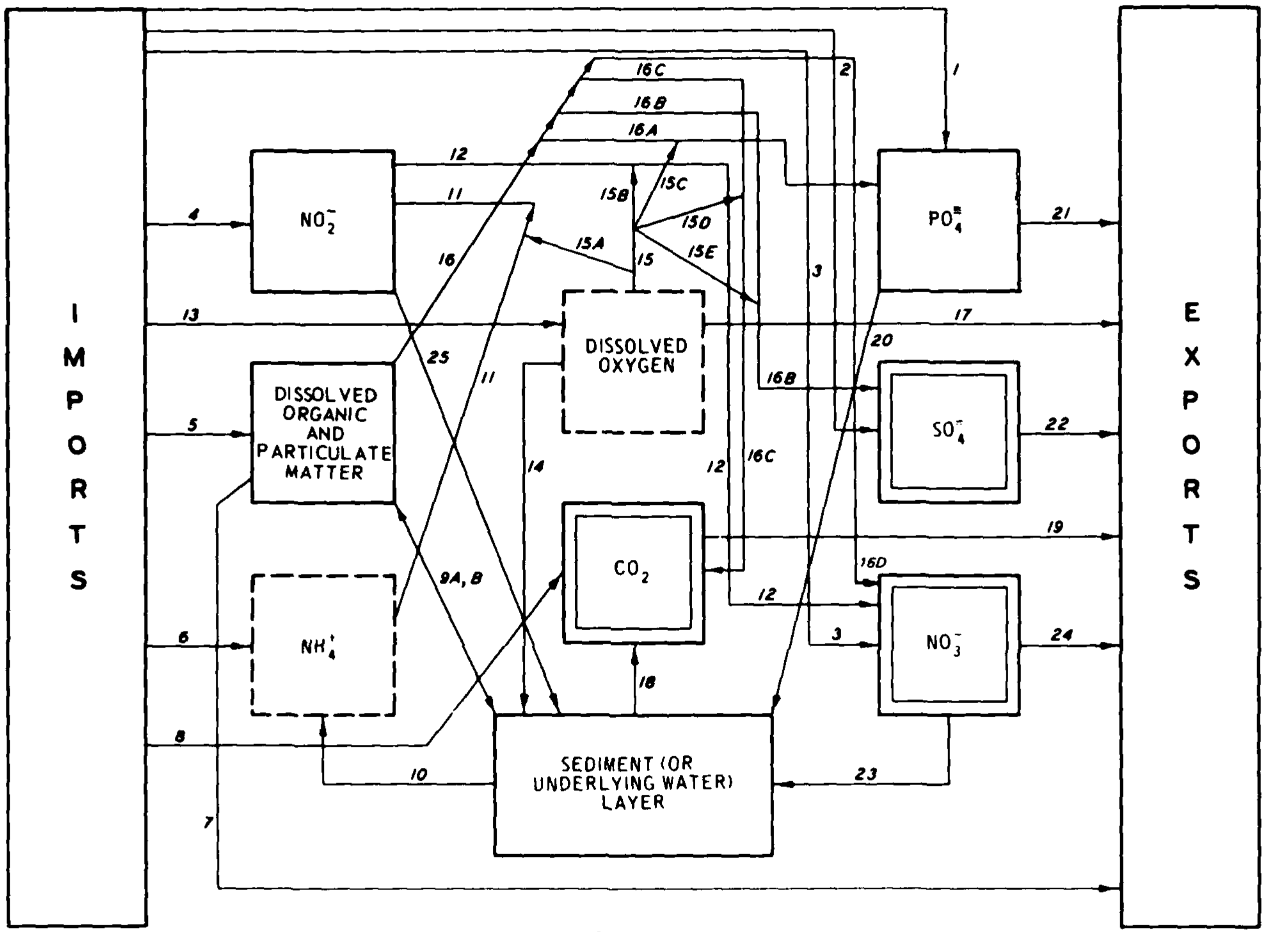
* Inflows are considered major movements of water into the hypolimnion from streams/rivers that flow into the reservoir and plunge below the thermocline.



PHASE I - DO DEPLETE

Figure 11. Major chemical changes and pathways associated with Phase I of the DOSAP algorthim

Arrow No.	Processes Represented by Arrows
5	Import of dissolved organic and particulate matter (dissolved organic matter with inflows; particulate matter settling from metalimnion and with inflows).
6	Import of ammonium with inflows.
7	Export of dissolved organics and particulate matter with outflows.
8	Import of dissolved carbon dioxide (predominantly as HCO_3^-) with inflows.
9A	Sedimentation of particulate organic matter from this water layer to underlying sediment or water layer.
9B	Release of dissolved organic matter from sediment (or water layer beneath layer of concern) to this water layer by diffusion, advection.
10	Diffusion of ammonium from sediment (or underlying water layer) to this water layer.
11	Oxidation of ammonium to nitrite (nitrification).
12	Oxidation of nitrite to nitrate (nitrification).
13	Import of DO with inflows.
14	Depletion of DO by diffusion into sediments (or underlying water) layer.
15	Oxygen depletion through uptake by chemical oxygen demand and biological oxidation processes, which may be split into:
15A	O_2 required for oxidation of $NH_4^+ \rightarrow NO_2^-$.
15B	O_2 required for oxidation of $NO_3^- \rightarrow NO_3^-$.
15C	O_2 required for oxidation of organically bound phosphate to release inorganic phosphate ($PO_4^{\equiv}$).
15D	O_2 required to oxidize organic carbon to $\rightarrow CO_2$.
15E	O_2 required to oxidize organic sulfide $\rightarrow SO_4^{=}$.
16	Decomposition of dissolved organics and particulate matter through chemical and biological processes to yield additional dissolved organics (retained within compartment), and carbon dioxide and dissolved inorganic phosphate, sulfate, and nitrate. Process may be split into:

(Continued)

Arrow No.	Processes Represented by Arrows
16A	Oxidation of organically bound phosphate to release inorganic phosphate ($PO_4^{\equiv}$).
16B	Oxidation of organic sulfide/sulfate to release inorganic sulfate ($SO_4^{=}$).
16C	Oxidation of organic carbon to carbon dioxide (CO_2).
16D*	Oxidation of organic nitrogen to inorganic nitrate (NO_3^-).
17	Export of DO with outflows.
18	Diffusion of carbon dioxide from sediment (or underlying water) layer into water layer of concern.
19	Export of dissolved carbon dioxide (as HCO_3^-) with outflows.
20	Precipitation of dissolved inorganic phosphate through formation of insoluble ferric and manganic phosphates and by sorption to other precipitating materials.
21	Export of dissolved inorganic phosphate with outflows.
22	Export of dissolved inorganic sulfate with outflows.
23	Diffusion of inorganic nitrate from water layer of concern into sediment (or underlying water) layer.
24	Export of dissolved inorganic nitrate with outflows.
25	Diffusion of inorganic nitrite from water layer of concern into sediment (or underlying water layer).

* Differentiated from ammonification under aerobic conditions.

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

Component	Factors Influencing Change of Concentration of Component
	Dissolved
d DO/dt =	Inflows - Outflows - DO [NO_2 Nitrate Formation + Dissolved Organic Matter Decay + Particulate Organic Decay + NH_4^+ + Nitrite Formation + Sediment Decay + BOD Demand + $S^{=}$ Sulfate Formation].
d NH_4^+/dt =	Inflows + Diffusion from Sediments or Underlying Anoxic Water Layer + Ammonification - NH_4^+ [NH_4^+ Nitrite Formation + Biological Uptake + Diffusion into Overlying Water Layer].
d NO_2^-/dt =	Inflows + NO_2^- [NH_4^+ Nitrite Formation] + NO_2^- [NO_3^- Nitrate Reduction] - Inflows - NO_2^- [NO_2^- Nitrate Formation + Diffusion into Sediments or Underlying Anoxic Water Layer + Diffusion into Overlying Water Layer].
d DOM*/dt =	Inflows + Sediment Release + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].
d CO_2/dt =	Inflows + CO_2 [Diffusion Out of Sediments or Underlying Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay] - Outflows - CO_2 [Carbonate Formation + Diffusion into Overlying Water Layer].
d $PO_4^{\equiv}$/dt =	Inflows + $PO_4^{\equiv}$ [Dissolved Organic $PO_4^{\equiv}$ Decay + Particulate Organic $PO_4^{\equiv}$ Decay + Cellular Release of $PO_4^{\equiv}$] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitates and Coprecipitates + Biological Uptake].
d $SO_4^{=}$/dt =	Inflows + $SO_4^{=}$ [Dissolved Organic Sulfate Decay + Particulate Organic Decay + $S^{=}$ Sulfate Formation] - Outflows - $SO_4^{=}$ [Biological Uptake].

(Continued)

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* DOM = dissolved organic matter.

Component	Factors Influencing Change of Concentration of Component
$d\ NO_3^-/dt$ =	Inflows + NO_3^- [NO_2^- Nitrate Formation] - Outflows - NO_3^- [Biological Uptake + NO_3^- Reduction + Diffusion into Sediments or Underlying Anoxic Water Layer].
	Particulate
d POM*/dt =	Inflows + Settling from Overlying Water Layer - Outflows - POM [Particulate Organic Matter Decay + Settling to Underlying Water or Sediment Layer].
d PIM**/dt =	Inflows + Settling from Overlying Water Layer - Outflows - PIM [Settling to Underlying Water or Sediment Layer].

* POM = particulate organic matter - includes microorganisms.

** PIM = particulate inorganic matter.

Phase II: DO Exhaustion (DO EXHAUST)

74. The pH range over which the phase is functional is 6.3 to 7.5.

75. The Eh is poised at approximately +400 mV.

76. The DO concentration is greater than or equal to 0 mg/ℓ and less than 2 mg/ℓ.

77. Synopsis of phase. Dissolved oxygen concentration in the water layer has dropped well below the 2-mg/ℓ level. Redox is poised at ≅ +400 mV (at pH 7.0) by the NO_2-NO_3 couple. Sufficient DO is present to continue oxidation of ammonium to nitrite and nitrate; however, the rate is much diminished, and ammonium is present in readily detectable quantities. Moreover, the oxygen depletion rate (arrows 14, 15, and 17) is quite rapid. The redox will not drop below ≅ + 400 mV even after DO has reached 0 mg/ℓ as long as a sufficient concentration of NO_2-NO_3 remains. As in Phase I, nitrate can still enter the system with inflows and is still produced by oxidation of ammonium through nitrite. However, removal of nitrate by flushing out of the system and by diffusion into sediments (or underlying anoxic water layer) has become appreciable and nitrate can no longer be considered as being

actively accumulated. Inorganic sulfate and inorganic phosphate formation and precipitation as iron phosphate remain as in Phase I.

