

January 1981

Natural Salinity Removal Processes in Reservoirs

Jay J. Messer

Eugene K. Israelsen

V. Dean Adams

Follow this and additional works at: https://digitalcommons.usu.edu/water_rep



Part of the [Civil and Environmental Engineering Commons](#), and the [Water Resource Management Commons](#)

Recommended Citation

Messer, Jay J.; Israelsen, Eugene K.; and Adams, V. Dean, "Natural Salinity Removal Processes in Reservoirs" (1981). *Reports*. Paper 214.

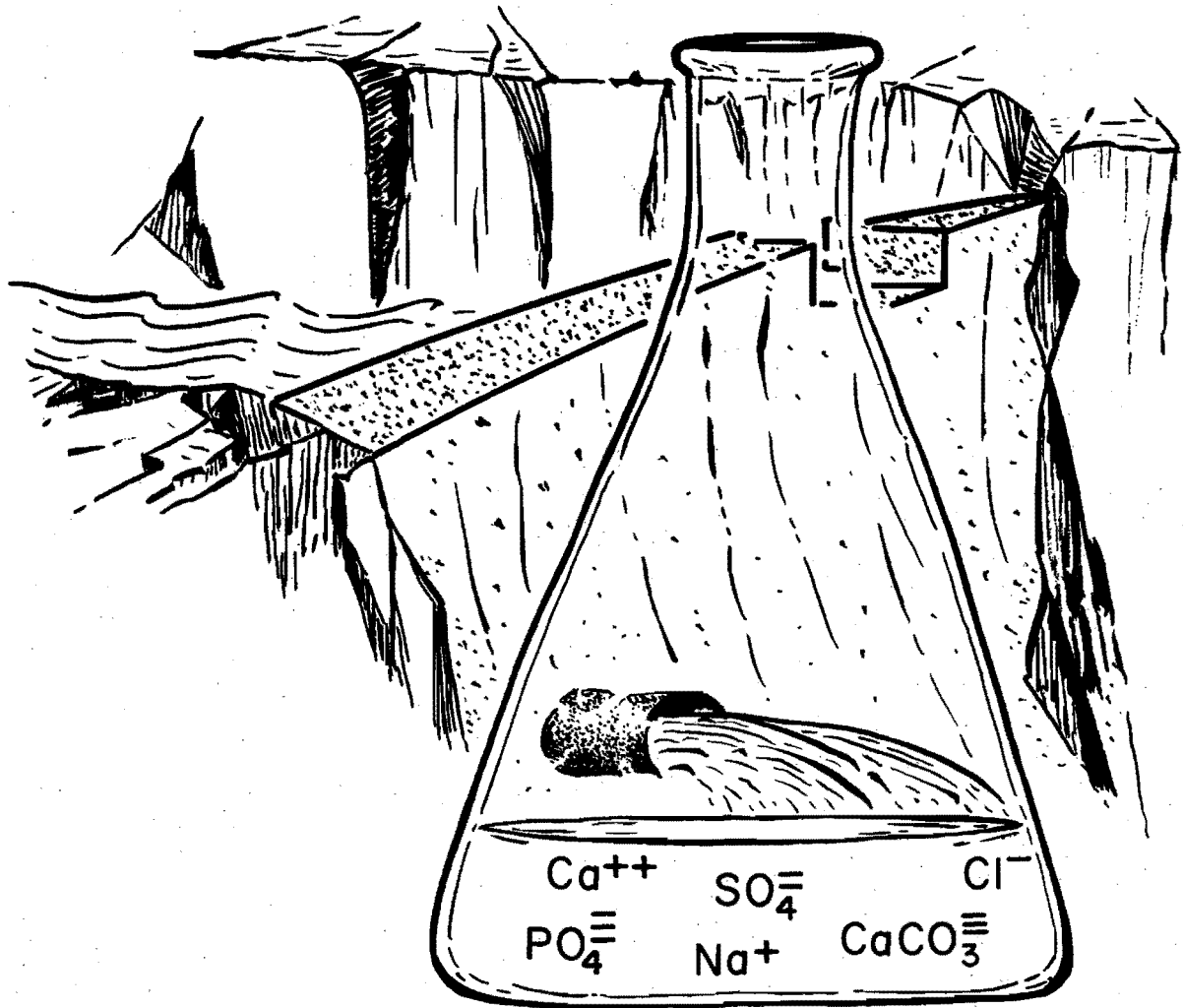
https://digitalcommons.usu.edu/water_rep/214

This Report is brought to you for free and open access by the Utah Water Research Laboratory at DigitalCommons@USU. It has been accepted for inclusion in Reports by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.



Natural Salinity Removal Processes In Reservoirs

Jay J. Messer
Eugene K. Israelsen
V. Dean Adams



Utah Water Research Laboratory
Utah State University
Logan, Utah 84322

August 1981

WATER QUALITY SERIES
UWRL/Q-81/03

NATURAL SALINITY REMOVAL PROCESSES
IN RESERVOIRS

by

Jay Messer, Eugene K. Israelsen, V. Dean Adams

WATER QUALITY SERIES
UWRL/Q-81/03

Utah Water Research Laboratory
Utah State University
Logan, Utah 84322

August 1981

ABSTRACT

A small but significant amount of salinity removal has been reported by various authors to occur in mainstem Colorado River reservoirs. Recalculation of some of these salinity budgets, together with a review of the data bases used, suggests that removal has not often been conclusively demonstrated. Laboratory microcosm experiments and field data indicate that calcium carbonate precipitation, perhaps with some coprecipitation of magnesium carbonate, is the mechanism responsible for most of the salinity removal in Oneida Reservoir, Idaho. Coprecipitation processes (including ion exchange), coagulation, and bioassimilation do not appear to be important natural salinity removal mechanisms. Finally, loss of calcium, relative to monovalent cations, may decrease water quality for irrigation purposes through increasing the sodium adsorption ratio (SAR), despite a gross decrease in the TDS. The potential role of various reservoir operation options in managing natural salinity removal processes and the value of such removal is discussed.

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance of L. Baker, G. Wylie, and D. Nero in the laboratory and field. L. D. James, J. Jurinak, D. Bowles, M. Clinton, and D. Merritt provided invaluable criticism and comments on the final report. We thank P. Brunson and A. Rivers for their art work, D. Falkenborg for editorial help, and L. Johnson for her highly competent typing and production efforts. Special thanks go to S. Petersen for allowing us to use his equilibrium model as a basis for our thermodynamic calculations.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGMENTS	iv
LIST OF FIGURES	vii
LIST OF TABLES	ix
Chapter	
I INTRODUCTION	1
II EVIDENCE OF SALINITY REMOVAL AS A RESULT OF IMPOUNDMENT IN WESTERN RESERVOIRS	3
Introduction	3
Review of Western Reservoir Studies	4
Lake Mead	4
Lake Powell	4
Flaming Gorge Reservoir	8
Bighorn Lake	9
Canyon Reservoir	9
Summary	9
III NATURAL SALINITY REMOVAL PROCESSES	11
Introduction	11
Precipitation	11
Carbonate Precipitation	11
Precipitation of Noncarbonate Species	18
Coprecipitation (Incongruent Precipitation)	19
Authigenesis (Diagenesis) of Clay Minerals	19
Reactions at the Solid-Solution Interface	20
Coagulation	21
Physical-chemical Processes	21
Bioflocculation	22
Biochemical Assimilation	22
Refractory Material	23
Emergence and Migration	23
Summary	23
IV STUDY AREA, METHODS AND MATERIALS	25
Description of Study Area	25
Methods	25
Field Sampling	25

TABLE OF CONTENTS (Continued)

	Page
Laboratory Studies	27
Analytical Methods	30
V SALINITY REMOVAL IN ONEIDA NARROWS RESERVOIR	31
Evidence for Ion Removal Based on Changes in Chemical Concentrations	31
Bear River Study	31
Bear River Synoptic Study	31
Thermodynamic Analysis of Carbonate Supersaturation	35
Homogeneous Precipitation of Other Species	39
Other Salinity Removal Mechanisms	41
Summary	42
VI LABORATORY EXPERIMENTS ON NATURAL SALINITY REMOVAL PROCESSES	43
Experiment I. Aphotic Coagulation/ Precipitation	43
Experiment II. Effects of Photosynthesis	43
Experiment III. Mixing of Upstream Water	51
Experiment IV. Effects of Saline Influent on Precipitation and Coagulation	51
Experiment V. Heterogeneous Precipitation	53
Summary	55
VII CONCLUSIONS AND RECOMMENDATIONS	57
Caveats Regarding Managing Calcite Precipitation as a Salinity Removal Process	58
Suggestions for Further Research	60
REFERENCES	63
APPENDIX A. DATA	69
APPENDIX B. CHEMICAL EQUILIBRIUM PROGRAM USED TO CALCULATE SUPERSATURATION OF CARBONATE SOLID PHASES GIVEN ANALYTICAL CONCENTRATIONS OF CONSTITUENT IONS AND TEMPERATURE	79

LIST OF FIGURES

Figure	Page
2.1. Reservoir studies with extensive hydrochemical data . . .	4
2.2. Conductivity (salinity) distribution in Lake Powell before (April) and after (June) the spring runoff (Reynolds and Johnson 1974)	5
2.3. Anion compositions of Lake Powell and the Green, Colorado, and San Juan Rivers (Reynolds and Johnson 1974)	6
2.4. USGS gaging stations used to calculate Lake Powell salinity mass balance	7
3.1. Examples of biogeochemical processes that could potentially transfer dissolved solids (dashed boundaries) to a particulate phase (solid boundaries) in natural waters	12
3.2. pC-pH diagram for a 10^{-3} m carbonic acid system	14
3.3. Stability relations of K-feldspar, muscovite, kaolinite, and gibbsite at 25°C and 1 atm, as functions of $\log [K^+]/[H^+]$ and $\log [H_4SiO_4]$	20
4.1. Bear River basin between Soda Point Reservoir and Glendale Reservoir, Idaho	26
4.2. Oneida Narrows Reservoir, Idaho. For location see rectangle A in Figure 4.1	26
4.3. Depth volume curve for Oneida Narrows Reservoir	27
4.4. Schematic diagram of three phase microcosm	28
5.1. Concentrations of various chemical constituents in Bear River on June 26, 1980 (mg/l except for alkalinity which is in mg/l as $CaCO_3$)	33
5.2. Specific conductance and temperature in the Bear River on March 10, 1981	33
5.3. Dendrogram representing the results of a cluster analysis of the data collected at stations shown in Figure 5.1 for the variables Ca^{++} , Na^{++} , K^+ , TDS alkalinity, Cl^- , and silica	35
5.4. Concentrations of chemical constituents in the vicinity of Oneida Narrows Reservoir on June 16, 1979	37
5.5. Concentrations of chemical constituents in the vicinity of Oneida Narrows Reservoir on July 15, 1980	37
5.6. Concentration of chemical constituents in the vicinity of Oneida Narrows Reservoir on August 1, 1980	38
5.7. Concentrations of chemical constituents in the vicinity on Oneida Narrows Reservoir on August 8, 1980	38

LIST OF FIGURES (Continued)

Figure	Page
5.8. Ion activity product of calcium and carbonate at Soda Point between July 8, 1971, and September 9, 1972	40
5.9. Ion activity product of calcium and carbonate below Oneida Narrows Reservoir tailrace between July 8, 1971 and September 9, 1972	40
6.1. Changes in concentrations of chemical species resulting in a mixture of Bear River waters at 15°C for 6 days	44
6.2. Changes in dissolved oxygen (DO) and pH before and during incubation of Oneida Narrows Reservoir water in the light (-) or dark (--) in semicontinuous 3-phase microcosms	45
6.3. Changes in calcium, magnesium, and alkalinity in Oneida Narrows Reservoir water during incubation in light (Groups I and II) and dark (Group III) in semicontinuous 3-phase microcosms	47
6.4. Changes in electrical conductivity occurring during incubation of Oneida Narrows Reservoir water in light (Groups I and II) and dark (Group III) 3-phase semicontinuous microcosms	48
6.5. Changes in silica concentration in Oneida Narrows Reservoir water incubated in light and dark semicontinuous, 3-phase microcosms	48
6.6. Relationship between calcium and alkalinity removal in individual microcosms between the beginning (days 0 and 1) and end days (11 and 13) of incubation	50
6.7. Changes in alkalinity, calcium, and sodium concentrations during incubation of Oneida Narrows Reservoir water under ambient laboratory conditions in the absence of a sediment phase	52
6.8. Changes in total dissolved solids during incubation of Oneida Narrows Reservoir water under ambient laboratory conditions in the absence of a sediment phase	53
6.9. Changes in chemical concentrations during incubation of a 1:7 mixture of Maple Grove hot springs water with Oneida Narrows Reservoir water under ambient laboratory conditions in the absence of a sediment phase	53
6.10. Change in TDS 48 hours after addition of various Bear River watershed soils to synthetic Oneida Reservoir water containing different concentrations of Ca ⁺⁺ (expressed as mg/l CaCO ₃)	54
6.11. Final TDS and calcium hardness concentrations in experimental flasks containing various amounts and types of soil and in soil-free control flasks incubated with various initial concentrations of calcium ion	55

LIST OF TABLES

Table	Page
2.1. Accumulation or release of ion loads in Flaming Gorge Reservoir between September 1972 and September 1974 (modified from Bolke 1979)	8
2.2. Major ion budget for Bighorn Reservoir, Montana, during 1968 and 1969 (based on data from Soltero et al. 1973)	9
3.1. Standard enthalpies of reaction, equilibrium constants, and analytical expressions for temperature corrections relating to freshwater carbonate chemistry (Plummer 1975 after various sources)	16
3.2. Solubility of potential important lacustrine carbonates (after Kelts and Hsü 1978, data from Garrels and Christ 1965, Truesdell and Jones 1974, Krauskopf 1978)	17
3.3. Factors which may affect carbonate precipitation in western reservoirs (greatly modified from Kelts and Hsü 1978)	18
3.4. Ion exchange of clays with solutions of CaCl ₂ and KCl of equal equivalent concentration (Wiklander 1964)	21
4.1. Results of five-day bioassays of microcosm water spiked with nitrate (10 mg NO ₃ -N/L) and phosphate (10 mg PO ₄ -P/L); results are means of duplicate analyses	29
4.2. Methods for water analyses	30
5.1. Comparison of paired samples taken upstream (Alexander) and downstream (Oneida Narrows Reservoir tailrace) several hours apart (data from Hill et al. 1973, Appendix F)	32
5.2. Comparison of ion:chloride ratios of samples taken several hours apart at Alexander, Idaho, and at the Oneida Narrows Reservoir tailrace (data from Hill et al. 1973, Appendix F)	32
5.3. Constituent concentrations in Oneida Narrows Reservoir on July 16, 1979	36
5.4. Saturation indices for calcite in Oneida Narrows Reservoir on three sampling dates	41
5.5. Comparison of TDS determined on filtrates of Bear River samples using filters with different pore sizes (GFC = 2 µm, millipore = 0.45 µm, and nucleopore = 0.22 µm)	42
6.1. Changes in concentrations, adjusted for dilution of selected constituents over the course of incubation under light (Groups I and II) or dark (Group III) conditions for 11 days	49