78. Summary of processes. Figure 12 presents the components and pathways of importance for Phase II. These are identical to those for Phase I; only the rates have changed. See Phase I (paragraph 72) for description of processes represented by arrows.

79. Algorithms summarizing the various processes operative on each component in Figure 12 are given below:

Component — Factors Influencing Change of Concentration of Components

Dissolved

d DO/dt = Inflows - Outflows - DO [NO_2^- Nitrate Formation + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + NH_4^+ Nitrite Formation + Sediment Decay + BOD Demand + $S^=$ Sulfate Formation].

d NH_4^+/dt = Inflows + Diffusion from Sediments or Underlying Anoxic Water Layer + Ammonification - NH_4^+ [NH_4^+ Nitrite Formation + Biological Uptake + Diffusion into Overlying Water Layer].

d NO_2^-/dt = Inflows + NO_2^- [NH_4^+ Nitrite Formation] + NO_2^- [NO_3^- Nitrate Reduction] - Outflows - NO_2^- [NO_2^- Nitrate Formation + Diffusion into Sediments or Underlying Anoxic Water with Ensuing Denitrification + Diffusion from Overlying Water Layer].

d NO_3^-/dt = Inflows + NO_3^- [NO_2^- Nitrate Formation] - Outflows - NO_3^- [Biological Uptake + NO_3^- Reduction + Diffusion into Sediments or Underlying Anoxic Water Layer with Ensuing Denitrification + Diffusion from Overlying Water Layer].

d DOM/dt = Inflows + Sediment Release + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].

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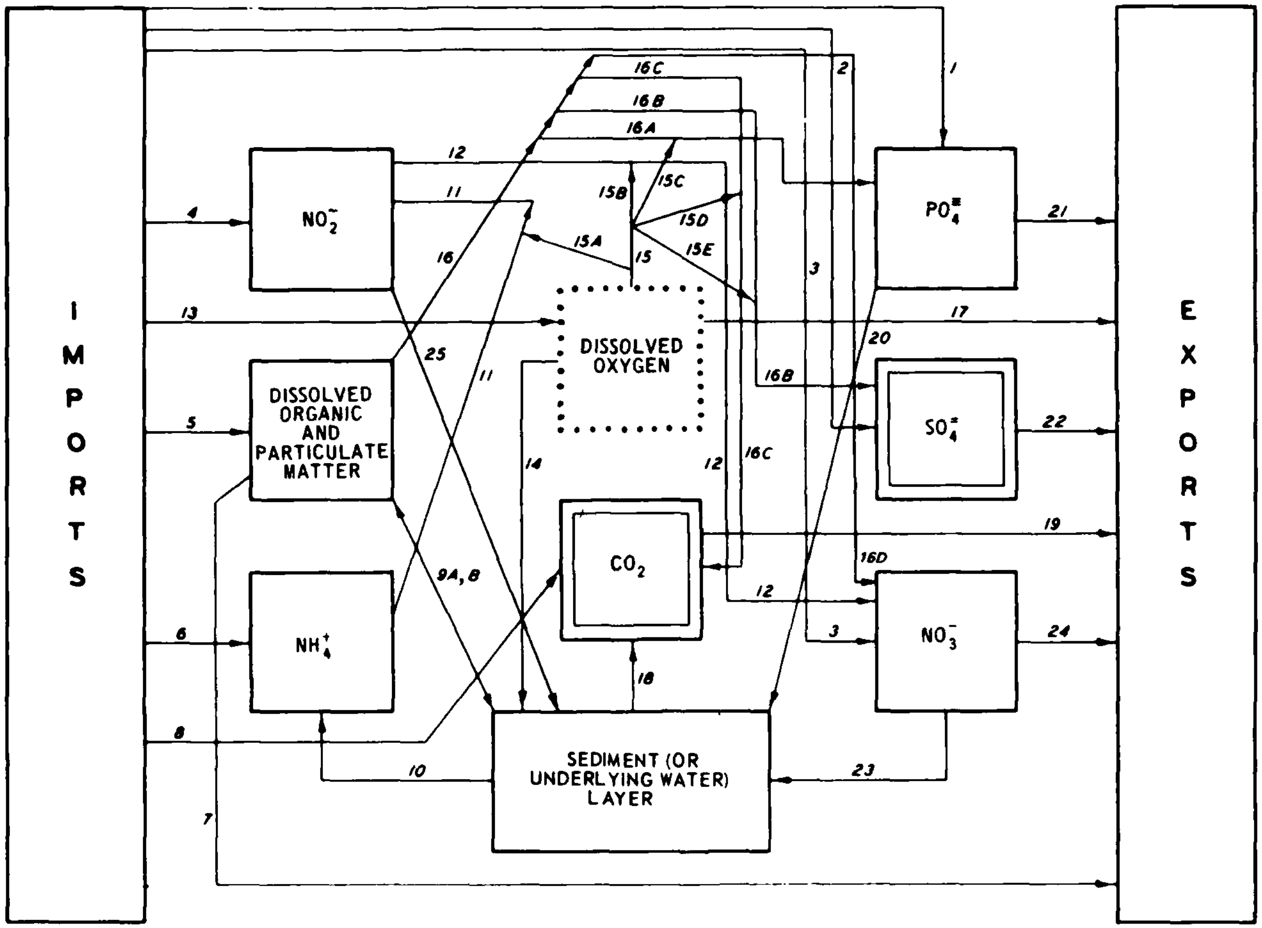

PHASE II - DO EXHAUST

Figure 12. Major chemical changes and pathways associated with Phase II of the DOSAP algorithm

Component	Factors Influencing Change of Concentration of Component
$d\,CO_2/dt$ =	Inflows + CO_2 [Diffusion Out of Sediments or Underlying Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay] - CO_2 [Outflows + Carbonate Formation + Diffusion into Overlying Water Layer].
$d\,PO_4^{\equiv}/dt$ =	Inflows + $PO_4^{\equiv}$ [Dissolved Organic PO_4 Decay + Particulate Organic PO_4 Decay + Cellular PO_4 Release] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitates and Coprecipitates + Biological Uptake].
$d\,SO_4^{=}/dt$ =	Inflows + $SO_4^{=}$ [Dissolved Organic Decay + Particulate Organic Decay + $S^{=}$ Sulfate Formation] - $SO_4^{=}$ [Outflows + Biological Uptake].

Particulate

d POM/dt = Inflows + Settling from Above - Outflows - POM [Particulate Organic Matter Decay + Settling to Below].

d PIM/dt = Inflows + Settling from Above - Outflows - PIM [Settling to Below].

Phase III: Ammonium Accumulation (AMMON ACCUM)

80. The pH range over which the phase is functional is 6.6 to 7.4.

81. The Eh is poised at approximately +300 mV (+400 > +200 mV).

82. The DO concentration is less than 1.5 to 0 mg/ℓ.

83. Synopsis of phase. Dissolved oxygen has been nearly or totally depleted. Nitrate is now being actively removed, and, although some nitrate may continue to be introduced in inflows, the rate of nitrate input (arrow 3) is exceeded by the removal in outflows (arrow 21) and by a large rate of diffusion into underlying sediment or the anoxic water layer. The concentration of nitrate is sufficiently low that nitrate reduction (nitrate respiration) is of little consequence. Ammonium is being actively accumulated now that nitrification is unavailable as a sink. Moreover, as oxygen disappears, ammonification

of organic materials in the water column (arrow 11) supplements the diffusion of ammonium from the sediments. Ammonium can be found in waters withdrawn from the hypolimnion. With decreasing redox values in the total absence of oxygen, very low concentrations of reduced manganese begin to appear in the water; however, at redox potentials $\cong +300$ mV, iron and manganese tend to reoxidize and are precipitated out of solution (arrows 7 and 12).

84. Summary of processes. Figure 13 gives the components and pathways of importance for Phase III. Arrows in Figure 13 are explained below:

Arrow No.	Processes Represented by Arrows
1	Import of dissolved inorganic phosphate with inflows.
2	Import of dissolved inorganic sulfate with inflows.
3	Import of dissolved nitrate with inflows.
4	Import of dissolved and particulate organic matter (dissolved organic matter in inflows; particulate matter settling from metalimnion and with inflows).
5	Import of ammonium with inflows.
6	Export of dissolved organics and particulate matter in outflows.
7	Import of dissolved carbon dioxide (at this pH predominantly HCO_3^-) with inflows.
8	Fermentative decomposition of dissolved and particulate organic matter to yield organic acids (which for now are retained within the compartment) and carbon dioxide.
9A	Sedimentation of particulate organic matter from water layer of concern to sediment (or water layer beneath it).
9B	Release of dissolved organic matter from sediment (or anoxic water layer beneath layer of concern) to water by diffusion.
10	Diffusion of ammonium from sediment (or anoxic water layer beneath layer of concern) to water.

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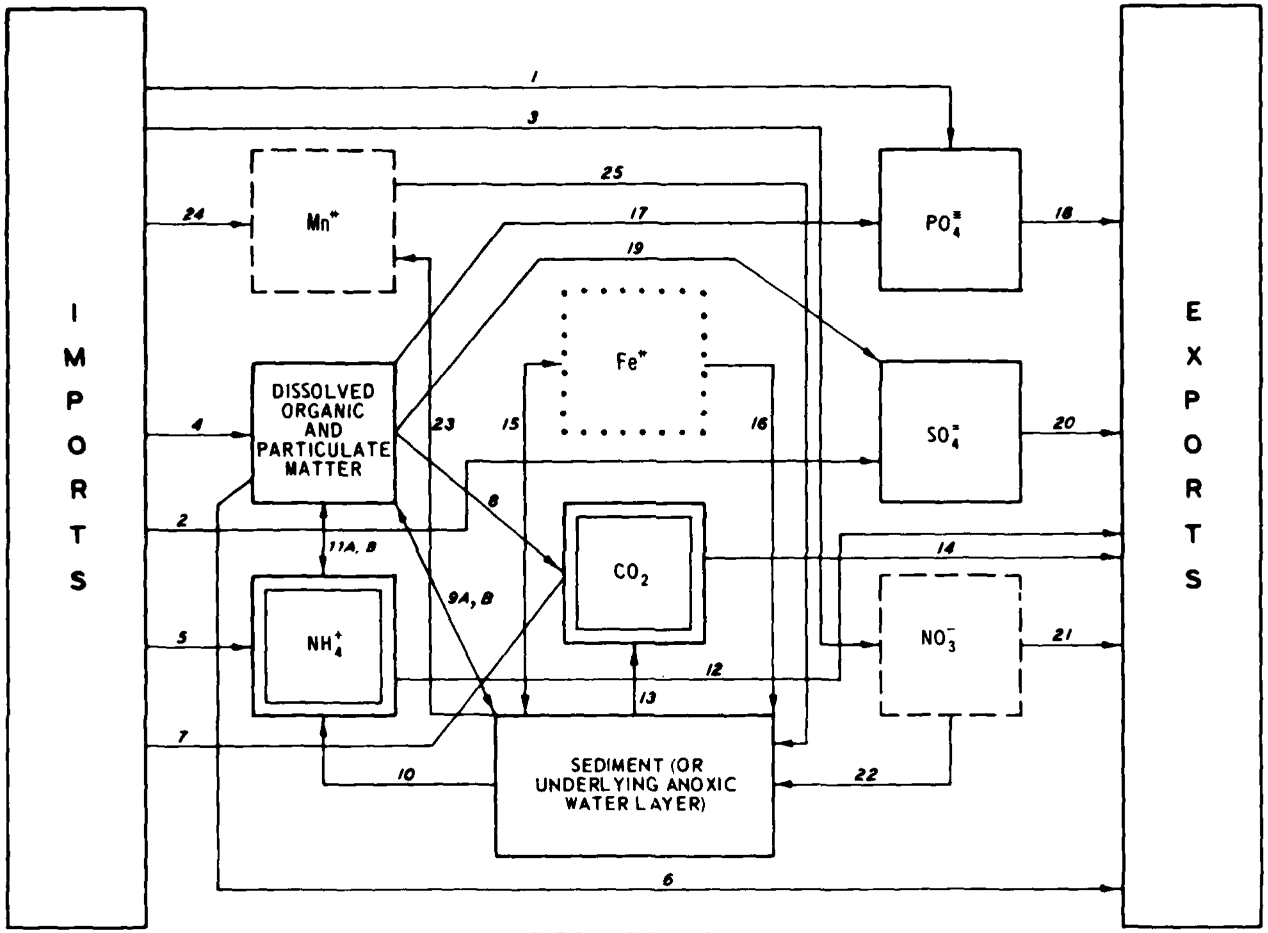

PHASE III – AMMON ACCUM

Figure 13. Major chemical changes and pathways associated with Phase III of the DOSAP algorithm

Arrow No.	Processes Represented by Arrows
11A	Ammonification of dissolved and particulate matter containing organic nitrogen.
11B	Immobilization of ammonium.
12	Export of ammonium in outflows.
13	Diffusion of dissolved CO_2 (at this pH range, mostly HCO_3^-) from sediments or underlying anoxic water layer into water layer of concern.
14	Export of dissolved CO_2 in outflows.
15	Diffusion of dissolved reduced (mostly chelated) iron out of sediment or underlying anoxic water layer into water layer of concern.
16	Oxidation and precipitation of iron from water layer of concern to sediment or underlying anoxic water layer.
17	Release of dissolved inorganic phosphate from anaerobically decomposing dissolved and particulate matter containing organic phosphates.
18	Export of dissolved inorganic phosphate in outflows.
19	Release of dissolved inorganic sulfate from anaerobically decomposing dissolved and particulate organic matter containing organic sulfates.
20	Export of dissolved inorganic sulfate in outflows.
21	Export of dissolved nitrate in outflowing waters.
22	Diffusion of dissolved nitrate from water into underlying sediment or anoxic water layer where it is reduced.
23	Diffusion of reduced Mn^{++} from sediments or underlying anoxic water layer into water layer of concern.
24	Import of reduced Mn^{++} with inflowing waters.
25	Oxidation and precipitation of manganese from water layer of concern to sediment or underlying sediment or underlying anoxic water layer.

85. Algorithms summarizing the various processes operative on each component in Figure 13 are given below:

Component — Factors Influencing Concentration of Components

Dissolved

d O/dt = 0. Once all O_2 has been exhausted, the solution to the equation: Inflows - Outflows - DO [NO_2^- Nitrate Formation + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + NH_4^+ + Nitrate Formation + Sediment Decay + BOD Demand + $S^=$ Sulfate Formation] = 0.

d NH_4^+/dt = Inflows + Diffusion from Sediment or Underlying Anoxic Water Layer + Ammonification - Outflows - NH_4^+ [Biological Uptake + Diffusion into Overlying Water Layer].

d NO_2^-/dt = Inflows + NO_2^- [NO_3^- Reduction] - Outflows - NO_2^- [Diffusion into Sediments or Underlying Anoxic Water Layer + Diffusion into Overlying Water Layer].

d NO_3^-/dt = Inflows - Outflows - NO_3^- [Biological Uptake + NO_3^- Reduction + Diffusion to Underlying Water or Sediment Layer] + Diffusion from Overlying Water Layer.

d CO_2/dt = Inflows + CO_2 [Diffusion from Sediments or Underlying Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay] - Outflows - CO_2 [Carbonate Formation + Diffusion to Above Water Layer].

d $PO_4^{\equiv}$/dt = Inflows + $PO_4^{\equiv}$ [Dissolved Organic PO_4 Decay + Particulate Organic PO_4 Decay + Cellular Release of Pi] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitates and Coprecipitates + Biological Uptake].

d $SO_4^=$/dt = Inflows + $SO_4^=$ [Dissolved Organic Sulfate Decay + Particulate Organic Sulfate Decay] - Outflows - $SO_4^=$ [Biological Uptake].

(Continued)

Component	Factors Influencing Concentration of Components
d DOM*/dt =	Inflows + Sediment Release + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].
	Particulate
d POM/dt =	Inflows + Settling from Above Water Layer - Outflows - POM [Particulate Organic Matter Decay + Settling to Underlying Water or Sediment Layer].
d PIM/dt =	Inflows + Settling from Above Water Layer - Outflows - PIM [Settling to Underlying Water or Sediment Layer].

* Will normally be present in waters withdrawn from hypolimnion.

Phase IV: Manganese Accumulation (MANG ACCUM)

86. The pH range over which the phase is functional is 6.6 to 7.4.

87. The Eh is +200 mV → +50 mV.

88. The DO concentration is 0 mg/ℓ.

89. Synopsis of phase. Redox has dropped to ≅ +200 mV, which is the changeover point from oxidizing to reducing conditions. Both dissolved ammonium and dissolved reduced manganese are being activity accumulated and are found in this water layer if it is being withdrawn as a part of reservoir releases. Continued withdrawal of this water will result in oxygen sag downstream (classical Streeter-Phelps) due to nitrification of ammonium and oxidation of reduced manganese to yield manganic hydroxides and oxides. Reduced iron is now appearing in solutions in easily detectable concentrations, although most of this will be complexed with dissolved organic matter; however, at a redox of +200 mV, most reduced iron is chemically reoxidized to yield insoluble ferric oxides and hydroxides that precipitate back out of the water. Thus, the concentration of iron in solution does not achieve high levels. Dissolved nitrate has been almost totally exhausted, and any residual nitrate is totally dependent upon the amount being supplied by external sources, i.e. arrow 3. Any nitrate entering the system will

almost immediately oxidize MN^{++} to MN^{+4}.

90. Summary of processes. Figure 14 depicts the major components and pathways that occur in Phase IV. Arrows in Figure 14 are explained below:

Arrow No.	Processes Represented by Arrows
1	Import of dissolved inorganic phosphate with inflows.
2	Import of dissolved inorganic sulfate with inflows.
3	Import of dissolved nitrate with inflows.
4	Import of dissolved organic and particulate matter (dissolved organic matter in inflows; particulate matter settling from metalimnion and with inflows).
5	Import of ammonium with inflows.
6	Export of dissolved organics and particulate matter with outflows.
7	Import of dissolved carbon dioxide (as HCO_3^-).
8	Fermentative decomposition of both dissolved and particulate organic matter to yield organic acids (which are retained within this compartment) and carbon dioxide.
9A	Sedimentation of particulate matter from water layer of concern to sediment.
9B	Release of dissolved organic matter from sediment to overlying water by diffusion.
10	Diffusion of ammonium from sediment or anoxic water layer beneath the water layer of concern to overlying water.
11A	Ammonification of dissolved organic and particulate matter containing organic nitrogen.
11B	Immobilization of ammonium.
12	Export of ammonium in outflows.
13	Diffusion of dissolved CO_2 (HCO_3^-) from sediment.
14	Export of dissolved CO_2 with outflows.
15	Diffusion of dissolved reduced (mostly chelated) iron.
16	Oxidation and precipitation of iron from water layer of concern to sediment.