LIST OF TABLES (Continued)

Table	Page
6.2. Changes in selected constituents in microcosms initially containing Oneida Narrows Reservoir water receiving daily replacement of 12 percent Bear River water versus 12 percent reservoir water (control)	51
6.3. Results of multiple ANOVA analysis of changes in TDS concentration relative to controls following incubation with different amounts of soils and sediments from the Bear River watershed in synthetic river water of varying initial calcium hardness	56
7.1. Effect of varying physical and chemical parameters of Oneida Narrows Reservoir water on the calcite saturation index as determined by equilibrium modeling (Appendix B)	60
A.1. Chemical concentrations in Bear River below Soda Point Reservoir (at Alexander) from Hill et al. (1973)	69
A.2. Chemical concentrations in Bear River below UPLC tailrace at Oneida, data from Hill et al. (1973)	69
A.3. Data collected on Bear River synoptic survey, June 26, 1980	70
A.4. Data collected on Oneida Narrows Reservoir synoptic study on July 15, 1980	71
A.5. Data collected on Oneida Narrows Reservoir synoptic study on August 1, 1980	72
A.6. Data collected on Oneida Narrows Reservoir synoptic study on August 19, 1980	72
A.7. Concentrations of various constituents in Experiment II. All data are in mg/l except conductivity (μ mhos/cm), alkalinity (mg/l as CaCO_3), Fe and Chlorophyll <u>a</u> (μ g/l), and temperature ($^{\circ}$ C)	73
A.8. Concentration of chemical constituents in microcosms during upstream/downstream experiment	74
A.9. Concentration of chemical constituents in microcosms during Experiment III	75
A.10. Chemical data for coagulation experiment	77
A.11. Final concentrations of constituents in control and experimental flasks following incubation with soil samples (Experiment V)	78

CHAPTER I
INTRODUCTION

Effective water resources management requires consideration of water quality in addition to water availability. One of the most important water quality variables in the semiarid western states is salinity. Each year increased salinity in western river basins results in substantial economic losses in the forms of lowered crop productivity and damage to pipes and fixtures resulting from lower quality water or, alternatively, higher costs of providing suitable water for irrigation and municipal uses. In the Lower Colorado River Basin, it has been estimated (USDI 1981) that each mg/l increment in average total dissolved solids (TDS) concentration in the annual discharge will result in an annual loss of \$450,000 in 1980 dollars to downstream users, approximately one third of which will be to agricultural users and the remainder to municipal and industrial supplies. The deleterious effects of increased salinity were recognized in the establishment of salinity criteria (target concentrations) for the Lower Colorado River Basin not to exceed 1972 concentrations (§120.5 40 CFR part 120). If further withdrawals of water for fossil fuel development and municipal uses in the Upper Basin decrease the availability of relatively fresh dilution water, the salinity problem will increase in the future.

Present attempts to mitigate the increasing salinity of the Colorado River include desalination facilities, diversion of saline springs and seeps, and shifts in water distribution and irrigation technologies (Narayanan et al. 1979, Temple 1980). Program cost projections (USDI 1977) exceed \$22 million/year and even then fail to include more than half of the proposed projects. As an additional alternative, two previous studies at the Utah Water Research Laboratory (UWRL) indicated that

significant quantities of total dissolved solids (salinity) that flow into some reservoirs are held there rather than being discharged through the outflow (UWRL 1975; Sorensen et al. 1976). If such "natural" salinity removal processes are of widespread occurrence in western reservoirs, and if reservoirs could be managed to enhance these removal mechanisms, the costs of salinity removal by utilizing more expensive techniques could be reduced.

The purposes of this research into natural salinity removal processes in reservoirs were twofold. The first was to review the literature to determine the frequency and magnitude of salinity removal occurring in western reservoirs. The results of this search are summarized in Chapter II. The second objective was to investigate possible mechanisms of salinity removal, together with the factors controlling these mechanisms, using both laboratory microcosms and data gathered from Oneida Reservoir, a small hydroelectric reservoir on the Bear River in southern Idaho. These studies focused on four hypothetical mechanisms for transferring salinity from the dissolved to the particulate state, i.e., natural salinity removal: 1) Congruent precipitation processes; 2) coprecipitation, including incongruent precipitation processes; 3) coagulation; and 4) biochemical assimilation. Following brief descriptions of the potential mechanisms for salinity removal in reservoirs in Chapter III, and a description of the Idaho study site and experimental methods in Chapter IV, the results of these experiments, together with brief discussions of the relevant chemistry, are presented in Chapters V and VI. Chapter VII summarizes the results of the study in the context of potential reservoir management practices.

CHAPTER II
EVIDENCE OF SALINITY REMOVAL AS A RESULT
OF IMPOUNDMENT IN WESTERN RESERVOIRS

Introduction

Interest in the effects of impoundment on water quality in western reservoirs began at least as early as 1937, following construction of Hoover Dam (Howard 1960). In a project co-sponsored by the U. S. Bureau of Reclamation, the Metropolitan Water District of Southern California, and the U. S. Geological Survey (Smith et al. 1960), Howard found evidence that, although salinity increased as a result of passage of Colorado River water through Lake Mead, almost half of the original increase was subsequently removed by precipitation of calcium, and to a lesser extent, silica within the lake. Since that time increasing interest in water quality has spawned many symposia and review papers dealing with effects of impoundment on water chemistry (e.g. USPHS 1965, Obeng 1969, Symons 1969, Ackerman et al. 1973, Ward and Stanford 1979). In addition, nearly 100 papers have been published in the last decade on the aquatic chemistry of impounded streams. However, few of the studies represented by these papers actually had as their primary purpose, the conclusive demonstration of salinity removal.

The occurrence of natural salinity removal in reservoirs has generally been demonstrated in one of three ways. The two most common methods are inferential. The easiest (and least conclusive) method is to demonstrate a lower concentration of dissolved constituents in the tailwater downstream from a reservoir than in the influent water. This method generally fails to take into account concentration or dilution brought about by influent springs, groundwater seepage, local precipitation and snowmelt, or evaporation from the lake surface.

A more conclusive demonstration of salinity removal can be obtained through the use of a mass balance on the constituents of interest. Such a balance employs a continuity equation of the form

$$\Delta m_{iR} = \Delta \sum c_{iR} D_{iR} = \sum c_{iIN} D_{iIN} - \sum c_{iOUT} D_{iOUT} - \Delta c_{iS} D_S \quad (2.1)$$

where m_i = the mass of the i 'th constituent;

c_i = the concentration of the i 'th constituent over some time period, t ; and D_i equals the volume of water represented by c_i . The subscripts R, IN, OUT, and S refer to removal, input, output, and storage, respectively. The input terms should include all inflow from the main stem, precipitation, snowmelt, seepage, and dry deposition ($D_i=0$). Output terms include tailwater and evaporation losses ($c_i=0$). The storage term should be measured accurately at the beginning and end of the period in question, and should include bank storage that can actively exchange ions with the water column.

It is seldom practical to measure all these terms accurately. Typically, at best only the major tributaries and tailwater are gaged. The most reliable data are at USGS stream gages, but they are often upstream or downstream of the ideal locations for establishing a mass balance in that they often include river reaches which are not part of the reservoir. Thus riverine processes may be confused with reservoir processes. Although precipitation may be gaged, chemical analyses of wet and dry deposition are seldom available, although such sources can contribute significantly to lake mineral budgets (Eisenreich 1981). Groundwater movements and chemistry are seldom known with accuracy, and minor tributaries are seldom gaged. Although in western states, water contributions from minor tributaries to lowland reservoirs are usually small, their flows may be highly mineralized and contribute disproportionately to the salt load. Streamflow outputs are often accurately monitored, but evaporation is usually estimated from the mass balance equation.

The third method for demonstrating salinity removal is deductive in nature: to observe, in situ, the occurrence of the suspected process itself. Such studies include observations of calcite formation and silica precipitation in the form of diatom frustules, and also sediment trap studies. Such investigations have been relatively rare in western reservoirs, although they have been performed more frequently in natural lakes. Because the nature of such studies is fundamentally different from mass balance methodologies, the removal processes will be reviewed separately in the following chapter.

In the following sections of this chapter, we shall critically review some of the previous studies conducted on western reservoirs for inferential evidence of natural salinity removal. In some cases, the primary intent of the writers was not to demonstrate salinity removal, but their data can be used to draw tentative conclusions toward that end. In other cases, the papers make a case for removal of salinity or specific ions. In such cases, we shall also attempt to make some judgment of the reliability of the data and the methodology employed to demonstrate removal.

We shall restrict our discussion to several western reservoirs located in arid or semiarid regions. The locations of these reservoirs are shown in Figure 2.1. They include: Bighorn Lake on the Bighorn River on the Wyoming-Montana border; Canyon Reservoir on the Guadalupe River in Texas; Flaming Gorge Reservoir on the Green River on the Utah-Wyoming border; Lake Powell on the Upper Colorado River in Southern Utah; and Lake Mead on the Lower Colorado River on the Nevada-Arizona border. These reservoirs were chosen on the basis of data availability and suitability, and because potential influences of the water balance and evaporitic lithology on reservoir water chemistry in these arid and semiarid systems are likely to be different than those in humid regions. Also shown in Figure 2.1 is the location of Oneida Reservoir on the Bear River in southern Idaho, the site chosen for intensive studies described in Chapters V and VI.

Review of Western Reservoir Studies

Lake Mead

As pointed out previously, Howard (1960) was the first to note the importance of salinity removal mechanisms in a western reservoir, using both concentration data and an incomplete mass balance. Howard noted that in the summer following closure of Hoover Dam in February 1935, total dissolved solids (TDS) concentrations became lower at the Willow Beach gage, 10 miles below the dam, than at Lee Ferry, Arizona, approximately 355 miles above the dam. He calculated that during the water years 1935-1948, 140×10^6 tons ($127 Tg$) of TDS were carried past the Lee Ferry station, and that another 8×10^6 tons were added by unmeasured tributaries above Lake Mead. Output was measured at the Willow Beach gage between 1935 and 1939, and immediately below the dam thereafter. The TDS in the outflow was 136×10^6 tons, resulting in a net decrease of 12×10^6 tons. Storage was calculated to be 22×10^6 tons, indicating a net increase in TDS of 10×10^6 tons ($8 Tg$) of TDS.

Although Howard does not describe his calculations, he estimated that 9×10^6 tons of calcium carbonate and 1×10^6 tons of silica precipitated in the lake, citing deposits of calcium and silica around the

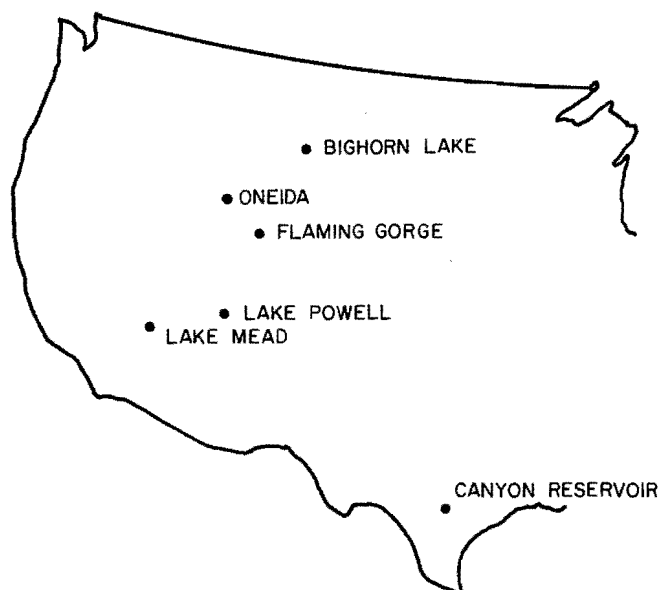


Figure 2.1. Reservoir studies with extensive hydrochemical data.

lake littoral as supporting evidence. From increases in sulfate and chloride output below the dam, however, Howard calculated that this removal of calcium and silica was overshadowed by the dissolution of gypsum, together with a smaller amount of halite, totaling 20×10^6 tons. Slight increases in magnesium, potassium, and nitrate concentrations were consistent with evaporative concentration, which accounted for 5 percent of the average annual inflow.

Howard thus suggests that approximately 6 percent ($10 \div 168$) of the total input of TDS to Lake Mead, including internal loading, is removed by calcium carbonate and less than 1 percent by silica precipitation. Data on inflows and outflows were taken from weighted annual average concentrations published by USGS. Neither the number of data points used to calculate fluxes or storage, nor the method of calculating calcium or silica precipitation or dissolution are presented. It is significant that the calculated removal rate is similar in magnitude to the estimated (unmeasured) salt input between Harper's Ferry, Arizona, and the head end of Lake Mead and about one half of the calculated change in storage. Considering that salinity may vary by a factor of two over space and depth in Lake Mead over a 4-day sampling cruise (Anderson and Pritchard 1960), the accuracy of the storage estimate is also subject to a magnitude of error that could substantially effect the calculated salinity removal.

Lake Powell

Much more is known regarding the salinity of Lake Powell than that of Lake Mead, because it has been the object of an in-

tensive National Science Foundation (RANN) study (e.g., Reynolds and Johnson 1974, Mayer 1977, Merritt and Johnson 1978, Johnson and Merritt 1979), which began in 1971. The introduction to the hydrodynamics of Lake Powell presented by Johnson and Merritt (1979) serves as good basis for discussion of salinity removal mechanisms later in this report.