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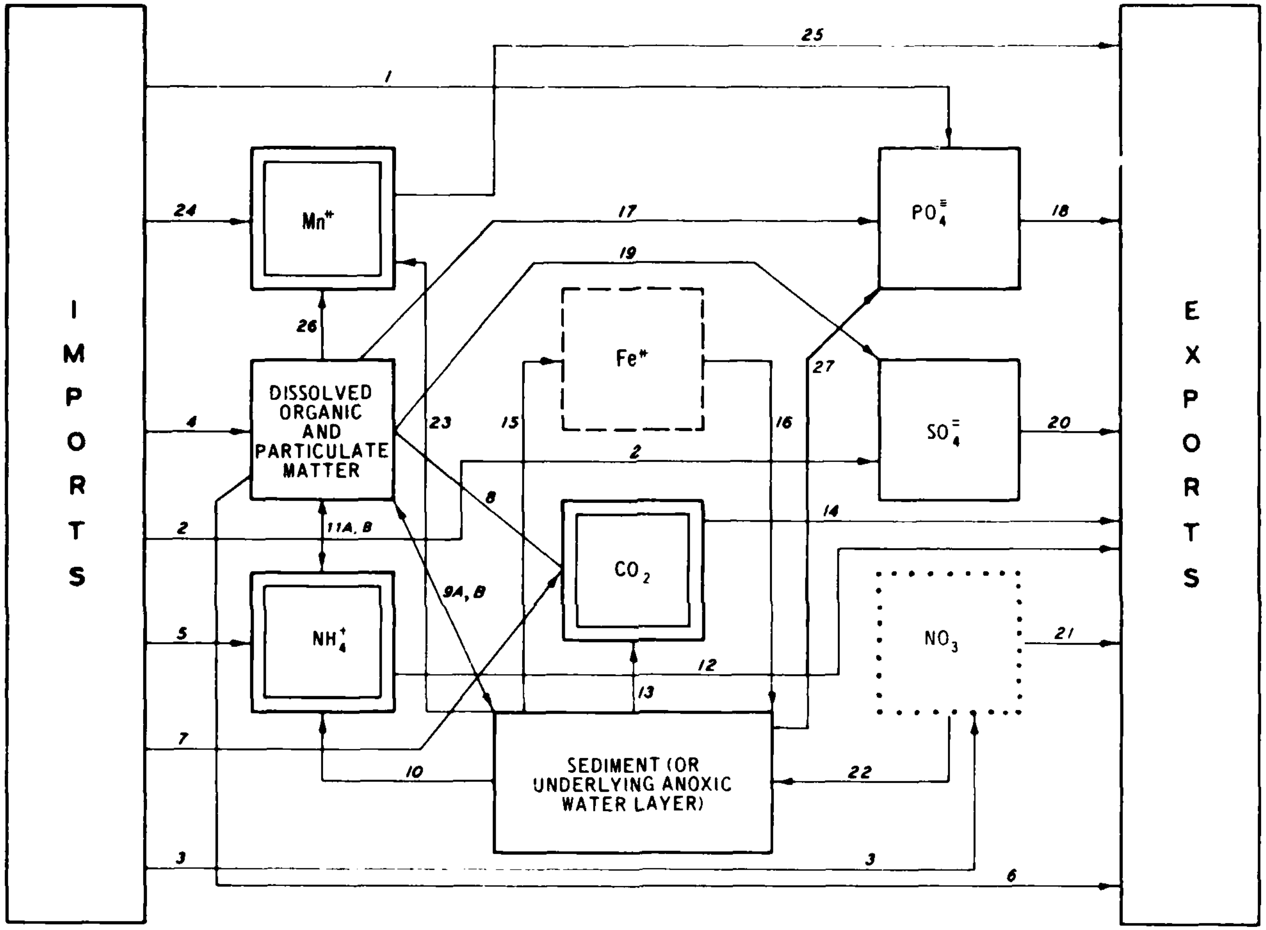

PHASE IV - MANG ACCUM

Figure 14. Major chemical changes and pathways associated with Phase IV of the DOSAP algorithm

Arrow No.	Processes Represented by Arrows
17	Release of dissolved inorganic phosphate from anaerobically decomposing dissolved and particulate matter containing organic phosphates.
18	Export of dissolved inorganic phosphate with outflows.
19	Release of dissolved inorganic sulfate from anaerobically decomposing dissolved and particulate matter containing organic sulfates.
20	Export of dissolved inorganic sulfate in outflows.
21	Export of dissolved nitrate with outflows.
22	Diffusion of dissolved nitrate from water into underlying sediment where it is denitrified.
23	Diffusion of reduced manganese from sediment into water layer of concern.
24	Import of reduced manganese with inflows.
25	Export of dissolved reduced manganese with outflows.
26	Release of dissolved reduced manganese from anaerobically decomposing dissolved and particulate matter containing organic and inorganic Mn.
27	Release of $PO_4^{\equiv}$ from underlying sediment or anoxic water layer.

91. Algorithms summarizing the various processes operative on each component in Figure 14 are given below:

Component	Factors Influencing Change of Concentration of Components
	Dissolved
$d\,O/dt$	= 0. DO concentration = 0 mg/ℓ.
$d\,NH_4^+/dt$	= Inflows + Diffusion from Sediment or Underlying Anoxic Water Layer + Ammonification − NH_4^+ [Biological Uptake + Diffusion into Overlying Water Layer + Outflows*].

(Continued)

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* Will normally be present in waters that are withdrawn from the hypolimnion.

Component	Factors Influencing Change of Concentration of Components
$d\ NO_2^-/dt$ =	0. NO_2^- concentration = 0 mg/ℓ.
$d\ NO_3^-/dt$ =	0. If > 0, then Inflows - Outflows - NO_3^- [Biological Uptake + NO_3^- Reduction + Diffusion into Sediment or Underlying Anoxic Water Layer] + Diffusion from Overlying Water Layer.
d DOM*/dt =	Inflows + Sediment Release + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].
$d\ CO_2/dt$ =	Inflows + CO_2 [Diffusion from Sediments or Underlying Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay] + Carbonate Formation + Diffusion to Overlying Water Layer].
$d\ PO_4^{\equiv}/dt$ =	Inflows + $PO_4^{\equiv}$ [Dissolved Organic PO_4 Decay + Particulate Organic PO_4 Decay + Biological PO_4 Release] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitates and Coprecipitates + Biological PO_4 Uptake].
$d\ SO_4^{=}/dt$ =	Inflows + $SO_4^{=}$ [Dissolved Organic Sulfate Decay + Particulate Organic Sulfate Decay - Outflows - $SO_4^{=}$ [Biological Uptake].
$d\ Mn^{++}/dt$ =	Inflows + Mn^{++} [Diffusion from Underlying Sediments or Anoxic Water Layer + Dissolved Organic Decay + Particulate Organic Decay + Reduction of Mn^{+4} in Suspended Particulate Inorganic Matter] - Outflows* - Mn^{++} [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates ($CO_3^{=}$) + Oxidation to Mn^{+4}].

(Continued)

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* Normally inconsequential.

Component — Factors Influencing Change of Concentration of Components

d Fe^{++}/dt = Inflows + Fe^{++} [Diffusion from Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Fe^{+++} in Suspended Particulate/Colloidal Inorganic Matter] - Outflows - Fe^{++} [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates ($S^{=}$) + Oxidation to Fe^{+++}].

Particulate

d POM/dt = Inflows + Settling from Overlying Water Layer - Outflows - POM [Particulate Organic Matter Decay + Settling to Underlying Water or Sediment Layer].

d PIM/dt = Inflows + Settling from Overlying Water Layer - Outflows - PIM [Settling to Underlying Water or Sediment Layer].

Phase V: Iron Accumulation (FERR ACCUM)

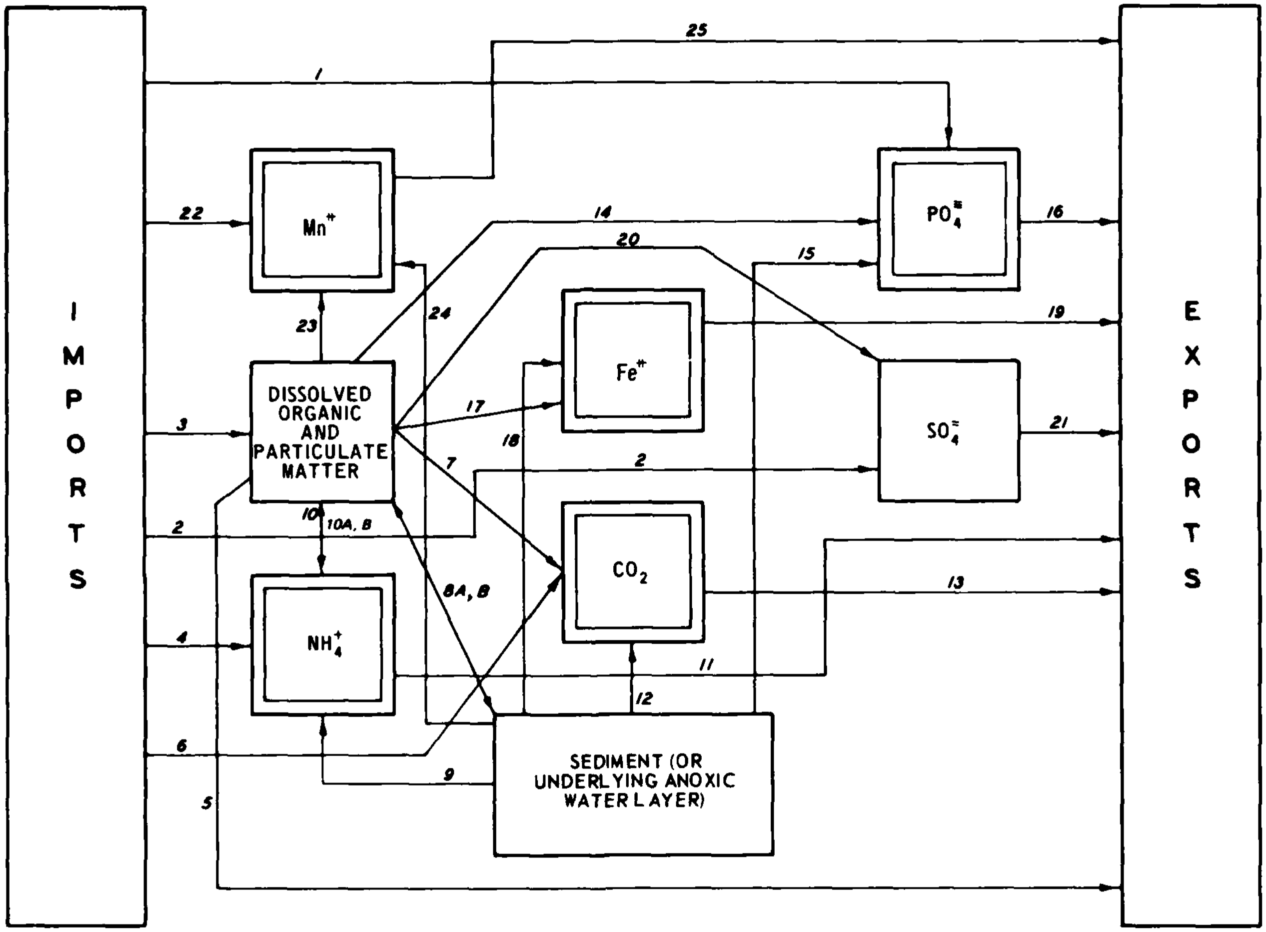
92. The pH range over which the phase is functional is 6.6 to 7.4.

93. The Eh is +50 mV.

94. The DO concentration is 0 mg/ℓ.

95. Synopsis of phase. Redox has dropped to +50 mV and reducing conditions have developed. Iron is being actively reduced, and inorganic phosphate is being brought into solution with iron. These reduction products are found in the outflows, if the reservoir has hypolimnetic withdrawal. Ammonium, manganese, iron, and carbon are being actively accumulated in the water, although the rates of accumulation of these materials are somewhat less than in previous phases; these will also be exported in the outflows from a system that has hypolimnetic withdrawal.

96. Summary of processes. Figure 15 presents the components and pathways of importance for Phase V. Arrows in Figure 15 are explained below:



PHASE V - FERR ACCUM

Figure 15. Major chemical changes and pathways associated with Phase V of the DOSAP algorithm

Arrow No.	Processes Represented by Arrows
1	Import of dissolved inorganic phosphate with inflows.
2	Import of dissolved inorganic sulfate with inflows.
3	Import of dissolved organics and particulate matter (dissolved organic matter in inflows; particulate matter settling from metalimnion and with inflows).
4	Import of ammonium with inflowing waters.
5	Export of dissolved organics and particulate matter with outflows.
6	Import of dissolved carbon dioxide (HCO_3^-) with inflows.
7	Fermentative decomposition of dissolved organics and particulate organic matter to yield organic acids (retained within dissolved organics compartment) and dissolved carbon dioxide.
8A	Sedimentation of particulate matter from the water layer of concern to the sediment layer beneath it.
8B	Release of dissolved organic matter from sediment (water layer) beneath the water layer of concern to water by diffusion.
9	Diffusion of ammonium from sediment or underlying anoxic water layer into water.
10A	Ammonification of dissolved organics and portions of particulate matter containing organic nitrogen.
10B	Immobilization of ammonium.
11	Export of ammonium in outflows.
12	Diffusion of dissolved CO_2 (HCO_3^-) from sediments or underlying anoxic water layer into water.
13	Export of dissolved CO_2 with outflows.
14	Release of dissolved inorganic phosphate via decomposition of dissolved organics and portions of particulate organic matter containing phosphate.

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Arrow No.	Processes Represented by Arrows
15	Release of dissolved inorganic phosphate from sediment following reductive decomposition of ferric phosphates.
16	Export of dissolved inorganic phosphate with outflows.
17	Release of reduced iron from anaerobically decomposing dissolved organics and particulate matter.
18	Diffusion of dissolved reduced (mostly chelated) iron out of sediment or underlying anoxic water layer into water layer of concern.
19	Export of reduced dissolved iron in outflows.
20	Release of dissolved inorganic sulfate from anaerobically decomposing dissolved organics and particulate matter.
21	Export of dissolved inorganic sulfate with outflows.
22	Import of reduced dissolved manganese with inflows.
23	Release of reduced dissolved manganese from anaerobically decomposing dissolved organic and particulate matter.
24	Diffusion of reduced dissolved manganese out of sediment or underlying anoxic water layer.
25	Export of reduced dissolved manganese with inflows.

97. Algorithms summarizing the various processes operative on each component in Figure 15 are given below:

Component	Factors Influencing Change of Concentration of Components
	Dissolved
$d\,O/dt$ =	0. DO concentration = 0 mg/ℓ.
$d\,NH_4^+/dt$ =	Inflows + Diffusion from Sediments or Underlying Anoxic Water Layer + Ammonification - Outflows - NH_4^+ [Biological Uptake + Diffusion into Overlying Layer].

(Continued)

Component	Factors Influencing Change of Concentration of Components
d NO_2^-/dt =	0. NO_2^- concentration = 0 mg/ℓ.
d NO_3^-/dt =	0. NO_3^- concentration = 0 mg/ℓ.
d DOM/dt =	Inflows + Sediment Release (or Underlying Water Layer) + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].
d CO_2/dt =	Inflows + CO_2 [Diffusion from Sediments or Underlying Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay] - Outflows - CO_2 [Carbonate Formation + Diffusion to Overlying Water Layer].
d $PO_4^{\equiv}$/dt =	Inflows + $PO_4^{\equiv}$ [Dissolved Organic PO_4 Decay + Particulate Organic PO_4 Decay + Biological PO_4 Release] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitates + Biological PO_4 Uptake].
d $SO_4^{=}$/dt =	Inflows + $SO_4^{=}$ [Dissolved Organic Sulfate Decay + Particulate Organic Sulfate Decay] - Outflows - $SO_4^{=}$ [Biological Uptake].
d MN^{++}/dt =	Inflows + Mn^{++} [Diffusion from Underlying Sediments or Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Mn^{+4} in Suspended Particulate Inorganic Matter] - Outflows* - Mn^{++} [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates** + Oxidation to Mn^{+4}].
d Fe^{++}/dt =	Inflows + Fe^{++} [Diffusion from Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Fe^{+++} in Suspended Particulate/Colloidal Inorganic Matter] - Outflows* Fe^{++} [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates† + Oxidation to Fe^{+++}].

* Present in outflows.

** Carbonates.

† Sulfides.

Component	Factors Influencing Change of Concentration of Components
d $S^=$/dt =	Inflows + $S^=$ [Diffusion from Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay* + Particulate Organic Matter Decay* + $SO_4^=$ (Reduction of Sulfate)] - Outflows - $S^=$ [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates** + Oxidation to S^o or $SO_4^=$].
	Particulate
d POM/dt =	Inflows + Settling from Overlying Water Layer - Outflows - POM [Particulate Organic Matter Decay + Settling to Underlying Water or Sediment Layer].
d PIM/dt =	Inflows + Settling from Overlying Water Layer - Outflows - PIM [Settling to Underlying Water or Sediment Layer + Particulate Inorganic Matter Decomposition].

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* Sulfhydryl groups that cannot be oxidized to $SO_4^=$ or S^o.

** Sulfides.

Phase VI: Sulfide Accumulation (SULFID ACCUM)

98. The pH range over which the phase is functional is 6.8 to 7.2.

99. The Eh is approximately -150 mV.

100. The DO concentration is 0 mg/ℓ.

101. Synopsis of phase. Redox has descended to -150 mV. Conditions have become highly reducing, and sulfide release from sediments or underlying reduced water layers has begun. Sulfate has begun to actively diffuse into sediment/underlying anoxic water layer; the dissimilatory sulfate reduction occurring in the sediments causes the underlying layers to serve as a sink for sulfate. Sulfate continues to move into the system via inflowing waters, and sulfate is also supplied via decomposition of organic sulfates. Ammonium, reduced iron, manganese, and phosphate continue to be released from the sediments and from the anaerobic decomposition of organic materials bearing them. Some sulfide has begun to be removed by formation of insoluble

ferrous sulfide. However, while sulfide is actively accumulating in the water layer, its concentration is, as yet, too low for significant precipitation by iron.

102. Summary of processes. Figure 16 presents the components and pathways of importance for Phase VI. Arrows in Figure 16 are explained below:

Arrow No.	Processes Represented by Arrows
1	Import of dissolved inorganic phosphate with inflows.
2	Import of dissolved inorganic sulfate with inflows.
3	Import of dissolved organics and particulate matter (dissolved organic matter in inflows; particulate matter settling from metalimnion and with inflows).
4	Import of ammonium with inflows.
5	Export of dissolved organics and particulate matter with outflows.
6	Import of dissolved carbon dioxide (at this pH, mostly HCO_3^-).
7	Fermentative decomposition of both dissolved and particulate organic matter to yield organic acids (retained within dissolved organics compartment) and dissolved carbon dioxide.
8A	Sedimentation of particulate matter from the water layer of concern to the sediment (or anoxic water layer) beneath it.
8B	Release of dissolved organic matter from sediment (or anoxic water layer) beneath the water of concern to water by diffusion.
9	Diffusion of ammonium from sediment or anoxic water in layer beneath the layer of concern to water by diffusion.
10A	Ammonification of dissolved organics and portions of particulate matter containing organic nitrogen.
10B	Immobilization of ammonium.
11	Export of ammonium in outflowing waters.