Lake Powell is classified as a warm monomictic lake, i.e., wind driven circulation fails to mix the warm reservoir water entirely to the bottom each summer, leaving a stagnant, salt rich chemolimnion at the bottom. Cold, relatively saline, inputs during the winter displace the older saline water out of the deepest portions of the reservoir, whence it is flushed from the reservoir by late March. The consequences of such hydrodynamics, depicted in Figure 2.2, are that summer surface overflows are generally lower in salinity than the lake average,

but over an entire year, the entire water volume is reasonably well mixed. That this is so can be seen from the intermediate nature of Lake Powell water chemistry with respect to its three major tributaries (Figure 2.3).

Reynolds and Johnson went on to determine that from 8 to 12 percent of the bicarbonate load of the influent water was being removed in Lake Powell, which would correspond to a salinity reduction of 19 to 29 mg/l, or approximately 5 percent of the 1965-1970 average salinity of 500 mg/l. The methodology involved assumptions similar to those used for our Lake Powell salinity budget that will be described at the end of this section. Corroborative evidence was gained from the fact that the surface water was everywhere supersaturated with respect to calcite. Subsequent experiments by Reynolds (1978), described in Chapter III, tend to support calcite precipitation as an

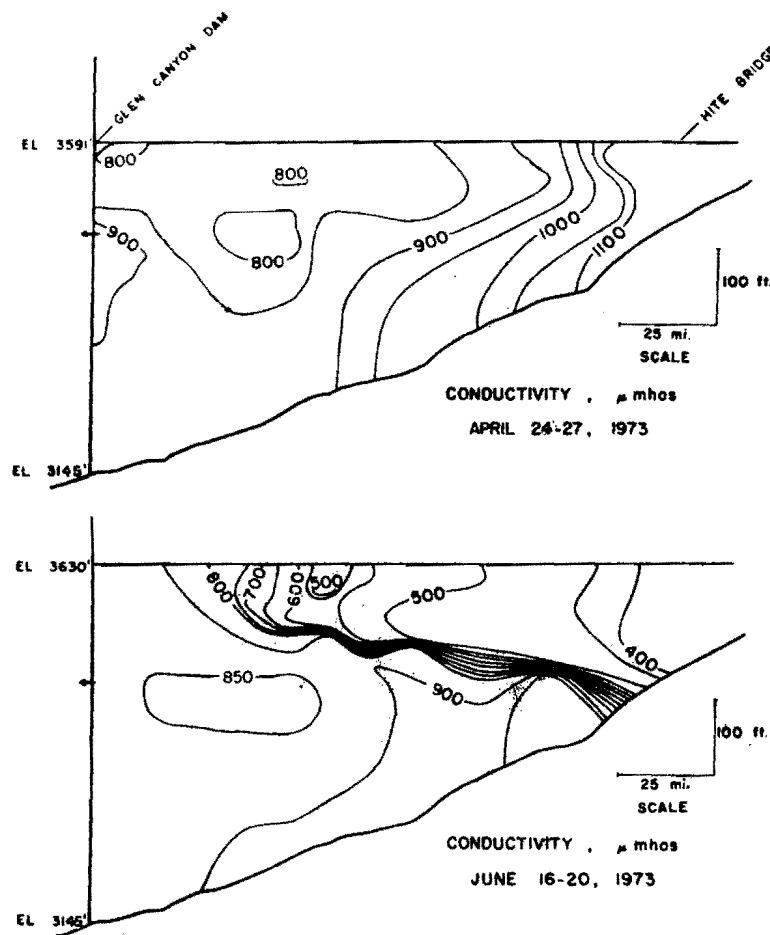


Figure 2.2. Conductivity (salinity) distribution in Lake Powell before (April) and after (June) the spring runoff (Reynolds and Johnson 1974).

important salinity removal mechanism. Mayer (1977) calculated a net loss (input minus output) of 1.3 to 2.9 mg/l of silica annually, with the higher value necessitating considerable bank storage of dissolved Si. Thus silica removal does not contribute substantially to salinity removal in Lake Powell. Neither of these studies, however, includes a reliable measurement of change in water column storage.

Inasmuch as salinity records (USU 1975, Table 1) for the Colorado River at Lake Powell seemed to indicate that as much as 11×10^6 g of salinity per day was being "stored" in the reservoir, and because no detailed calculations seemed to have been published, we decided to construct an input-output salinity model for the reservoir. We have chosen to present the model here, rather than in a later chapter, because we shall not turn again specifically to Lake Powell in our studies. The methodology is similar to that used by Reynolds and Johnson (1974), Mayer (1977), and Bolke (1979), except that a term is included for changes in water column and bank storage.

As is often the case, there is no gaging station immediately upstream from Lake Powell from which to directly derive the input data. Therefore, inputs were calculated using a linear regression model that relates the total annual salinity load from four streams tributary to the reservoir to the total salt load passing a downstream station prior to closing of the Glen Canyon dam in 1963. The upstream stations included the San Rafael River near the town of Green River, Utah, the Colorado River near Cisco, Utah, the Green River, also near Green River, Utah, the San Juan River near Bluff, Utah, and the Dirty Devil River above Poison Springs Wash near Hanksville, Utah. According to Iorns et al. (1965) the rivers at these stations contribute 96.8 percent of the salt load to Lake Powell. The downstream station was on the Colorado River near Lee Ferry, Arizona. The locations of these stations are shown in Figure 2.4. The period covered by the model included the 1941 through 1962 water years, and the data were taken from the USGS (e.g., USGS 1979).

The linear model took the form

$$M_{OUT} = 446 + 1.02.M_{IN} \quad \dots \dots \dots (2.1)$$

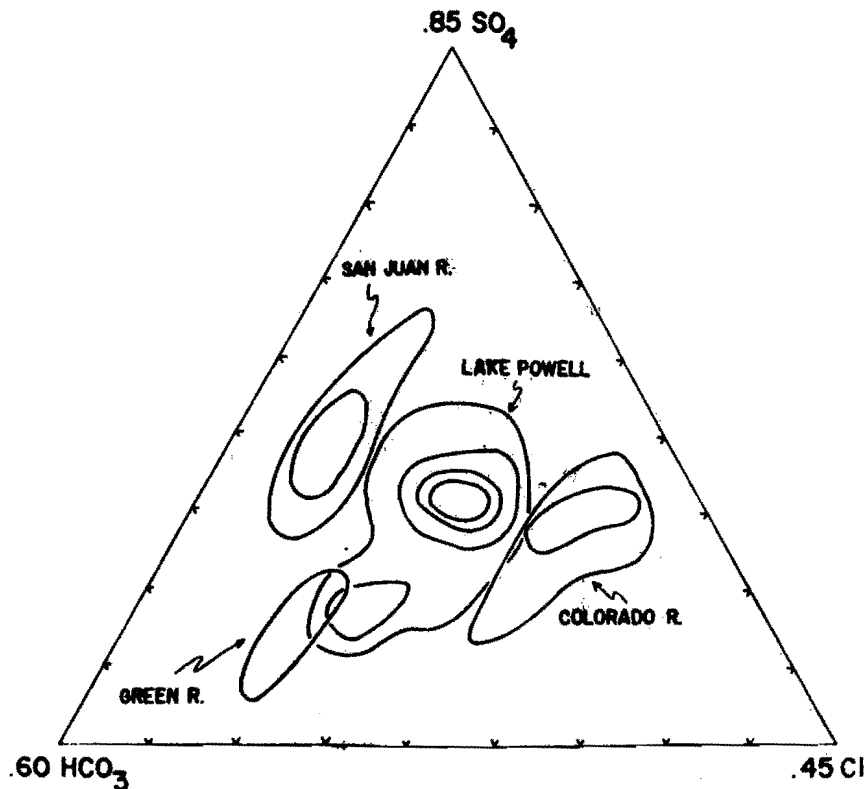


Figure 2.3. Anion compositions of Lake Powell and the Green, Colorado, and San Juan Rivers (Reynolds and Johnson 1974).

Data are expressed in ion equivalent percents.

in which the masses of total dissolved solids input and output, M_{IN} and M_{OUT} , respectively, are expressed in 10^9 g/yr. The regression accounted for 83 percent of the variation in annual salinity output ($r = 0.913$, $n = 22$) at Lee Ferry. Assuming that closure of the dam had no effect on salinity levels in the river, Equation 2.1 predicts that total salt output for the 13 water years 1963 through 1975 at Lee Ferry should have been 99.1×10^6 metric tons, whereas the observed salt load passing the station totaled only 76.2×10^6 metric tons, leaving 22.9×10^6 metric tons apparently stored in the reservoir.

The actual storage of salt in the water column can be estimated with reasonably good accuracy. The increase in water storage in the reservoir up until 1975 was 2.76×10^{10} m^3 . Total dissolved solids concentrations could be calculated by integrating specific conductance isopleths measured by Merritt and Johnson (1977, Figure 13) at the end of September in 1975, and using the empirical model chosen by these authors to relate TDS to specific conductance ($TDS = 17.48 + 0.684$ (EC) Hendrick (1973)). The volume weighted mean TDS concentration for the reservoir at this time was 579 mg/l. Multiplied by the storage volume of 2.76×10^{10} m^3 , this leads

to a total water column storage of 15.9×10^6 metric tons. This leaves 6.9×10^6 metric tons of salt, or 7 percent of the calculated input, to have been removed either in bank storage or by some natural removal process.

Bank storage of salinity depends on the movement of dissolved salts relative to stored water, in cracks, crevices, and permeable formations inundated by the reservoir water. Qualitatively, one may envision that, in a filling reservoir, if the hydraulic migration rate of water away from the reservoir exceeds the molecular diffusion rate back toward the reservoir of salts released to the water from the flooded minerals, bank storage may act as a sink for salinity. This is more likely to occur in permeable strata, which could also be expected to contribute more salt owing to the relatively large surface area in contact with the water, than in large channels and crevices. The latter may be characterized by rapid flooding, followed by subsequent out migration of dissolved salts. Additionally, during seasonal or secular decreases in reservoir water levels, salts would be flushed out of the banks as stored water drains back toward the reservoir.

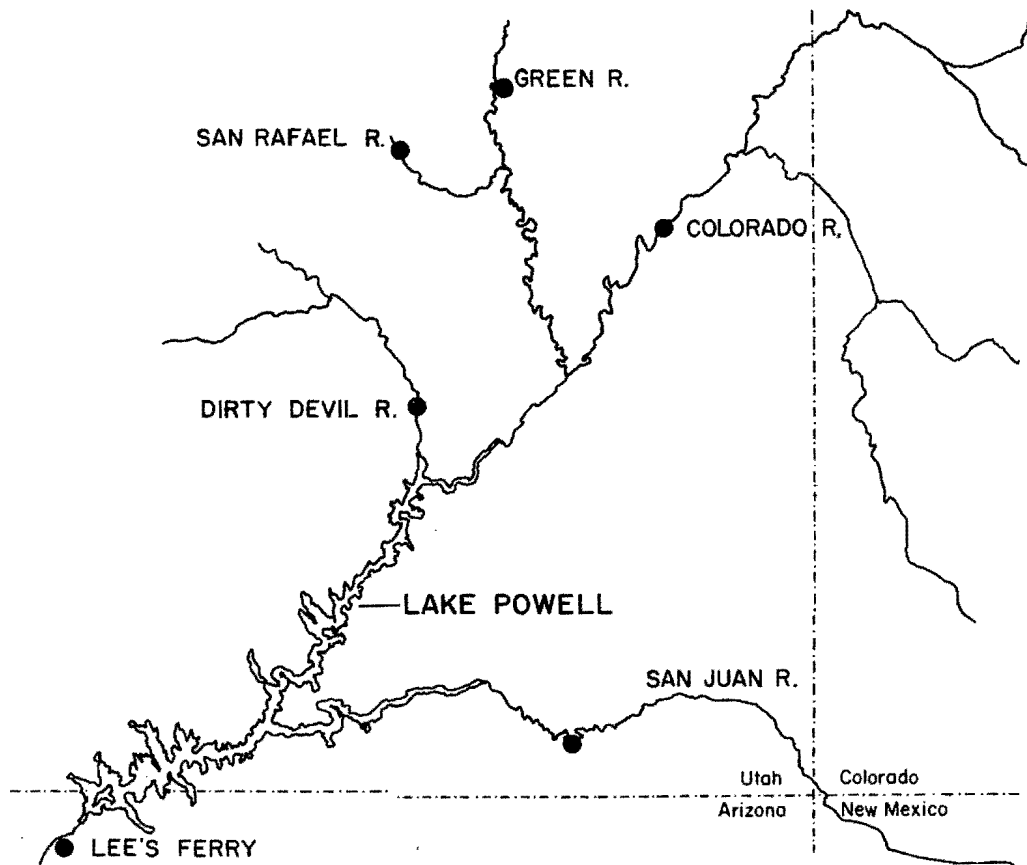


Figure 2.4. USGS gaging stations used to calculate Lake Powell salinity mass balance.

Although the magnitude of bank storage cannot be resolved with information presently available, a crude calculation may offer some perspective. Bank storage in Lake Powell, at the time water column salt storage was measured above, was approximately $11 \times 10^9 \text{ m}^3$ (Lee Morrison, Bureau of Reclamation, personal communication). If one assumes an average historical flow weighted TDS concentration of 560 mg/l was stored with this water (i.e., no biogeochemical interactions occurred), the storage of salt would be 6.2 metric tons, which would account for approximately 90 percent of the discrepancy between input and output, leaving only 0.7 percent of the input unaccounted for. Again, it is important to recall that this calculation is likely to represent an absolute maximum storage because it neglects biogeochemical salt loading from drowned rock and soil formations. Nonetheless, it suggests that massive biogeochemical salinity removal is in no way conclusively demonstrated by the salinity mass balance.

Flaming Gorge Reservoir

Closing of the Flaming Gorge Dam on the Green River in northern Utah in 1962 led to an increase in the flow-weighted average TDS concentration in the outfall, which led Bolke (1979) to construct a salt balance for the reservoir. His methodology was similar to that described earlier for Lake Powell. The TDS load immediately below the dam site was related to the load from three gaged upstream tributaries (Green River, Blacks Fork, and Henry's Fork) during 1957-1962 prior to closure of the dam, the difference being ascribed to unmeasured salt sources (nonpoint flows, minor tributaries, springs, etc.). The precipitated/leached salt load was calculated using the mass balance:

$$LL = DSL + OTL + DLF - 1.20 \text{ MINL} \quad \dots (2.2)$$

in which LL is the net gain or loss from biogeochemical reactions, DSL is the change in water column storage, OTL is the measured outflow load, DLF is a storage term for the smaller Fontanelle Reservoir, downstream from the gaging station on the Green River, and MINL is the measured inflow load. The nature of the calculation of the DLF term is not clear from Bolke's discussion, nor is the reliability of the data used to calculate DSL apparent.

The net biogeochemical loading rate, LL, was calculated for eight periods of various lengths, based (presumably) on the availability of data with which to calculate DSL (Bolke and Waddell 1975). The results indicated that, between the closing of the reservoir in 1962 and the end of the study in 1975, a net release of 1.95×10^6 metric tons of TDS to the Green River resulted following construction of the reservoir. The pattern of TDS release was 1) high during initial filling (3 yr) of the reservoir, 2) low during a following period of declining water levels (3 yr), and 3) a return to high rates

during subsequent filling to design capacity. Bolke suggested that the increases were primarily due to leaching of salts from newly inundated rocks, and that loadings would probably decrease in the future.

Bolke (1979) also calculated a dissolved ion budget for the period September 1972 to September 1975. The net changes in ion loads (LL) are shown in Table 2.1. Modest increases in sodium, magnesium, and chloride were accompanied by a large increase in sulfate, a large decrease in bicarbonate, and no change in calcium concentration. Bolke (1979) reasoned that if the increase in sulfate load were caused by gypsum dissolution, then $190 \times 10^6 \text{ kg}$ of calcium would be brought into solution, which would in turn precipitate $280 \times 10^6 \text{ kg}$ of carbonate in order to realize the zero balance of calcium inputs and outputs noted in Table 2.1. Bolke then noted that the dissolved bicarbonate calculated in the load budget was $390 \times 10^6 \text{ kg}$, thus leaving $110 \times 10^6 \text{ kg}$ unaccounted for.

Alternatively, one could approach the problem from the opposite direction. The precipitation of $130 \times 10^6 \text{ kg}$ of calcium would be accompanied (assuming it originated from gypsum) by $310 \times 10^6 \text{ kg}$ of sulfate. The remaining $180 \times 10^6 \text{ kg}$ of sulfate could be produced by sulfide oxidation or the dissolution of other sulfate minerals. Unfortunately, the discrepancy between the ion budgets (Bolke 1979, p. 32) and the TDS budget (p. 31) for the same period differ by over 100 percent (see Bolke 1979, Table 2.3). This discrepancy suggests serious flaws in either the data or, more likely, the budget calculations, which makes further speculation of rather limited value. If Bolke's calculations are correct, however, as much as 10 percent of the TDS (external plus internal)

Table 2.1. Accumulation or release of ion loads in Flaming Gorge Reservoir between September 1972 and September 1974 (modified from Bolke 1979).

Constituent	Accumulation (-) or release (+)		
	$\times 10^6 \text{ kg}$	$\times 10^9 \text{ equivalents}$	
Calcium	0	0	} +8
Magnesium	70	6	
Sodium	50	2	
Bicarbonate	-390 ^a	-6	} +5
Sulfate	460	10	
Chloride	30	1	
Total	+220		
TDS	564		

^aThis value is misprinted as -0.49×10^6 metric tons in Bolke (p.32).

load to the reservoir may be lost by calcium carbonate precipitation.

Bighorn Lake

Bighorn Lake is a multipurpose impoundment created by the closing of Yellowtail Dam on the Bighorn River, Montana, in November 1965. The chemistry and limnology of the reservoir have been described by Soltero et al. (1973, 1974) and Soltero and Wright (1975). Soltero et al. (1973) published discharge-weighted major ion concentrations of the inputs and outputs streams for the reservoir during calendar years 1968 and 1969. Hydrologic budgets for the period were also provided, enabling the construction of a budget with a net storage (water column plus biogeochemical changes) term only. The resulting budget is shown in Table 2.2.

As can be seen, most constituents were released to a small extent by the reservoir, except sodium and chloride, which showed a slight decrease in the effluent. Storage in the reservoir increased by $91 \times 10^6 \text{ m}^3$ during the budget period (Soltero et al. 1974), but no water column concentration data are available. No secular trend in the specific conductance of the effluent was noticeable during the budget period (Soltero et al. 1973, p. 346), and the writers noted that calcium carbonate precipitation was not likely to be important in Bighorn Lake because the Ca/Mg ratio does not change between the influent and effluent waters.

Table 2.2. Major ion budget for Bighorn Reservoir, Montana, during 1968 and 1969 (based on data from Soltero et al. 1973).

Constituent	Input	Output	Difference (%)
	$\times 10^9 \text{ kg}$		
Sodium	33.0	32.4	-2
Calcium	30.5	31.1	+2
Magnesium	9.55	9.63	+1
Chloride	4.7	4.4	-6
Bicarbonate	75.9	78.5	+3
Sulfate	111	116	+4

An attribute of the data given by Soltero et al. (1973) compared to that shown in Table 2.2 is worthy of notice. In the original data, flow weighted concentrations were presented, and these concentrations were typically 5-15 percent lower for the discharge than the inputs. The reason for this is the unaccounted for snowmelt along the sides of the reservoir, which dilutes the lake water. Thus the apparent salinity removal phenomenon disappears when the data are expressed as mass fluxes, as in Table 2.2.

Canyon Reservoir

Canyon Reservoir is an oligo-mesotrophic deep storage reservoir on the Guadalupe River in central Texas. Hannan (1979) has summarized earlier work by him and his colleagues on the biogeochemistry of the reservoir. Hannan and Young (1974) found that bicarbonate ion concentrations decreased near the center of the reservoir, which the writers associate with the areas of highest chlorophyll *a* concentrations. Examination of their data (p. 189), however, does not seem to justify such a simple relationship. Specific conductance also decreased between an upstream station and the dam, mostly in the upstream, riverine reach of the reservoir. The writers again attributed this effect to biogenic carbonate precipitation, but without offering either proof or calculations.

Hannan and Broz (1976) extended the earlier work, and reported the following average changes in concentrations between a station upstream for the reservoir and the tailrace: alkalinity, -20 to 30%, specific conductance, -34%, calcium, -25%, magnesium, -23%, sodium, -20%, potassium, +35%. No chloride or sulfate data were presented. There are no seasonal trends apparent in any of these concentration changes, which might be expected if the principal removal mechanism were calcium carbonate precipitation. Hannan et al. (1979) presented more detailed isopleths, and noted that bicarbonate reduction was positively correlated with primary productivity rates, although reference was made to an unpublished thesis, and no data were presented.

In summary, these studies gave circumstantial evidence of calcium carbonate acting to remove salinity from Canyon Reservoir. No mass balance was performed, however, and seepage of less saline water through an alluvial formation crossed by the reservoir could provide some dilution. Normal precipitation is low (< 16 cm/yr) in the area, which minimizes the impact of rainfall as a diluent. No mechanisms for sodium or magnesium removal were suggested.

Summary

Although the authors of reservoir studies in the semiarid western states have frequently suggested that salinity removal may occur, the magnitudes are usually small and within the range of error of the calculations. High estimates are 6 percent for Lake Mead, 3 to 8 percent for Lake Powell, 10 percent for Flaming Gorge, and a net gain of 3 percent in Bighorn Reservoir. Decreasing ion concentrations were observed in Canyon Reservoir, Texas, but no mass balance was done. Most published mass balance calculations are plagued by poor cation-anion balances, hidden calculations, and unexpressed or unsupported assumptions. In many cases, random sampling error in determining salt storage in the water column is

sufficient to account for the calculated removal. Determining bank storage of salinity is a particularly thorny problem.

Two points are worth considering when analyzing and interpreting these data, however. The first is that a very small reduction in the salinity load in a river could be worth millions of dollars annually to downstream users (DOI 1981). Related to the first point is the second: a small salinity reduction is difficult to demonstrate conclusively against a high and variable background. This is not to say that such a change is not susceptible to management or worth looking for. That existing studies do not conclusively demonstrate constant and substantial salinity removal in reservoirs is not meant to imply that certain mechanisms cannot be important during

some years or seasons in certain reservoirs. We shall return to this problem in the final chapter.

In general, such salinity removal as occurred appeared to be caused by calcium carbonate precipitation, although very minor biogenic silica removal was noted in Lake Powell and Lake Mead. The implication that carbonate precipitation can act to ameliorate gypsum dissolution in the relatively young Flaming Gorge Reservoir is interesting, inasmuch as a homeostatic biogeochemical mechanism may be implied. That is, if calcium carbonate failed to precipitate, thus reducing the calcium concentration in the overlying water, would gypsum continue to dissolve? This question will be pursued following a discussion of the relevant chemistry in the following chapter.

CHAPTER III

NATURAL SALINITY REMOVAL PROCESSES

Introduction

Biogeochemical processes that potentially could remove TDS from surface waters during transit through reservoirs include precipitation, coprecipitation, coagulation, and biochemical assimilation. These four processes are illustrated schematically in Figure 3.1. Precipitation is taken here to include congruent processes only; that is, processes in which two or more species in solution form a more or less crystalline precipitate, according to the principles of heterogeneous equilibria. Incongruent processes, involving solid phases as both reactants and products, will be considered as coprecipitation. Coagulation processes may be purely physico-chemical or may involve bridging by biological polymers. Biochemical assimilation includes incorporation of dissolved ions into shells, bones, tests, and other biogenic structures with long lifetimes relative to sedimentation rates. Each of these processes will be considered with respect to the relevant chemistry and previous in situ studies.

Precipitation

Although occasionally massive calcium carbonate deposition has been observed in hardwater midwestern lakes (Otsuki and Wetzel 1974), including the summer "whittings" of Lake Michigan (Strong and Eadie 1978), demonstrations of such precipitation in western reservoirs are less common. Extrapolation of laboratory experiments to chemical conditions in Lake Powell led Reynolds (1978) to conclude that calcite precipitation removed a significant fraction of the calcium input to Lake Powell, but that the phenomenon was restricted to a few weeks during the summer. Because calcite precipitation is strongly influenced by pH, and thus by photosynthesis and other biological processes, precipitation is likely to be strongly influenced by trophic state, residence time, and morphometry of reservoirs, and thus simple extrapolation from natural lakes to reservoirs must be done with caution. As a first step in evaluating the empirical evidence on the extent to which precipitation occurs, it is worthwhile to consider the factors which affect precipitation reactions in aquatic systems.

Carbonate Precipitation

The relative ubiquity of calcium and magnesium in freshwater ecosystems, together with the low solubility of their carbonates relative to monovalent ions, leads to the supposition that these species might be suspected to remove the majority of salts from hardwater reservoirs. Lucid presentations of carbonate precipitation with emphasis on freshwater ecosystems can be found in Garrels and Christ (1965), Kelts and Hsü (1978), and Stumm and Morgan (1981). The following discussion depends heavily on these sources.

Solubility product. The solubility product of calcite, the most ubiquitous carbonate, is reported to be 4.5×10^{-9} (Krauskopf 1978) at 25°C, i.e.

$$K_{sp}(\text{calcite}) = (\text{Ca}^{++})(\text{CO}_3^{=}) = 4.5 \times 10^{-9} = 10^{-8.35} \quad \dots (3.1)$$

where the quantities in parentheses refer to the activities of calcium and carbonate, respectively. The negative \log_{10} of the K_{sp} , 8.35, is customarily referred to as the pK_{sp} , and this term provides a convenient notation for equilibrium calculations. Activities of ions differ from their analytical concentrations (denoted by enclosure in brackets), in that activities represent the "effective" concentrations of each species with respect to a particular reaction. In dilute solution at environmental temperatures activities are somewhat lower than analytical concentrations, owing to interactions with other ions in solution.

Ion activities are calculated by multiplying an analytical concentration by a suitable activity coefficient (γ). In dilute aqueous solution (< 0.1 m), these coefficients are most conveniently calculated using the extended Debye-Hückel equation (e.g., Stumm and Morgan 1981, p. 134-137).

$$\log \gamma = -AZ^2 \frac{\sqrt{I}}{1+Ba\sqrt{I}} \quad \dots (3.2)$$

where

A = 1.82×10^6 (dielectric constant x Kelvin temperature)^{2/3} ≈ 0.5 in H₂O at 25°C

Z = ionic charge

B = 50.3 (dielectric constant x Kelvin temperature)^{1/2} ≈ 0.33 in H₂O at 25°C

a = ion size parameter (in 10⁻¹⁰ m assuming B ≈ 0.33)

I = ionic strength of the medium

Values of a are tabulated in Stumm and Morgan (1981, p. 135), e.g., 0.5 nm for CO₃²⁻ and 0.6nm for Ca⁺⁺. Ionic strength can be calculated using the formula

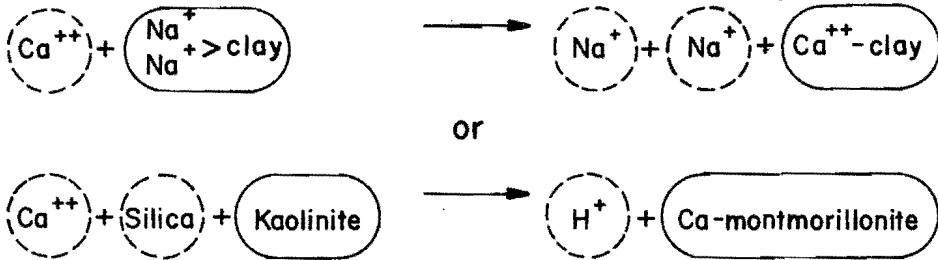
$$I = \frac{1}{2} \sum C_i Z_i^2 \quad \dots \dots \dots (3.3)$$

where C_i and Z_i represent the concentration and charge of ionic species i, respectively. When the complete analysis of a water is not available, Stumm and Morgan (1981) suggest using one of the approximations:

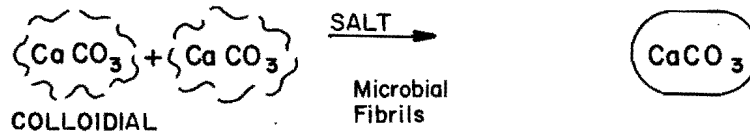
PRECIPITATION



COPRECIPITATION



COAGULATION



BIOASSIMILATION



Figure 3.1. Examples of biogeochemical processes that could potentially transfer dissolved solids (dashed boundaries) to a particulate phase (solid boundaries) in natural waters.

$$I = 4([\text{Ca}^{++}] + [\text{Mg}^{++}]) - \frac{\text{alkalinity}}{2} \quad (3.4)$$

or

$$I = 2.5 \times 10^{-5} \times \text{TDS} \quad (3.5)$$

where the total dissolved solids (TDS) is expressed in mg/l.