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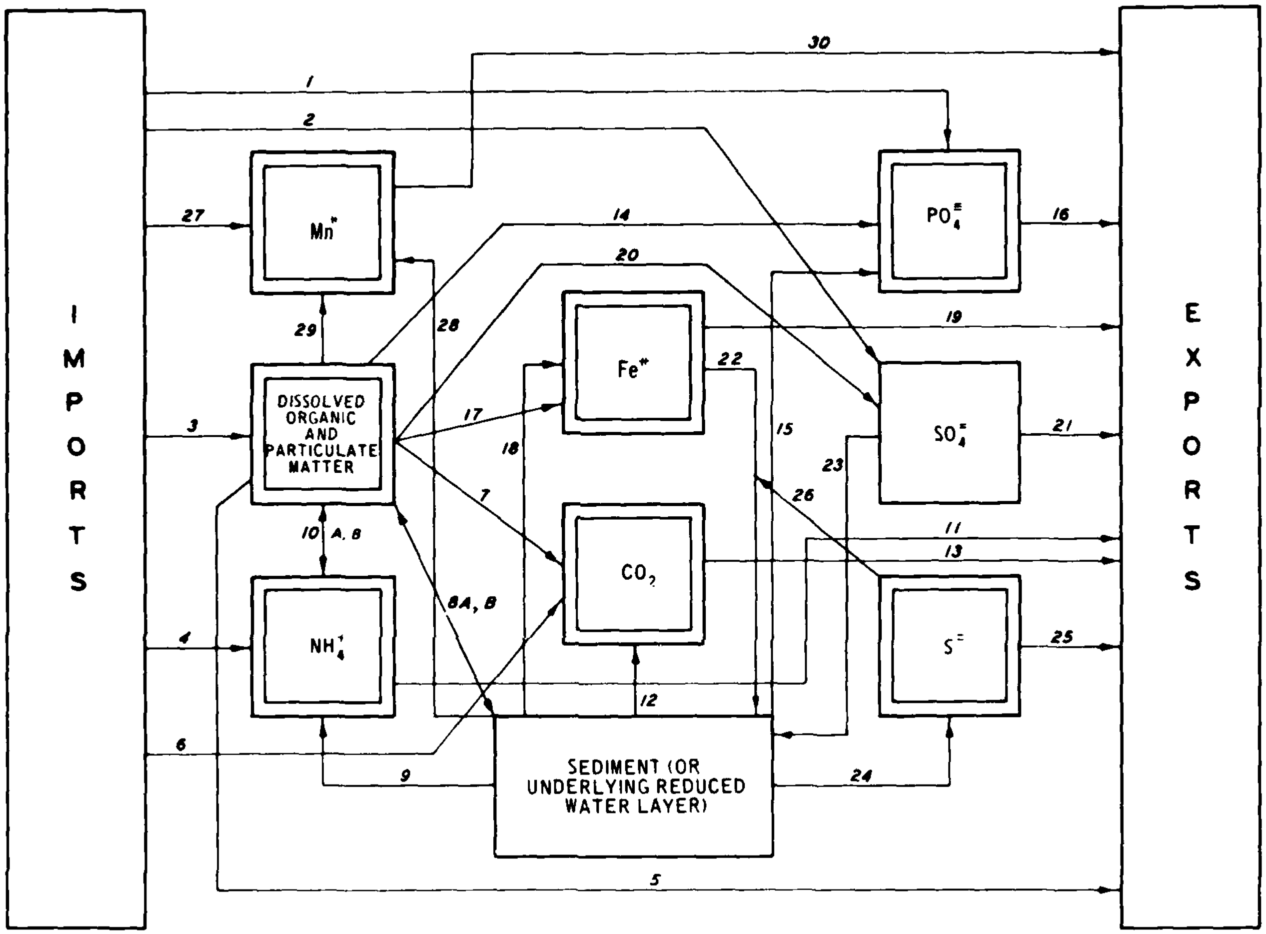

PHASE VI – SULFID ACCUM

Figure 16. Major chemical changes and pathways associated with Phase VI of the DOSAP algorithm

Arrow No.	Processes Represented by Arrows
12	Diffusion of dissolved CO_2 (HCO_3^-) from sediments or underlying anoxic water layer into water.
13	Export of dissolved CO_2 with outflows.
14	Release of dissolved inorganic phosphate via decomposition of dissolved organics and portions of particulate matter containing phosphate.
15	Release of dissolved inorganic phosphate from sediment following reductive decomposition of ferric phosphates.
16	Export of dissolved inorganic phosphate with outflows.
17	Release of reduced iron from anaerobically decomposing dissolved organics and particulate matter.
18	Diffusion of dissolved reduced iron out of sediment or underlying anoxic water layer into water layer of concern.
19	Export of dissolved reduced iron with outflows.
20	Release of sulfate from anaerobically decomposing dissolved organics and particulate matter.
21	Export of dissolved inorganic sulfate with outflows.
22	Precipitation of reduced dissolved iron to sediment or underlying anoxic water layer as a consequence of the formation of insoluble ferrous sulfide.
23	Diffusion of dissolved inorganic sulfate into sediment or underlying anoxic water layer.
24	Diffusion of dissolved inorganic sulfide out of sediment or underlying anoxic water layer.
25	Export of dissolved inorganic sulfide with outflows.
26	Precipitation of dissolved inorganic sulfide to sediment or underlying anoxic water layer as a consequence of the formation of insoluble ferrous sulfide.

(Continued)

Arrow No.	Processes Represented by Arrows
27	Import of reduced manganese with inflows.
28	Release of reduced manganese from underlying sediments or anoxic water layer.
29	Release of reduced manganese from anaerobically decomposing dissolved organics and particulate matter.
30	Export of reduced manganese with outflows.

103. Algorithms summarizing the various processes operative on each component in Figure 16 are given below:

Component	Factors Influencing Change of Concentration of Components
	Dissolved
$d\ O/dt$	= 0. DO concentration = 0 mg/ℓ.
$d\ NH_4^+/dt$	= Inflows + Release From Sediment or Underlying Water Layer + Ammonification - Outflows* - NH_4^+ [Biological Uptake + Diffusion into Overlying Layer].
$d\ NO_2^-/dt$	= 0. NO_2^- concentration = 0 mg/ℓ.
$d\ NO_3^-/dt$	= 0. NO_3^- concentration = 0 mg/ℓ.
$d\ DOM/dt$	= Inflows + Release from Sediment or Underlying Water Layer + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].
$d\ CO_2/dt$	= 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].
$d\ PO_4^{\equiv}/dt$	= Inflows + $PO_4^{\equiv}$ [Dissolved Organic PO_4 Decay + Particulate Organic PO_4 Decay + Biological PO_4 Release] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitates + Biological PO_4 Uptake].

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* Present in outflows.

Component	Factors Influencing Change of Concentration of Components
d $SO_4^{=}$/dt =	Inflows + $SO_4^{=}$ [Dissolved Organic Sulfate Decay + Particulate Organic Sulfate Decay] - Outflows - $SO_4^{=}$ [Biological Uptake].
d Mn^{++}/dt =	Inflows + Mn^{++} [Diffusion from Underlying Sediments or Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Mn^{+4} in Suspended Particulate Organic Matter] - Outflows* - Mn^{++} [Biological Uptake + Diffusion to Overlying Water + Formation of Insoluble Precipitates** + Oxidation to Mn^{+4}].
d Fe^{++}/dt =	Inflows + Fe^{++} [Diffusion from Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Fe^{+++} in Suspended Particulate/Colloidal Inorganic Matter] - Outflows* - Fe^{++} [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates** + Oxidation to Fe^{+++}].
d $S^{=}$/dt =	Inflows + $S^{=}$ [Diffusion from Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay† + Particulate Organic Matter Decay† + $SO_4^{=}$ Reduction] - Outflows* - $S^{=}$ [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitates** + Oxidation to $S^{o}/SO_4^{=}$].
	Particulate
d POM/dt =	Inflows + Settling from Overlying Water Layer - Outflows - POM [Particulate Organic Matter Decay + Settling to Underlying Water or Sediment Layer].

(Continued)

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* Present in outflows.

** Sulfides.

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

Component	Factors Influencing Change of Concentration of Components
d PIM/dt =	Inflows + Settling from Overlying Water Layer - Outflows - PIM [Settling to Underlying Water or Sediment Layer + Particulate Inorganic Matter Decomposition].

Phase VII: Methanogenesis

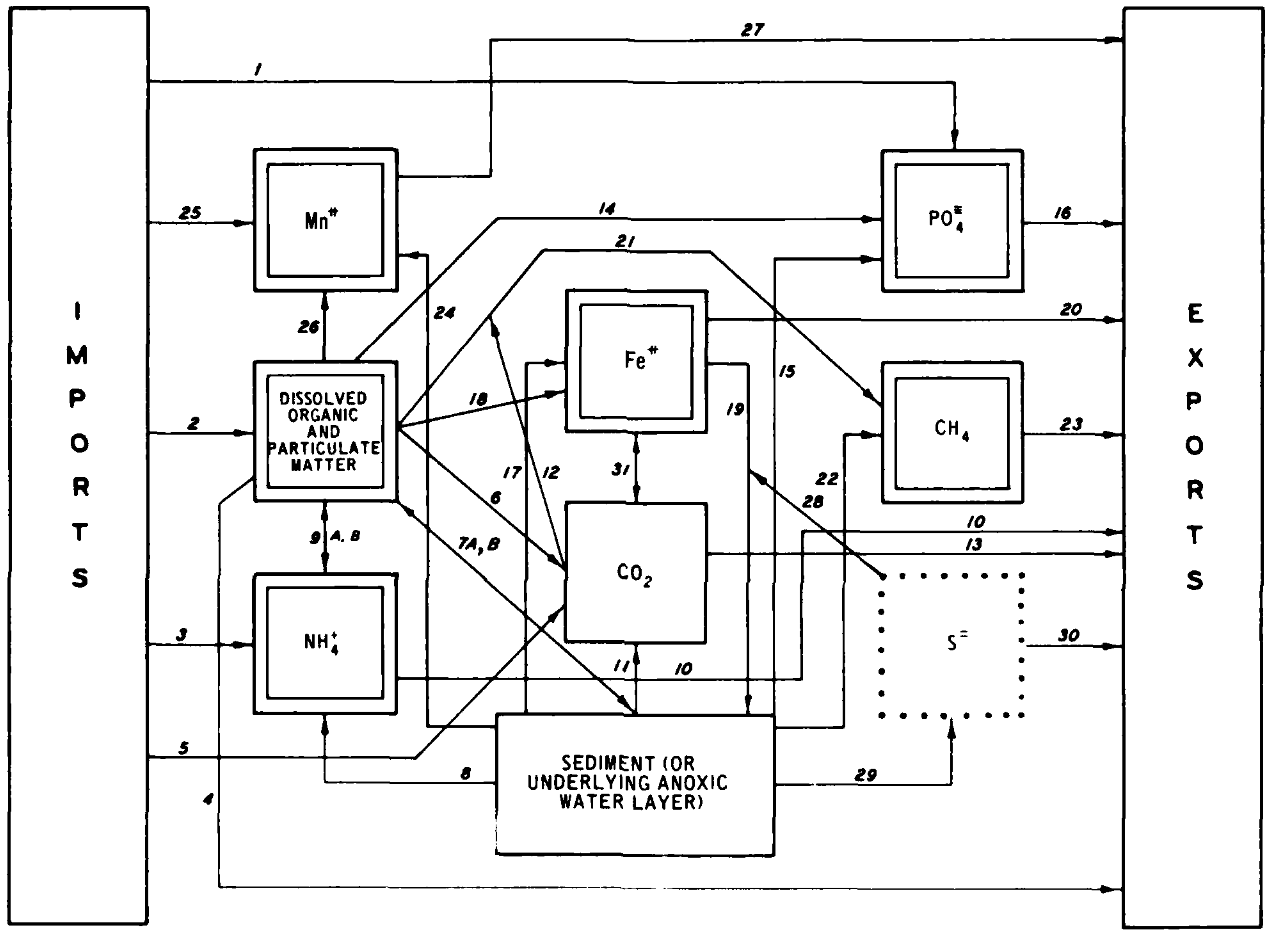
104. The pH range over which the phase is functional is 6.6 to 7.4.