Calcite solubility then can be shown to equal the square root of the K_{sp} divided by the activity coefficients for Ca^{++} and CO_3^{--} . Specifically,

$$(\gamma_{\text{Ca}^{++}}[\text{Ca}^{++}])(\gamma_{\text{CO}_3^{--}}[\text{CO}_3^{--}]) = K_{sp}(\text{calcite}) \quad (3.6)$$

and

$$[\text{Ca}^{++}] = [\text{CO}_3^{--}]$$

thus

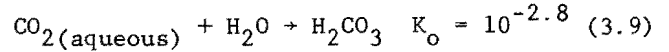
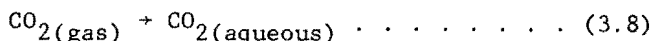
$$[\text{Ca}^{++}] = \left[\frac{K_{sp}}{\gamma_{\text{Ca}^{++}}\gamma_{\text{CO}_3^{--}}} \right]^{1/2} \quad (3.7)$$

By similar reasoning, if a water is saturated with calcite, the ion activity product, $(\gamma_{\text{Ca}^{++}}[\text{Ca}^{++}])(\gamma_{\text{CO}_3^{--}}[\text{CO}_3^{--}]) = \text{IAP}$, will exactly equal the K_{sp} . Supersaturated water will exhibit an IAP/K_{sp} ratio > 1.0 , and undersaturation will result in a ratio < 1.0 .

The importance of the effect of ionic strength on calcite solubility has been pointed out by Plummer (1975). Equilibrium calculations indicate that mixing saline water ($< 10\%$ sea water) with fresh groundwater saturated with respect to calcite invariably results in undersaturation. The extent of undersaturation increases greatly with increasing P_{CO_2} above $10^{-3.0}$ atm and with decreasing temperature. The undersaturation is attributable to the indifferent ion effect as expressed through the activity coefficients. This phenomenon may be important in increasing calcite solubility near saline seeps in rivers or reservoirs.

In surficial waters three major factors influence solid/solution equilibrium; carbonate is a conjugate base in the carbonic acid system (as is bicarbonate); the carbonic acid system exists in equilibrium with a gaseous component, CO_2 ; and CO_3^{--} participates in ion pairing reactions that compete with calcite precipitation. The first two factors, which are interrelated, are considered together.

Carbonic acid system. Carbonic acid is a diprotic acid which exists in equilibrium with atmospheric carbon dioxide. It becomes aquated when it enters solution

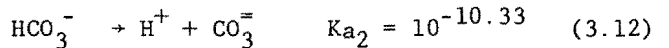
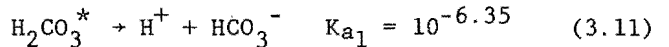


The sum of $\text{CO}_2(\text{aqueous}) + \text{H}_2\text{CO}_3$ is typically represented as H_2CO_3^* . CO_2 solubility is determined by Henry's Law,

$$\text{CO}_2(\text{aqueous}) = K_H \cdot P_{\text{CO}_2} \quad (3.10)$$

where K_H is Henry's Law constant for CO_2 and P_{CO_2} is the partial pressure of CO_2 in the gas phase (atmosphere). K_H is dependent on temperature and equals $10^{-1.42}$ moles/atm-1 at 25°C (CRC 1976). P_{CO_2} is typically $10^{-3.5}$ atmospheres in ambient air. $[\text{CO}_2(\text{aqueous})]$ thus should be $10^{-4.9}$ M. Upon dissolution only a small fraction ($\approx 3\%$) of the $\text{CO}_2(\text{aqueous})$ becomes aquated, however, the K_o for reaction (3.9) being only $10^{-2.8}$ at 25°C .

H_2CO_3^* next dissociates into bicarbonate, which may in turn further dissociate to yield carbonate ion



the K values given being for infinite dilution ($I=0$) and 25°C (Harned and Scholes 1941). $K_{a1} \approx K_{\text{H}_2\text{CO}_3}/K_o$ from Equation 3.9, where $K_{\text{H}_2\text{CO}_3}$ represents the dissociation constant of true H_2CO_3 .

By combining Equations 3.8 to 3.12 with the mass balance condition for total inorganic carbon, C_T and neglecting H_2CO_3 ,

$$C_T = (\text{H}_2\text{CO}_3^*) + (\text{HCO}_3^-) + (\text{CO}_3^{--}) \quad (3.13)$$

It can be shown that

$$(\text{CO}_3^{--}) = \alpha_2 C_T \quad (3.14)$$

where

$$\alpha_2 = \frac{K_{a1}K_{a2}}{K_{a1}K_{a2} + K_{a1}(\text{H}^+) + (\text{H}^+)^2} \quad (3.15)$$

Activities of the remaining fractions, $(\text{H}_2\text{CO}_3^*)$ and (HCO_3^-) , can be calculated similarly (Stumm and Morgan 1981) to yield a concentration/pH diagram similar to Figure 3.2. It can be seen that the carbonate activity becomes equal to the bicarbonate activity where the activity lines intersect at $\text{pH} \approx 10.33$, the $\text{p}K_{a2}$ of carbonic acid. This explains why carbonates precipitate only with basic pH.

From the discussion above, we thus may compute the IAP for calcite as

$$\text{IAP} = \frac{(\gamma_{\text{Ca}^{++}})([\text{Ca}^{++}]) \{K_{a1}K_{a2}P_{\text{CO}_2}K_H\}}{(\text{H}^+)^2} \quad (3.16)$$

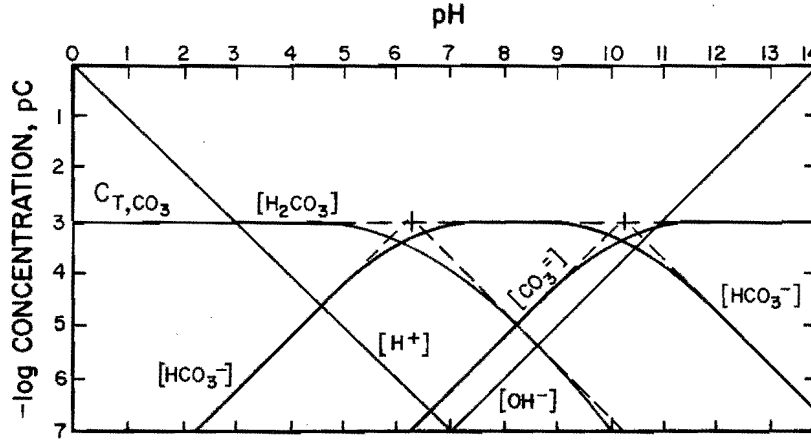


Figure 3.2. pC-pH diagram for a 10^{-3} m carbonic acid system.

When the alkalinity is predominantly ($> 95\%$) HCO_3^- , i.e., $\text{pH} = 7.3-9.3$, and the system is in equilibrium with atmospheric CO_2 ($\text{PCO}_2 = 10^{-3.5}$) at 25°C , Equation 3.16 can be simplified to

$$\text{IAP} = (\gamma_{\text{Ca}^{++}})[\text{Ca}^{++}] (\gamma_{\text{CO}_3^{=}}) \frac{K_{a2} \text{ALK}}{(\text{H}^+)} \quad (3.17)$$

These equations indicate that the precipitation of calcium carbonate will be enhanced by the increasing pH that results from the loss of CO_2 (H_2CO_3^*) from the system. This may result from CO_2 escaping from supersaturated groundwater or from hypolimnetic water that has been subjected to decay processes and subsequently exposed to the atmosphere. Carbonate encrustations of dead moss and rocks surrounding spring outlets illustrate this process. Also CO_2 can be removed by photosynthesis, as will be discussed in a subsequent section. First, however, we shall consider the third process, ion pairing, which competes for calcium and carbonate ions.

Ion pairing and complexation. In addition to insoluble precipitates, calcium may form ion pairs with inorganic ligands such as $\text{CO}_3^{=}$ and $\text{SO}_4^{=}$, or with organic ligands such as the polyphenolic acids responsible for the brown or yellow color of waters draining from decaying vegetation. Similarly, carbonate may be complexed by calcium, or by other metals (e.g. Hassett and Jurinak 1971). Such reactions are characterized by stability constants which describe such reactions as



There are models presently available that calculate the fraction of various species

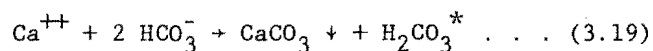
held in complexes and ion pairs (e.g., Truesdell and Jones 1974, Ingle et al. 1978, 1980, and summaries in Pagenkopf 1978). Applications of these models generally require extensive water quality analyses, however, and less comprehensive models are frequently used which deal only with key species, i.e., those which complex a significant fraction of the species of interest. Complexation is often ignored in natural aquatic systems because other factors may be expected to cause at least as much, if not more, uncertainty (e.g. Kramer 1967). However, Otsuki and Wetzel (1973) demonstrated that fulvic acids may complex significant amounts of calcium in waters containing substantial organic color. Such compounds also have been shown to interfere with the kinetics of calcite precipitation, as discussed below.

Effects of temperature on carbonate equilibria. In one of the earlier studies of the effects of temperature on freshwater carbonate equilibria, Kindle (1929) recognized the importance of PCO_2 on the deposition of lacustrine marls. Kramer (1967) developed a model which took into account the effects of temperature and ionic strength on carbonate equilibria in Great Lakes water, but failed to include ion pairing (which is probably not highly significant in the < 2 mM water of these lakes). Kramer concluded that colder water, typical of the mass of water below the thermocline, was undersaturated with respect to calcite or dolomite. Water warmer than $13-14^\circ\text{C}$ was supersaturated with respect to both phases, but aragonite saturation resulted only above 20°C . Kramer reasoned that because of the long residence times characteristic of Great Lakes waters, that the undersaturation in the hypolimnion was the result of supersaturation with CO_2 , the equilibrium concentration of which exceeded that in the atmosphere by a factor

of 3 at 5°C. The supersaturation was assumed to result from slow mixing.

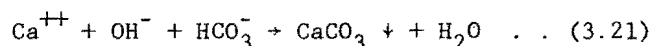
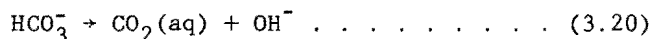
Plummer (1975) summarized the effects of temperature on the various equilibrium constants as shown, along with additional pertinent equilibrium constants, in Table 3.1. Temperature can be seen to decrease CO₂ solubility, shift the carbonate equilibria toward CO₃⁼, and decrease the K_{sp}, thus decreasing calcite solubility by several mechanisms.

Effects of biological activities on nonbiogenic calcite precipitation. It has been known for some time that the removal of CO₂(aqueous) or HCO₃⁻ by photosynthesis in the euphotic zone of lakes results in calcium carbonate precipitation. The reaction can be described



Thus the removal of one mmol of CO₂ (H₂CO₃^{*}) would result in the precipitation of one mmol of Ca⁺⁺ and a subsequent reduction in 2 meq of alkalinity, provided the IAP/K_{sp} ratio equaled or exceeded 1.0 prior to uptake of CO₂ by autotrophs. Chemoautotrophs such as nitrifiers and *Thiobacillus* may assume local importance, as may anaerobic uptake by heterotrophic microorganisms in aerobic, aphotic environments (e.g. Sorokin 1969). However, carbon fixation rates by these processes are generally much lower than those resulting from photosynthesis by algae and macrophytes.

It should be noted that uptake of HCO₃⁻ rather than CO₂ would result in



which, when added, result in Equation 3.19. The first phenomenon, represented in Equation 3.20 was demonstrated by Steeman Nielsen and Kristiansen (1949) and is catalyzed by the enzyme carbonic anhydrase. The carbon species fixed is thus unimportant in its effect on carbonate production. Of course plants fixing HCO₃⁻ in alkaline waters are more likely to produce sufficient CO₃⁼ to exceed the K_{sp} for calcite than would be obligate CO₂ fixers, such as the aquatic moss *Fontinalis*, which is limited to slightly acidic waters (Hutchinson 1975).

Most reservoirs in the west have rather steep sides, and consequently harbor only a meager littoral zone. Thus most of the photosynthetic production occurs in the phytoplankton community. However, if shallow, upstream reaches of reservoirs have extensive growths of macrophytes or benthic algal mats, these communities are particularly capable of precipitating large amounts of calcite, as has been demonstrated by Otsuki and Wetzel (1974) and others. The benthic

macroalga *Chara* is particularly effective in this regard.

Kinetics. Calcite crystal growth occurs by a surface controlled mechanism such as spiral dislocation (Nancollas and Reddy 1971, Wiecherst et al. 1975, Reynolds 1978). Reddy (1975) has demonstrated that crystal growth can be described by the second order equation

$$\frac{dN}{dt} = -k_s N^2 \dots (3.22)$$

where

N = total molar concentration of all dissolved calcium species minus the equilibrium Ca⁺⁺ concentration, i.e., the excess calcium available for precipitation

k = crystal growth rate constant

s = seed crystal concentration (= available crystal surface area)

The value of k was found to be approximately 2.17 (+10 percent) l²/mol-min-mg seed in an inorganic solution, but with increasing additions of glycerophosphate, k decreased to as low as 0.081 l²/mol-min-mg seed for a 0.3 mM/l concentration of glycerophosphate. Additional experiments indicated that the inhibition of crystal formation was caused by interference with the growth process, rather than by ion pairing with calcium or formation of a metastable solid phase at the crystal surface.

Such experiments led Reynolds (1978) to investigate the possibility that interference with crystal growth by polyphenolic organics was responsible for calcite supersaturation observed in Lake Powell. Experiments similar to those performed by Reddy in artificial lake water which contained no polyphenolic organics yielded the rate expression

$$\frac{dc}{dt} = k_s \left[(\text{Ca}^{++})(\text{CO}_3^{=}) - \frac{K_{sp}}{(\gamma_{\text{Ca}^{++}})(\gamma_{\text{CO}_3^{=}})} \right] \dots (3.23)$$

which gave a linear plot with a zero intercept, thus confirming Equation 3.22. Additional experiments with natural Lake Powell water containing polyphenolic organics, however, fit the expression

$$\frac{dc}{dt} = k_s C^n \dots (3.24)$$

where C = (CO₃⁼), and n≠4. Reynolds interpreted these experiments as pointing to crystal growth by the relatively efficient spiral dislocation nucleation process in the absence of inhibiting species. In the presence of inhibiting species, however, growth occurred by the much slower surface nucleation and spreading process with carbonate, rather than calcium (cf. Reddy 1975), being the rate controlling species.

Table 3.1. Standard enthalpies of reaction, equilibrium constants, and analytical expressions for temperature corrections relating to freshwater carbonate chemistry (Plummer 1975 after various sources).

Reaction	ΔH_r^0	Log K ₍₂₅₎
$\text{CaOH}^+ = \text{Ca}^{++} + \text{OH}^-$	-1.19	-1.40
$\text{CaSO}_4^0 = \text{Ca}^{++} + \text{SO}_4^{--}$	-1.65	-2.309
$\text{CaCO}_3^0 = \text{Ca}^{++} + \text{CO}_3^{--}$	-3.13	-3.20
$\text{MgOH}^+ = \text{Mg}^{++} + \text{OH}^-$	-2.14	-2.60
$\text{MgSO}_4^0 = \text{Mg}^{++} + \text{SO}_4^{--}$	-4.92	-2.238
$\text{MgHCO}_3^+ = \text{Mg}^{++} + \text{HCO}_3^-$	-10.37	-0.928
$\text{MgCO}_3^0 = \text{Mg}^{++} + \text{CO}_3^{--}$	-0.058	-3.398
$\text{NaSO}_4^- = \text{Na}^+ + \text{SO}_4^{--}$	-2.229	-0.226
$\text{Na}_2\text{SO}_4^0 = 2\text{Na}^+ + \text{SO}_4^{--}$	2.642	-1.512
$\text{NaHCO}_3^0 = \text{Na}^+ + \text{HCO}_3^-$..	0.250
$\text{NaCO}_3^- = \text{Na}^+ + \text{CO}_3^{--}$	-8.911	-1.268
$\text{Na}_2\text{CO}_3^0 = 2\text{Na}^+ + \text{CO}_3^{--}$..	-0.672
$\text{NaCl}^0 = \text{Na}^+ + \text{Cl}^-$..	1.602
$\text{KCl}^0 = \text{K}^+ + \text{Cl}^-$..	1.585
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	13.345	-13.998
$\text{CaMg}(\text{CO}_3)_2(\text{dolomite}) = \text{Ca}^{++} + \text{Mg}^{++} + 2\text{CO}_3^{--}$	-8.29	-17.00
$\text{CaCO}_3(\text{calcite}) = \text{Ca}^{++} + \text{CO}_3^{--}$	Analytical expression	
	Log K(T) = 13.870 - 0.04035T - 3059T	
$\text{H}_2\text{CO}_3^0 = \text{H}^+ + \text{HCO}_3^-$	Log K(T) = 14.8435 - 0.032786T - 3404.71/T	
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{--}$	Log K(T) = 6.498 - 0.02379T - 2902.39/T	
$\text{KSO}_4^- = \text{K}^+ + \text{SO}_4^{--}$	Log K(T) = 3.106 + 637.6/T	
$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{--}$	Log K(T) = 5.3505 - 0.0183412T - 557.2461/T	
$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^0$	Log $\alpha_{\text{H}_2\text{CO}_3^0} = \log P_{\text{CO}_2} - 14.0184 + 0.015246T$ + 2385.73/T - I(0.84344 - 0.004471T + 0.000006667T ²)	

As Reynolds added tannic acid or cold water extracts from Tamarix, or cottonwood or oak leaves to the water, K decreased. A regression of log K on log TTE (total tannic acid equivalents) showed a correlation coefficient of -0.94. Ultraviolet radiation restored the original K value, and other organics (pyrogallol and citric, acetic, tartaric, and glycolic acids) failed to inhibit crystal growth. Reynolds hypothesized that the polyphenolic substances which

enter the reservoir during spring runoff adsorb onto the crystals, thus inhibiting spiral dislocation growth and forcing the crystals to grow by the slower mechanism of surface nucleation and spreading. The implication for Lake Powell was that, although the water is supersaturated during much of the year, calcite precipitation occurs predominantly in the downstream surface waters of the reservoir during the summer months.

Precipitation of carbonates other than calcite. Carbonate precipitates that could conceivably form in natural waters are shown in Table 3.2, along with representative values for their respective K_{sp} 's at infinite dilution. Although most of the transition metal carbonates could exert control over the concentration of the metal in alkaline waters, the amount of the available metal is insufficient to account for substantial removal of dissolved carbonate in typical reservoir waters. The most prevalent of these, Fe^{++} , is only present in un-oxygenated water, and there it is competed for effectively by $S^{=}$ which forms the highly insoluble mineral, pyrite ($K_{sp} = 10^{-18.1}$ as opposed to $10^{-10.7}$ for siderite). Even then, the Fe^{++}/Ca^{++} ratio must exceed 0.05 for siderite, rather than calcite, to be the stable solid phase. Precipitation of other alkaline earth carbonates (e.g., Ba^{++} , and Sr^{++}) are similarly restricted by low ambient concentrations of the metals.

Many of the magnesium-rich carbonates, e.g. huntite, magnesite, hydromagnesite, and nesquehonite, are found only in saline lakes dominated by evaporative regimes, and then only as diagenetic products (Kelts and Hsü 1978). Dolomite also is formed only over geologic time periods, owing probably to the very low entropy of the crystal structure (Garrels et al. 1960). The remaining primary

precipitates are apparently controlled largely by the Mg^{++}/Ca^{++} ratio.

Müller et al. (1972) found that generally waters with a Mg^{++}/Ca^{++} ratio less than 2 were dominated by calcite precipitation. Waters whose ratio exceeded 12 were almost invariably dominated by aragonite precipitation, while intermediate ratios led to the precipitation of magnesium calcites and aragonite. This phenomenon has alternatively been explained to result from poisoning by Mg^{++} of the calcite lattice structure (Folk 1974) or from increased solubility of the Mg^{++} salt through incongruous solution (Berner 1975). Maximum solubility occurs at 6.0-8.5 mole percent Mg^{++} , which separates the high from low-magnesian calcites in Table 3.2. Monohydrocalcite precipitation has been demonstrated only in Lake Kivo in Africa (Stoffers and Fischbeck 1974) under a Mg^{++}/Ca^{++} ratio of 4-30. Thus, if the Mg^{++}/Ca^{++} ratio remains below 2 in reservoirs, it should be possible to focus on calcite as the primary solid carbonate phase responsible for precipitation from the water column.

Case studies. Many case studies (as opposed to equilibrium models involving dissolved species) are found in the limnological and oceanographic literature, and several deserve special mention because of their particular insights or controver-

Table 3.2. Solubility of potentially important lacustrine carbonates (after Kelts and Hsü 1978, data from Garrels and Christ 1965, Truesdell and Jones 1974, Krauskopf 1978).

Species		pK_{SP}
Primary precipitates		
$CaCO_3$	Calcite	8.35
$Mg_x Ca_{(1-x)} CO_3$		
$x = 0.005-0.07$	Low Mg-calcite	*
$x = 0.07-0.3$	High Mg-calcite	*
$CaCO_3 \cdot H_2O$	Monohydrocalcite	
$CaCO_3$	Aragonite	8.22
Diagenetic in sediments		
$Ca_{0.45-0.55} Mg_{0.55-0.45} (CO_3)_2$	Dolomite	17-19
$CaMg_3(CO_4)_3$	Huntite	30
$MgCO_3$	Magnesite	7.5
$Mg_5(OH(CO_3)_2)_2 \cdot 4H_2O$	Hydromagnesite	36.8
$BaCO_3$	Witherite	8.3
Uncertain origin		
$FeCO_3$	Siderite	10.7
$SrCO_3$	Strontianite	9.0
$MnCO_3$	Rhodochrosite	9.3
$ZnCO_3$	Smithsonite	10.0

*Depends on Mg/Ca ratio.

siality. Among these are the works of Megard (1968) on Minnesota lakes and Otsuki and Wetzel (1974) on extremely hard water lakes in Indiana. Both studies found that photosynthesis was empirically coupled strongly to calcite precipitation. Megard found that the 4 moles of CO₂ fixation were accompanied by the precipitation of 1 mole of CaCO₃, which is far less than that predicted by Equation 3.19. The reason for this discrepancy was not clear.

Brunskill (1969) monitored meromictic Fayetteville Green Lake in upstate New York over a 14-month period for evidence of calcite precipitation and its causes. The IAP/K_{sp} ratio was calculated using an algorithm that took into account concentration, diverse ion effects, ion pairing, temperature, and HS⁻ contributions to alkalinity. Also, suspended calcite crystal inventories were conducted periodically by filtration, and sedimentation rates were monitored using sediment traps suspended in the monolimnion.

Brunskill concluded that, although the mixolimnion of the lake was supersaturated with respect to calcite throughout the year, a three- to fourfold increase in supersaturation (to values ranging from 6.6 to 9.4) occurred from May to late August. This was attributed to the effects of temperature on the dissociation constants of carbonic acid and the equilibrium activity product of calcite. Calcite precipitation (2g/m²-day) began in late May, and was followed one month later by a decline of 2 moles CO₂/m² which persisted into October. The crystals settled at a rate of 2-4 m/day during the spring, a rate consistent with Stokes' law. Calcite precipitation and sedimentation were greatly reduced during the remainder of the year. Both chemical data and sedimentation traps indicated an annual sedimentation rate of 230-240 g CaCO₃/m²-yr.

Kelts and Hsü (1978) summarized their experiments on carbonate sedimentation in Zurichsee in Switzerland. Calcite precipitation occurred in two peaks during early summer and early fall, both of which followed peaks of algal biomass. Precipitation also roughly corresponded with the IAP/K_{sp} ratio and the highest epilimnetic temperatures, but the correspondence was, at best, general. Calcite crystals tended to be large (5-15 μm) during the spring peak and smaller (1-4 μm) during the autumn peak, perhaps owing to different crystal growth processes. Calculations based on observed alkalinity changes and crystal dissolution rates suggested net deposition of 4 mm sediment annually, compared to an observed value of 1-3 mm/yr.

Summary of carbonate precipitation processes. Factors capable of affecting the chemical precipitation of carbonates in reservoirs, together with some of the processes affecting them, are summarized in Table 3.3. The influence of some of these factors can be studied using equilibrium

chemical approaches, and others require *in situ* monitoring or laboratory experiments. Rather than speculating further here, we shall discuss the likely importance of these factors in the context of the research on Oneida Reservoir in subsequent chapters.

Precipitation of Noncarbonate Species

Unlike the carbonates, there appears to be little evidence for the congruent precipitation of other solid phases in freshwater environments (Jones and Bowser 1978). Typically, the cycle of weathering reactions for clay minerals in freshwater systems involves the weathering of feldspars to kaolinite (see e.g. Stumm and Morgan 1981), which releases alkali or alkaline earth metals and perhaps some silica. Authigenic formation of Na- or Ca-montmorillonite also reduces dissolved metal and silica concentrations and may occur in some lacustrine sediments, but such a process involves incongruent precipitation and so will be discussed in a subsequent section.

The failure of aluminosilicates to precipitate in congruent reactions has been attributed by Hem and Lind (1974) to the high energy requirements for deprotonation of AlOH and SiOH to form Al-O-Si bonds. Kittrick (1970) found precipitation of kaolinite from aqueous suspension of aluminosilicates to require 3 to 4 years in the laboratory, a period clearly too long to be of interest in a periodically mixed reservoir with a detention time of 1-2 years. Precipitation of metal sulfides, oxides, and oxy-

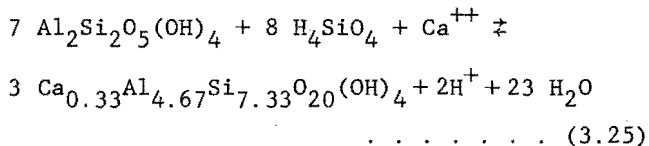
Table 3.3. Factors which may affect carbonate precipitation in western reservoirs (greatly modified from Kelts and Hsü 1978).

<u>Equilibrium factors</u>	
Saturation Index (IAP/K _{sp})	
Evaporation	
Temperature	
Alkalinity	
Loss of CO ₂ from supersaturated water	
pH (especially photosynthesis)	
Ionic strength	
Groundwater mixing	
Evaporation	
Mg/Ca Ratio	
<u>Kinetic factors</u>	
Availability of seed crystals	
Rate of seeding	
Rate of nucleation	
Rate of supersaturation	
Inhibitors (phosphates, organic films)	

hydroxides, and of calcium phosphates and fluorides, may be important in exerting control on the solubility of their constituent ions (see Jones and Bowser 1978). However, it is unlikely that in most relatively fresh surface waters, stoichiometrically limiting ions are present in sufficient concentration to affect total salinity greatly. The precipitation of biogenically reduced iron originating from sedimented iron oxides in the form of nontronite (e.g. Müller and Foerstner 1973) or vivianite (Emerson and Widmer 1978) may be important in limiting the diffusion of ferrous ion into the overlying water, but cannot be responsible for reducing salinity unless the iron oxides and oxyhydroxides originally entered the lake in colloidal ("dissolved") form.