105. The Eh is less than or equal to -175 mV.

106. The DO concentration is 0 mg/ℓ.

107. Synopsis of phase. Redox has now reached -175 mV. Ammonium, soluble manganese and iron, and phosphate continue to be produced, and these materials continue to appear in the tailwaters of projects with hypolimnetic withdrawal. In those impoundments having low sulfide levels in their sediments, and having high iron levels, the rate of sulfide release to the water column has been severely diminished. Consequently, removal of sulfide by formation of insoluble ferrous sulfide and by export from the system--either in outflows or by the activity of sulfide-oxidizing bacteria at the metalimnetic-hypolimnetic interface--results in a net depletion of sulfide in the water column. Lack of sulfate as an electron acceptor has also caused a decrease in the sulfide formation rate. The decrease in activity by sulfate reducers has removed the source of competition for organic substrates that formerly existed between the sulfate reducers and the methane-producing bacteria and methanogenesis has become the dominant process. As a result, the Eh has shifted from -150 to -175 mV and is now being poised by methanogenesis. Carbon dioxide is being actively utilized in the methane-forming process.

108. Summary of processes. Figure 17 depicts the components and pathways of importance for Phase VII. Arrows in Figure 17 are explained below:



PHASE VII - METHANOGENESIS

Figure 17. Major chemical changes and pathways associated with Phase VII of the DOSAP algorithm

Arrow No.	Processes Represented by Arrows
1	Import of dissolved inorganic phosphate with inflows.
2	Import of dissolved and particulate organic matter (dissolved organic matter in inflows; particulate matter settling from metalimnion and with inflows).
3	Import of ammonium with inflows.
4	Export of dissolved organics and particulate matter with outflows.
5	Import of dissolved carbon dioxide (HCO_3^-) with inflows.
6	Fermentative decomposition of both dissolved and particulate organic matter to yield organic acids (retained within the dissolved organics compartment) and dissolved carbon dioxide.
7A	Sedimentation of particulate matter from the water layer of concern to the sediment or anoxic water layer beneath it.
7B	Release of dissolved organic matter from the sediment or anoxic water layer beneath the layer of concern into the water in the layer of concern by diffusion.
8	Diffusion of ammonium from the sediment or anoxic water layer beneath the layer of concern into the water in the layer of concern.
9A	Ammonium release by ammonification of dissolved organics and portions of particulate matter containing organic nitrogen.
9B	Ammobilization of ammonium.
10	Export of ammonium with outflows and advection.
11	Release of dissolved CO_2 (HCO_3^-) from sediments or underlying anoxic water layer into the water in the layer of concern by diffusion.
12	Uptake of dissolved CO_2 (HCO_3^-) by methanogenesis.
13	Export of dissolved CO_2 (HCO_3^-) with outflows and advection.

(Continued)

Arrow No.	Processes Represented by Arrows
14	Release of dissolved inorganic phosphate via fermentative decomposition of dissolved organics and portions of particulate matter containing phosphate.
15	Release of dissolved inorganic phosphate from sediment or underlying anoxic water layer by diffusion of the phosphate after reductive decomposition of ferric phosphates.
16	Export of dissolved inorganic phosphate with outflows and advection.
17	Release of dissolved reduced iron from the sediment or underlying anoxic water layer by diffusion of the iron after reductive decomposition by ferric phosphates.
18	Release of dissolved reduced iron from anaerobically decomposing dissolved organics and particulate matter.
19	Precipitation of reduced dissolved iron to sediment or underlying anoxic water layer as a consequence of the formation of insoluble ferrous sulfide.
20	Export of reduced dissolved iron with outflows and advection.
21	Production of methane during fermentation of dissolved organics in water layer.
22	Release of methane to the water layer from sediment or underlying anoxic water layer.
23	Export of methane from system--primarily as rising bubbles of gas.
24	Release of dissolved reduced manganese from underlying sediment or anoxic water layer by diffusion into the layer of concern.
25	Import of reduced manganese with inflows and advection.
26	Release of reduced manganese from anaerobically decomposing dissolved organics and particulate matter.
27	Export of reduced manganese with outflows and advection.

(Continued)

Arrow No.	Processes Represented by Arrows
28	Precipitation of dissolved sulfide to sediment or underlying anoxic water layer as a consequence of the formation of insoluble ferrous sulfide.
29	Release of dissolved sulfide from sediment or underlying anoxic water layer to water layer of concern by diffusion.
30	Export of dissolved sulfide with outflows and advection.

109. Algorithms summarizing the various processes operative on each component in Figure 17 are given below:

Component	Factors Influencing Change of Concentration of Components
	Dissolved
$d\ O/dt$	= 0. DO concentration = 0 mg/ℓ.
$d\ NH_4^+/dt$	= Inflow + Release from Sediment or Underlying Water Layer + Ammonification - Outflows - NH_4^+ [Biological Uptake + Diffusion into Overlying Layer].
$d\ NO_2^-/dt$	= 0. NO_2^- concentration = 0 mg/ℓ.
$d\ NO_3^-/dt$	= 0. NO_3^- concentration = 0 mg/ℓ.
$d\ DOM/dt$	= Inflows + Release from Sediment or Underlying Water Layer + DOM [Particulate Organic Matter Decay] - Outflows - DOM [Dissolved Organic Matter Decay].
$d\ CO_2/dt$	= 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].
$d\ PO_4^{\equiv}/dt$	= Inflows + $PO_4^{\equiv}$ [Dissolved Organic PO_4 Decay + Particulate Organic PO_4 Decay + Biological PO_4 Release] - Outflows - $PO_4^{\equiv}$ [Formation of Precipitate + Biological PO_4 Uptake].

(Continued)

Component	Factors Influencing Change of Concentration of Components
d $SO_4^{=}$/dt =	Inflows + $SO_4^{=}$ [Dissolved Organic Sulfate Decay + Particulate Organic Sulfate Decay] - Outflows - $SO_4^{=}$ [Biological Uptake].
d Mn^{++}/dt =	Inflow + Mn^{++} [Diffusion from Underlying Sediments or Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Mn^{+4} in Suspended Particulate Organic Matter] - Outflows - Mn^{++} [Biological Uptake + Diffusion to Overlying Water + Formation of Insoluble Precipitates + Oxidation to Mn^{+4}].
d Fe^{++}/dt =	Inflows + Fe^{++} [Diffusion from Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + Reduction of Fe^{+++} in Suspended Particulate/Colloidal Inorganic Matter] - Fe^{++} [Biological Uptake + Diffusion or Overlying Water Layer + Formation of Insoluble Precipitates + Oxidation to Fe^{+++}].
d $S^{=}$/dt =	Inflows + $S^{=}$ [Diffusion for Underlying Sediment or Anoxic Water Layer + Dissolved Organic Matter Decay + Particulate Organic Matter Decay + $SO_4^{=}$ Reduction] - Outflows - $S^{=}$ [Biological Uptake + Diffusion to Overlying Water Layer + Formation of Insoluble Precipitate + Oxidation to $SO_4^{=}$].
d CH_4/dt =	CH_4 [Diffusion from Underlying Sediment or Anoxic Water Layer] + CH_4 [Methanogenesis (Dissolved Organic Matter Decay + Particulate Organic Matter Decay)] - Outflows - CH_4 [Oxidation + Diffusion to Overlying Water Layers].
	<u>Particulate</u>
d POM/dt =	Inflows + Settling from Overlying Water Layer - Outflows - POM [Particulate Organic Matter Decay + Settling to Underlying Water or Sediment Layer].

(Continued)

Component	Factors Influencing Change of Concentration of Components
d PIM/dt =	Inflows + Settling from Overlying Water Layer - Outflows - PIM [Settling to Underlying Water or Sediment Layer + Particulate Inorganic Matter Decomposition].

PART V: EVALUATION OF RELEVANT RATE DATA

110. Little information exists in the literature on rate data for anaerobic processes in reservoirs included in DOSAP. By contrast, there is considerable information on these processes in marine and freshwater ecosystems other than reservoirs. Rather than furnishing a compendium of nonreservoir related data, a tabulation is presented herein of ranges of values that are specific for reservoirs (Table 1); values for nonreservoir systems are included only when there are no data for particular processes in reservoirs (Table 1). For convenience in making comparisons with data from the authors own studies and in order to establish a common mode for data assembly, all of this information is expressed in terms of milligrams of the component being released or depleted per square metre of surface per day ($mg \cdot m^{-2} \cdot day^{-1}$).

111. While extensive use has been made of the literature on flooded soils as a source of concepts for the DOSAP algorithm, this area has not been used as a source of rate information. There are several reasons for this. Many of the flooded soils experiments that have been done were conducted at temperatures in the 25° to 35°C range. Since temperatures in reservoir hypolimnions typically are in the 5° to 15°C range, the rates obtained from these studies tend to be higher than anticipated for reservoir situations. Moreover, many flooded soils experiments tend to use large amendments of the particular substrate being studied, and this may also yield above-normal rates. Also, the previous history of many test soils with respect to flooding is not described in the literature in which the experiments are presented. Thus, the applicability of data obtained using these soils is somewhat dubious; the authors cannot be certain whether the rate data obtained in such studies would be typical of newly flooded soils, soils located in the flood pool region of a reservoir, or reservoir sediments. Finally, experiments on flooded soils often use a very thin layer of water over the soil surface. This practice results in a larger potential capacity for diffusive exchange of oxygen throughout the entire layer of water over the soil surface than would be expected in the typical

reservoir situation. The larger potential capacity would tend to produce a higher concentration of oxidized chemical species in the water over the flooded soil than would be anticipated for all but the shallowest, most well-mixed reservoirs.