Coprecipitation (Incongruent Precipitation)

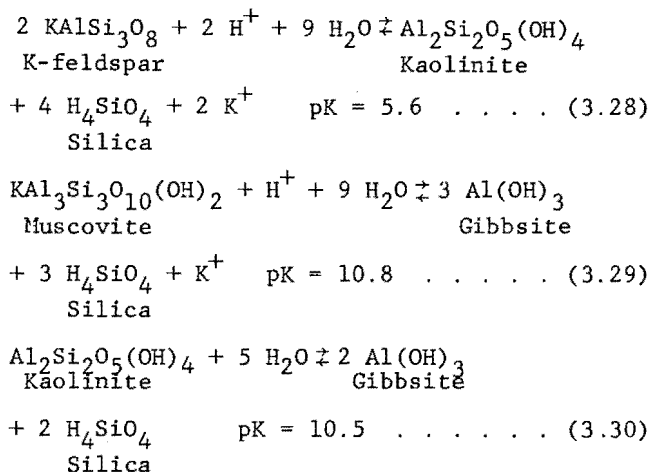
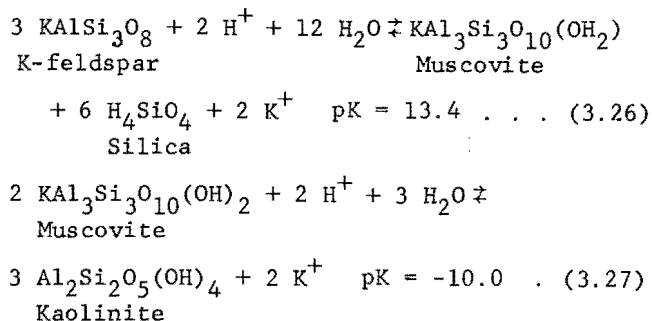
Coprecipitation (incongruent precipitation) processes are those involving more than one solid phase. A classical situation is exemplified by the authigenic conversion of kaolinite to Ca-montmorillonite (Stumm and Morgan 1981, p. 530)



Such a reaction would essentially reduce the dissolved solids by 99.7 percent, providing the solid phases were truly nonfilterable. In addition to such chemically "well-defined" processes, we shall also include ion-exchange on surfaces of suspended particles (Table 3.1), as well as precipitation of metal oxides and oxyhydroxides, phosphates, and organic coatings on the surfaces of suspended particulates (Jenne 1977), as examples of incongruent processes.

Authigenesis (Diagenesis) of Clay Minerals

The most convenient method of displaying information about clay mineral equilibria is the stability of predominance diagram pioneered by Sillén. Krauskopf (1978, p. 157-158) offers the following example involving K-feldspar, muscovite, kaolinite, and gibbsite. The reactions, together with the negative logarithms of their equilibrium constants, are:



The equilibrium expressions can be written with two unknowns; $\log [K^+]/[H^+]$ and $\log [H_4SiO_4]$:

$$2 \log \frac{[K^+]}{[H^+]} + 6 \log [H_4SiO_4] = -13.4 \quad (3.26')$$

$$2 \log \frac{[K^+]}{[H^+]} = 10.0 \quad (3.27')$$

$$2 \log \frac{[K^+]}{[H^+]} + 4 \log [H_4SiO_4] = -5.6 \quad (3.28')$$

$$\log \frac{[K^+]}{[H^+]} + 3 \log [H_4SiO_4] = -10.8 \quad (3.29')$$

$$2 \log [H_4SiO_4] = -10.5 \quad (3.30')$$

Equations 3.26' through 3.30' can consequently be represented as straight lines on a graph (Figure 3.3) with these axes. As can be seen from the diagram, kaolinite is the stable phase for intermediate ($10^{-5.3}$ to $10^{-2.7}$ m/l) silica concentrations, except under conditions of high K^+ concentrations or very high pH, where muscovite (a K-mica) becomes predominant.

Kramer (1967) plotted chemical analyses of Great Lakes water on stability diagrams for sodium and potassium species. He found summer lake water and sediment pore water to be in equilibrium with kaolinite, although winter lake water was in apparent equilibrium with gibbsite. Only seawater was sufficiently rich in K^+ and Na^+ to near the stability fields for k-feldspar and montmorillonite (or albite), respectively. This finding generally underscores the idea that diagenesis of kaolinite to the smectites (e.g. montmorillonite) is generally limited to marine sedimentary environments.

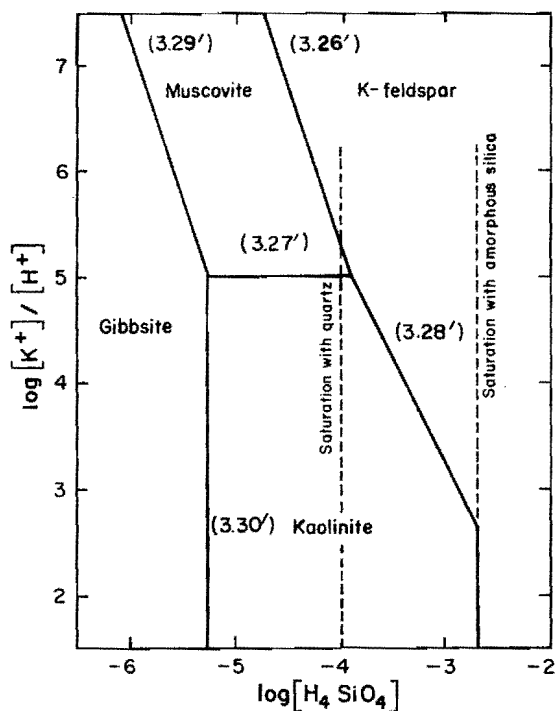


Figure 3.3. Stability relations of K-feldspar, muscovite, kaolinite, and gibbsite at 25°C and 1 atm, as functions of $\log [K^+]/[H^+]$ and $\log [H_4SiO_4]$. Numbers in parentheses refer to Equations 3.26' to 3.30'.

Notes of caution regarding conclusions based on equilibrium models are given by Sutherland (1970) and Zen (1972), among others. Uncertainty in thermochemical data upon which equilibrium constants must be based, variable composition and crystallinity of solid phases, and metastability resulting from slow kinetics may confuse interpretations. Furthermore, Jones and Bowser (1978) point out that many of the diagenetic reactions are highly influenced by H_4SiO_4 concentrations, which may be temporally highly variable in the euphotic zone due to uptake by diatoms. The latter authors deduce from a thorough review of the literature on fresh water lacustrine sediments, however, that no evidence exists to dispute the view that sediment composition is controlled entirely by the distributive signature of lake currents superimposed on allochthonous inputs of minerals from the watershed.

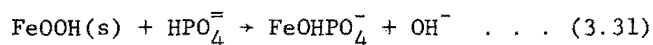
Reactions at the Solid-Solution Interface

Natural waters contain many particulates with specific surface areas of several hundred m^2/g and surface energies on the order of 10^9 erg/g (Stumm and Morgan 1981). These particulates provide active sites for many reactions in aquatic systems. The

simplest of these involve the adsorption of nonpolar solutes or poorly hydrated ions or complexes onto surfaces because of their low affinity for the aqueous phase. More complicated reactions occur as a result of chemical interactions, covalent bonding, ion-exchange, hydrogen bonding, or London or van der Waals forces. Although much is known about the nature of these interactions in well-defined laboratory systems, the work in natural waters remains mostly empirical, owing largely to the ill-defined composition of the particulate milieu.

It is beyond the scope of this research to construct state-of-the-art models to describe coagulation reactions in western reservoirs. The purpose of the experiments to be described subsequently is to demonstrate the possible importance of such reactions, with a basic description of the most important processes and the factors that control them, for subsequent application in interpreting the experimental results. Further background can be found in Stumm and Morgan (1981, p. 599-684), Kavanaugh and Leckie (1980), and the references found therein. The following discussion is based primarily on these sources.

Particulate surfaces in most natural waters are negatively charged because of one of three basic processes; chemical reactions, isomorphous replacement, and ion adsorption. Chemical reactions such as the deprotonation of metal hydroxides, silanol, or organic functional (e.g. carboxyl) groups leads to negatively charged surface sites which vary as a function of pH. Surfaces may become positively charged at low pH because of protonation of amino groups, and become neutrally charged at a pH referred to as the "zero point of charge," or ZPC. Charged surfaces may also result from coordinative binding of solutes to solid surfaces, e.g.



This process is called adsorption or specific adsorption.

Isomorphous replacement results when Si^{4+} is replaced by Al^{3+} , or Al^{3+} by Mg^{2+} , in a clay crystal lattice, resulting in a net negative charge which must be neutralized by a counter ion. Such charges are not influenced by pH, although H^+ ion may compete with other dissolved ions for positions on the exchange site. Clay minerals thus have an ion exchange capacity having a pH dependent component resulting from deprotonated silanol groups at plate edges, and a pH-independent component, much of which is exhibited at interlayer positions in expanding lattice clays.

The affinity for cations exhibited by these charged surfaces is a function of the surface charge, clay structure, and the hydrated radius of the adsorbed cation. In dilute solution, divalent cations are selec-

tively adsorbed over monovalent cations. The exchange can be represented by a selectivity coefficient, Q, e.g. for the replacement of sodium by calcium on an exchange site (Stumm and Morgan 1981, p. 643-644):

$$Q_{(NaR \rightarrow CaR)} = \frac{X_{CaR}}{X_{NaR}^2} \frac{[Na^+]^2}{[Ca^{++}]} \dots \dots \dots (3.32)$$

where X represents the equivalent fraction of the counter-ion on the exchange surface, R. (e.g. $X_{CaR} = 2[CaR^{++}] / 2[CaR^{++}] + [NaR^+]$). Values for Q depend on a host of environmental variables, such as ionic strength and composition of the clay particles. Selectivity for divalent ions decreases with increasing ionic strength, as can be seen in Table 3.4, and the magnitude of the effect is highly dependent on clay type. The combined effects of hydrated radius and charge can be summarized by the Hofmeister or Lyotropic series: $Sr^{++} > Ca^{++} > Mg^{++} > H^+, NH_4^+ > K^+ > Na^+$ (e.g. Shainberg and Kemper 1967), although some zeolites produce the opposite behavior.

The final mechanism for creating a surface charge is ion adsorption due to London-van der Waals forces or hydrogen bonding (as opposed to the chemical bonding described above). Examples include the adsorption of surfactants on clays, and humic or fulvic acids or multinuclear hydroxy-metal compounds on calcite or silica surfaces. The ZPC on such particles is determined by the relative concentrations of potential-determining ions in solution, including pH. Such reactions are undoubtedly important in controlling heavy metal distribution in aquatic systems (e.g. Jenne 1977) and in interfering with crystal growth kinetics as described earlier.

The consequences of such reactions may be to remove TDS by either substituting heavier ions for lighter ions, or by transferring soluble species to newly created exchange sites. In the first case, such a mechanism may involve replacement of one Ca^{++} by two Na^+ ions, if ionic strength in the reservoir is higher than in the tributary water, owing either to evaporation or input from saline springs or seeps.

Replacement of K^+ by Na^+ would also decrease salinity. Finally, weathering of kaolinite to montmorillonite in sediments could increase the available ion exchange capacity if the sediment were subsequently released into the overlying water column during wind mixing or overturn. However, such an event would be more likely to increase the salinity, by stirring more concentrated interstitial water into the overlying water column.

Coagulation

Natural waters hold in dispersion many types of particulates, which have diameters small enough to pass through a standard glass fiber filter (Stumm and Morgan 1981). Glass fiber filters typically pass 50 percent of the particles as large as 0.7-0.9 μm (Sheldon 1972) which thus appear as total dissolved solids (\equiv filterable residue, EPA 1978, APHA 1975) in the analysis. Any mechanism which results in the coagulation of these particles would thus appear to remove salinity, even though there would be no actual reduction in the truly dissolved species. Two processes which could effect such coagulation in reservoirs are physical-chemical coagulation and bioflocculation.

Physical-chemical Processes

Physical-chemical coagulation depends on neutralizing the chemically induced surface charges, which tend to disperse similarly charged colloids, and physical transport processes that bring about interparticle contact (Hahn et al. 1980, O'Melia 1980). The ionic double layer that surrounds charged colloids in aquatic systems is compressed with increasing ionic strength, allowing the similarly charged particles to approach closely enough to flocculate, thus increasing their sedimentation velocity sufficiently to remove much of their mass to the sediment. This process accounts for the well-known sedimentation of river-borne clays in estuaries (e.g. Edzwald et al. 1974) and has also been demonstrated in a sewage outfall plume in a river (Hahn et al. 1980), an environment of much lower ionic strength. Transport mechanisms that allow the coagulation of colloids include Brownian motion, which leads

Table 3.4. Ion exchange of clays with solutions of $CaCl_2$ and KCl of equal equivalent concentration (Wiklander 1964).

Clay	Exchange Capacity, meq g ⁻¹	Ca^{++}/K^+ Ratios on Clay			
		Concentration of Solution $2[Ca^{++}] + [K^+]$, meq liter ⁻¹			
		100	10	1	0.1
Kaolinite	0.023	-	1.8	5.0	11.1
Illite	0.162	1.1	3.4	8.1	12.3
Montmorillonite	0.810	1.5	-	22.1	38.8

to perikinetic coagulation and gravitational settling, and fluid shear, which results in orthokinetic coagulation. The last of these processes may provide the most efficient transport mechanism in well mixed environments. Coagulation is a reversible process, in that redispersion of suspended colloids may occur if ionic strength were to decrease in a reservoir or river reach.

Unfortunately there is very little literature on physical-chemical coagulation of very small (< 2 μm) colloids in natural freshwater systems. Physical modeling has lead O'Melia (1980) to conclude that coagulation is extremely effective at removing submicron particles from lake ecosystems. The principal problem thus far has been the absence of a rapid, low-cost method for determining particle size fractions in the <1 μm range.

Stumm and Morgan (1981, p. 671) present two equations for determining steady state colloid concentrations in completely mixed (one-box) reservoirs resulting either from perikinetic or orthokinetic processes. These are:

$$\text{Perikinetic: } N = \frac{\tau^{-1} \pm \tau^{-2} + \sqrt{4 k_p N_0 \tau^{-1}}}{2 k_p} \dots (3.33)$$

and

$$\text{Orthokinetic: } N = \frac{\tau^{-1} n_0}{\tau^{-1} + k_o} \dots (3.34)$$

in which N = steady state concentration of aggregates

o = concentration of aggregates entering the reservoir

Q = inflow - outflow rate

V = reservoir volume

τ = residence time = V/Q

k_o, k_p = orthokinetic and perikinetic rate constants, respectively.