112. It is apparent from the data presented in Table 1 that there is some information available on almost all of the anaerobic release processes of DOSAP. Inflow and outflow rates are necessarily site specific for a given reservoir and will not be considered herein. However, because of the restricted amount of data available for reservoirs, there are a number of limitations on what may be done with the data. For example, the flux rates presented in Table 1 are a useful indication of the range of concentrations of anaerobic products that may be expected in reservoirs; however, no indications are given of the rates of releases to be expected, and rates are mandatory for DOSAP to be used as the basis for a mathematical subroutine simulating anaerobic processes. Moreover, the data in Table 1 are also limited relative to the number of environmental situations to which they may be applied. For example, the anoxic reservoir hypolimnion data presented in Table 1 were taken from one environment and the temperature range in this case was 10° to 14°C; the coastal marine sediment data were taken from a 4°C environment; and the denitrification data obtained from the sediment of the small eutrophic lake were obtained at a third temperature. The question that immediately arises is what would the values in Table 1 be if they were all obtained from the same system at the same temperature. To accomplish this, however, studies must be conducted under highly controlled conditions.

113. The data presented in Table 2* illustrate the use of sediment water reaction chambers to provide data for DOSAP. While the data in Table 2 are expressed as fluxes (net rate and direction of release), they could also have been given as first-order rate coefficients or other desired means of expression. The central point here is that all

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* Table 2 presents the results of studies conducted by the authors on sediment water reaction in DeGray Reservoir, Arkansas.

the rate data necessary for DOSAP can be collected using this procedure. To provide a complete set of rate coefficients for DOSAP under a wide range of geographic conditions, the authors are studying the anaerobic release of these same components from sediments taken from various CE reservoir projects in different sections of the continental United States. Rate coefficients obtained from these studies will be summarized in an Engineering Technical Letter (ETL) on data preparation and coefficient selection (September 1982). This ETL will also give detailed instructions on the methods to be used in collecting the data (or for making estimates, when necessary) required for DOSAP. For illustrative purposes, Table 3 presents a compendium of the methods used to obtain data required for use in the DOSAP model and is intended as preliminary guidance prior to publication of the ETL.

PART VI: CONCLUSIONS

114. The occurrence of DO depletion and anaerobic processes in the hypolimnion of CE reservoirs can adversely impact water quality and directly affect CE Civil Works activities.

115. A review of the literature and discussions with authorities on anaerobic processes confirmed the feasibility of formulating a realistic conceptual model of anaerobic processes that, along with appropriate process rate data, could serve as a basis for a subroutine for numerical reservoir water quality models. A numerical model with the ability to simulate deoxygenation and anaerobic processes is required to provide the CE with the ability to address problems associated with low DO and anaerobic conditions in reservoirs.

116. Some of the data required to use DOSAP will be site specific, and pertinent field data must be collected for each reservoir application to provide a description of initial conditions and to update input variables. However, for developing and verifing DOSAP as an anaerobic subroutine for widespread field application, a broad base of data obtained from a variety of different reservoirs is required. Sediment water reaction chambers offer the most viable means for obtaining such information. These required studies are being accomplished as part of the Corps' EWQOS Program.

117. Application of the DOSAP subroutine in a numberical water quality model to various CE reservoir projects using data obtained from the projects offers a viable means for examining the effectiveness of various management strategies upon problems associated with low DO and anaerobic conditions. Under proper conditions and through the use of data obtained from neighboring bodies of water, a water quality model equipped with the DOSAP subroutine should also be applicable to preimpoundment investigations that involve a concern for the probability of a new project to develop anoxic conditions.

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Table 1

Reduction and Release of Various Components in Reservoirs and Other Freshwater Environments

Component	Environment	Rate	Reference
Organic N release	Anoxic reservoir hypolimnion	$0.0112\ g\ Org\ N \cdot m^{-2} \cdot day^{-1}$	Gordon (1976)
NH_4-N release	Anoxic reservoir hypolimnion	$0.026\text{-}0.076\ g\ NH_4\text{-}N \cdot m^{-2} \cdot day^{-1}$	Gordon (1976)
N_2 production (denitrification)	Sediment of small eutrophic lake	$0.016\ g\ N \cdot m^{-2} \cdot day^{-1}$	Chan and Knowles (1979)
Fe^{++} release	Anoxic reservoir hypolimnion	$0.112\text{-}0.350\ g\ Fe^{++} \cdot m^{-2} \cdot day^{-1}$	Gordon (1976)
Mn^{++} release	Anoxic reservoir hypolimnion	$0.49\text{-}0.74\ g\ Mn^{++} \cdot m^{-2} \cdot day^{-1}$	Gordon (1976)
Soluble P release	Anoxic reservoir hypolimnion	$0.038\ g\ P \cdot m^{-2} \cdot day^{-1}$	Gordon (1976)
Sulfide production	Anaerobic sediments	$0.403\ g\ S^{=} \cdot m^{-2} \cdot day^{-1}$	Orr and Gaines (1974)
H_2S release	Coastal marine sediments	$0.22\text{-}5.2\ g\ S^{=} \cdot m^{-2} \cdot day^{-1}$	Hansen, Ingvorsen, and Jørgensen (1978)
Total P release	In situ sediment chambers	$7.0\ mg\ P \cdot m^{-2} \cdot day^{-1}$	Sonzogni et al. (1977)
Total P release	Five anoxic lakes	$4.0\text{-}10.8\ mg\ P \cdot m^{-2} \cdot day^{-1}$	Sonzogni et al. (1977)

Table 2

Net Flux of Various Components from Water Column Above a Sediment Composite Taken from DeGray Reservoir, Arkansas*

Component	Flux for Sediment Treatment $g \cdot m^{-2} \cdot day^{-1}$	Component	Flux for Sediment Treatment $g \cdot m^{-2} \cdot day^{-1}$
Dissolved oxygen (DO) depletion	-123	Orthophosphate phosphorus (OPO_4-P) accumulation	-12.4
Total Kjeldahl nitrogen (TKN) depletion	-1.00	Total organic carbon (TOC) accumulation	-30.0
Ammonium nitrogen (NH_4-N) accumulation	+8.70	Total soluble iron (Fe) accumulation	+10.2
Nitrate nitrogen (NO_3-N) depletion	-1.36	Total soluble manganese (Mn) accumulation	+9.50
Total phosphorus (TP) accumulation	-1.82	Dissolved sulfate (SO_4) depletion	-41.0

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* Study was done in sediment water reaction chambers at 20°C under conditions simulating those found in the hypolimnion of DeGray Reservoir.

Table 3

Summary of Methods Used to Obtain Data Required for Use in the DOSAP Model

Component	Method*	References
Dissolved oxygen	Biochemical oxygen demand probe with associated DO meter; calibrated by Iodometric Method for DO measurement	Standard Methods (1976)
Oxidation-reduction potential	Platinum electrode and standard pH calomel *reference* electrode used with ± millivolt scale of a standard millivolt-pH meter. Measure in situ	Platinum electrode preparation as in Mann and Stolzy (1972) Oxidation-reduction procedure described in general in American Society for Testing and Materials (1977)
Soluble nutrients	Filter sample through 0.45-μm membrane filter. NOTE: if sample is taken from anoxic waters, all sample collection and filtration must be conducted under a nitrogen atmosphere. Suggest using a peristaltic pump to take sample that is then pumped into a filtration chamber continuously purged with nitrogen during the collection and filtration processes. Preserved by immediate freezing to -20°C	
Total Kjeldahl nitrogen	Kjeldahl digestion followed by phenate or Nesslerization methods	Standard Methods (1976)
Ammonia nitrogen	Phenate or Nesslerization Method	↓
Nitrite-nitrate nitrogen	*Cadmium reduction method*	↓
Total phosphorus	Perchloric acid digestion or persulfate digestion followed by vanadomolbdo*phosphoric acid colorimetric method*	↓
Orthophosphate phosphorus	Ascorbic Acid Method	↓
Dissolved organic carbon	Combustion-infrared	↓
Sulfate	Barium-perchlorate titration	↓
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-μm membrane filter; preserve with 11.6 N HCl *(0.2 ml acid/15 ml of sample)*. Analyze by *flame photometry*	↓
Total inorganic carbon	Filter through 0.45-μm membrane filter under N_2 pressure. Store at 4°C in 10-ml serum vials until analyzed. Determine titrimetrically (if dissolved iron less than 1.0 mg/ℓ)	↓
Total sulfide	Collect and preserve using zinc acetate; analyze within 24 hr using titrimetric method	↓
Sediment and interstitial water	Use detailed methods described by Brannon et al. (1976) in sections entitled "Experimental Methods (Sampling Procedures)" and "Selective Extraction of Sediments"	Brannon et al. (1976)

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* All sampling and filtration procedures should be conducted under a nitrogen atmosphere.

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Gunnison, Douglas
Characterization of anaerobic chemical processes in reservoirs: Problem description and conceptual model formulation : Final report / by Douglas Gunnison, James M. Brannon (Environmental Laboratory) : prepared for Office, Chief of Engineers, U.S. Army. -- Vicksburg, Miss. : U.S. Army Engineer Waterways Experiment Station ; Springfield, Va. : available from NTIS, 1981.
80, [3] p. : ill. ; 27 cm. -- (Technical report / U.S. Army Engineer Waterways Experiment Station ; E-81-6)
Cover title.
"April 1981."
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Bibliography: p. 76-80.

1.Bacteria, Anaerobic. 2. Computer programs. 3. Computer simulation. 4. DOSAP (Computer program). 5. Mathematical models. 6. Reservoirs. 7. Water -- Dissolved oxygen.

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