These rate constants depend on the following factors.

$$k_p = \alpha_p 8 D \pi a \dots (3.35)$$

$$k_o = \alpha_o \cdot \frac{4}{\pi} V_m \frac{du}{dz} \dots (3.36)$$

where

α = collision efficiency factor

D = Brownian diffusion coefficient = Einstein-Stokes coefficient

a = particle radius

V_m = volume fraction occupied by suspended particles

d_u/d_z = velocity gradient

Such calculations lead to a half-time for reduction of 10⁶ particles/ml (in water of 20°C and α = 1) of 6 days by perikinetic coagulation versus 3.7 days for orthokinetic coagulation if a = 1.0 μm and d_u/d_z = 5 sec⁻¹.

Bioflocculation

Bioflocculation results from the tendency of bacteria to aggregate at surfaces in order to take advantage of the increased availability of nutrients drawn to charged sites (Marshall 1971) and perhaps also to exert an ameliorative effect on an otherwise harsh environment. Bacteria and viruses are widely known to armor themselves with clay platelets, which may enhance their survival in aquatic systems (e.g. Bitton and Mitchell 1974), and recent work by Massalski and Leppard (1979a,b) has indicated that a substantial portion of the dissolved organic carbon (DOC) fraction of lakes may be present as colloidal microfibrils associated with bacteria.

The significant aspects regarding the microfibrils were their ubiquity and their apparent role in the ecology of the bacteria. The 2-40 nm fibrils were found at different depths in the water column, at the sediment surface, as a coating on algae and bacteria, as an apparent adhesive between particles, and as a component of froth at the air-water interface in nine different Canadian Lakes. Agglomerations caused by fibrillar adhesion included colloids such as clay particles, viruses, and copepod fecal pellets. Ferrante and Parker (1977) have shown that such fecal pellets are surrounded by a polysaccharidic peritrophic membrane that is broken down by microbial activity within 6-14 days under conditions found in Lake Michigan. Inasmuch as the settling rate was found to average 4.7 m/day, this would allow the pellet to reach a reservoir bottom that was shallower than 25 m, but, in the absence of downwelling turbulence, probably sets a maximum depth at 65 m for the process to be effective as an apparent salinity removal mechanism. The longevity of the pellet in the sedimentary environment was not studied.

Biochemical Assimilation

Biochemical assimilation or bioassimilation is the uptake of dissolved substances by organisms and their incorporation into biomass. In examining bioassimilation as a potential salinity removal mechanism, it is important to look at situations in which the subsequent mineralization and release of the substances does not occur rapidly with respect to the residence time of the reservoir. For example, consider an algal bloom occurring toward the head end of a reservoir and having a lifetime of 24 to 48 hours. If

the algae decomposed entirely within another 48 hours after death, they would not significantly affect the net dissolved solids concentration of a reservoir with an effective detention time in the euphotic zone of 10-12 days. The most likely bioassimilation processes to affect salinity removal would thus be those that incorporate dissolved solids into refractory material that contribute to long term sediment production, or into components of the food chain that emigrate from the reservoir.

Refractory Material

The refractility of various components of biomass depends largely on its composition, although environmental factors undoubtedly play a major role in supplying the energy of activation needed for various decomposition processes. It is somewhat surprising that algal decomposition rates are rather slow, although highly variable. Gunnison and Alexander (1975) found that dead blue green algae showed signs of radical decomposition after several days, but that microscopic evidence of decomposition in many species of green algae did not appear for 1 to 2 weeks. Species of Pediastrum and Staurastrum did not show evidence of damage, even at the termination of the incubation 30 days following the start of the experiment.

Wetzel (1975, p. 592-595) has summarized the work of some previous investigators, who found that decomposition typically results in a rapid release of dissolved organic matter (DOM), probably resulting from cellular autolysis. This is followed by a less rapid (approximately first order) release until the more resistant components of the cell walls remain. At 20°C, organic carbon of dead green algae was reduced to 45 percent in 5 days under aerobic conditions, whereas 60 days were required to reduce the particulate organic carbon to 50 percent of its original value. Dead zooplankton, benthos, and fish showed highly variable rates of decay, with 28% (fish) to 68% (Tubifex) loss of total particulate biomass within 24 hr under aerobic conditions at 20°C. Decomposition was found to be strongly affected by temperature, pH, and major ion ratios and concentrations.

The end result of this relatively slow degradation is the production of some fraction of the lake sediment that is autochthonous in origin. It is important to note, however, that the carbonaceous fraction of this resistant biomass entered the system largely as a gas, or the assimilated bicarbonate soon was replaced by CO₂ from the atmosphere. Thus bioassimilated inorganic carbon is not likely to provide a viable salinity removal mechanism, provided equilibration with the atmosphere is rapid relative to the effective residence time of the reservoir. Such is usually the case in high productive bodies of water (Emerson 1975). Therefore calcitic and aragonaceous structures, the opaline siliceous tests of

diatoms, and vertebrate skeletal structures would seem to be the most likely means of removal of salinity by bioassimilation.

Calcitic structures include the carapaces of ostracods, otoliths (ear bones) of fish, oogonia cysts of Chara spp., pelycepod shells, and (rarely) tests of the green, nonnoplanktonic alga, Phacotus. Aragonitic structures include gastropod shells, and some pelycepods. A few pelycepods may secrete magnesian calcite shells (Kelts and Hsü 1978). Skeletons and scales of aquatic vertebrates are also calcified. Finally, diatom species are protected by a frustule of opaline silica.

The long-term survival of such hard parts depends on the depositional environment. Parker and Edgington (1976) found that solubilization rates of diatom frustules in Lake Michigan sediments, which are under-saturated with respect to silica, approximately equaled the accumulation rate. However, diatom frustules, carapaces of ostracods, and mollusc shells survive long enough in many lacustrine sediments to make them valuable paleolimnological indicators (e.g., Frey 1974). Thus some long-term salinity removal must occur by such processes in suitable reservoirs.

Emergence and Migration

Two other biological mechanisms that do not depend on the refractory nature of hard parts remaining in the sediment include insect emergence and fish migration. Although very little data are available for the former phenomenon in western reservoirs, Menzie (1980) has recently reviewed the literature and found that Chironomidae (midges) account for the majority of production in most typical lake ecosystems, typically 10-20 g dry weight/m²-yr. If one assumes that assimilated carbon is ultimately replenished by the atmosphere, a maximum of about 15 percent of this dry weight could be composed of nitrogen, phosphorus, and inorganic minerals (e.g. Bowen 1980), thus accounting for removal from a reservoir with a mean depth of 10 m, only 0.2 mg dissolved solids/l-yr. Similarly a small lake fishery (10 g/m²-yr) would remove a similar amount. Thus emergence and migration are not likely to significantly decrease dissolved solids in natural reservoir ecosystems.

Summary

The biogeochemical processes that could contribute significantly to natural salinity removal in reservoirs include homogeneous precipitation; incongruous precipitation processes that include clay diagenesis and ion exchange reactions which replace lighter counter ions with heavier ones; coagulation, including biocoagulation; and bioassimilation followed by sedimentation or emigration. Of the precipitation processes, calcite precipitation driven either by photosynthetically induced increases in pH or by increasing

temperature, looks the most promising in western reservoirs. There is evidence of this process occurring in natural lakes, although the stoichiometry does not always correspond to that predicted. Homogeneous precipitation of other carbonates and authigenic precipitation of clay minerals do not appear important in relatively fresh waters.

Of the remaining processes, less is known. Past research indicates that in-

congruous clay mineral diagenesis is restricted to sediment environments, except in unusual or particularly saline waters. Coagulation, either as a result of the input of saline spring water or through the trapping effect of bacterial fibrillar colloids, has not been thoroughly investigated. Bioassimilation may be important in controlling chemicals incorporated into refractory hard parts, but emigration is unlikely to be of sufficient magnitude to represent an important chemical sink in saline waters.

CHAPTER IV

STUDY AREA, METHODS AND MATERIALS

Description of Study Area

Oneida Narrows Reservoir is a hydroelectric reservoir operated by Utah Power and Light Company on the Bear River between the towns of Cleveland and Preston in southeastern Idaho (Figure 4.1). The narrows occur where the reservoir passes through a ridge that separates Gem Valley to the north (including the southern portion of the valley called Gentile Valley) from the lower lying Cache Valley to the south. Both valleys are vertical fault block structures filled with alluvial and glacial deposits overlying the Cenozoic rock which forms the valley floor, thus providing means for extensive groundwater movements in the valley bottoms. The alluvial deposits from ancient Lake Thatcher are overlain by Pleistocene fractured olivine basalt in the valley, which is in turn overlain by approximately 6 feet of loess and, in the areas adjacent to the mountains, alluvium and colluvium of recent origin. Haws and Hughes (1973) provide a thorough description of the Oneida subbasin of the Bear River Drainage, from which the following description derives.

Annual hydrologic inputs to the Oneida subbasin average 555 km^3 from the Bear River mainstem, where a quaternary lava flow blocked the river from its original northwesterly course near Alexander, Idaho; 187 km^3 (44 cm) of precipitation, distributed approximately evenly throughout the year; and approximately 154 km^3 of groundwater inflow from the Blackfoot River drainage to the north. Outflow from the basin occurs through the Oneida Narrows Dam discharge, which averages $656 \text{ km}^3/\text{yr}$, and $18 \text{ km}^3/\text{yr}$ in irrigation exports to the Blackfoot River drainage to the north. The remaining $222 \text{ km}^3/\text{yr}$ return to the atmosphere as evapotranspiration. Thus approximately 61 percent of the hydrologic inputs to the unit are exported through the reservoir. The mean annual temperature in the subbasin is 6.7°C , and the mean elevation is 1800 m. The low topography of the valley bottoms, ample water, and rich soil make the Oneida subbasin one of the richest agricultural areas within the Bear River Valley. Principal crops include alfalfa, pasture, other hay, and small grains, with lesser amounts of sugar beets and potatoes.

The reservoir itself is located in a steep sided canyon (Oneida Narrows) which

separates Gentile Valley to the north from Cache Valley to the south (Figure 4.2). Although the morphometry of the basin is known, virtually no previous chemical or biological data are available for the reservoir. At full storage (spillway level = 1485 m above M.S.L.), the reservoir occupies a volume of 14.2 km^3 and has a surface area of 208 ha (Utah Power and Light Co., personal communication). A depth-volume curve is shown in Figure 4.3. The depth of the reservoir varies over a range of approximately 0.5-1 m both daily and seasonally with operation of the hydroelectric station, and the upstream reach grades imperceptibly into the Bear River below Cottonwood Creek. The surrounding peaks rise to an elevation of 1750-1875 m, thus there is undoubtedly a substantial input of snowmelt to the reservoir during the spring and summer. Also, several hot springs in the immediate vicinity discharge small amounts of hot ($\sim 50^\circ\text{C}$), saline water into the reservoir.

Methods

Field Sampling

Two synoptic sampling surveys and several reservoir surveys were conducted to see if changing concentration patterns could be used to reveal the extent and location of salinity removal processes in the river reach between Soda Point and the tailrace of Oneida Reservoir.

Synoptic studies. Samples were collected on June 26, 1980, in downstream order from the USGS gaging station below Soda Point Reservoir (approximately 8:15 a.m. MDT) to the bridge across the Oneida Narrows, 2 km below the Oneida Narrows Reservoir tailrace (approximately 4:30 p.m. MDT). Samples were collected at the following locations (a sampling map is presented in Chapter V).

- 1) North side of riverbank 40 m below USGS gaging station at Soda Point.
- 2) Middle of dam at irrigation diversion at Grace.
- 3) Middle of bridge above Grace power plant.
- 4) West bank above bridge near cheese factory.

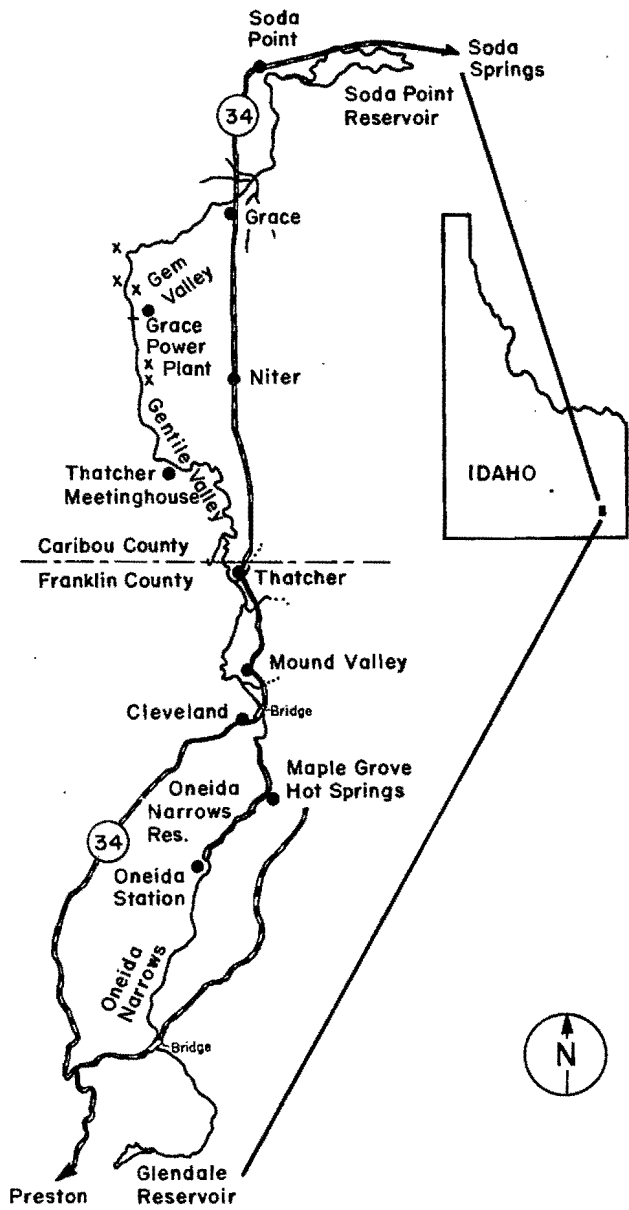


Figure 4.1. Bear River basin between Soda Point Reservoir and Glendale Reservoir, Idaho.

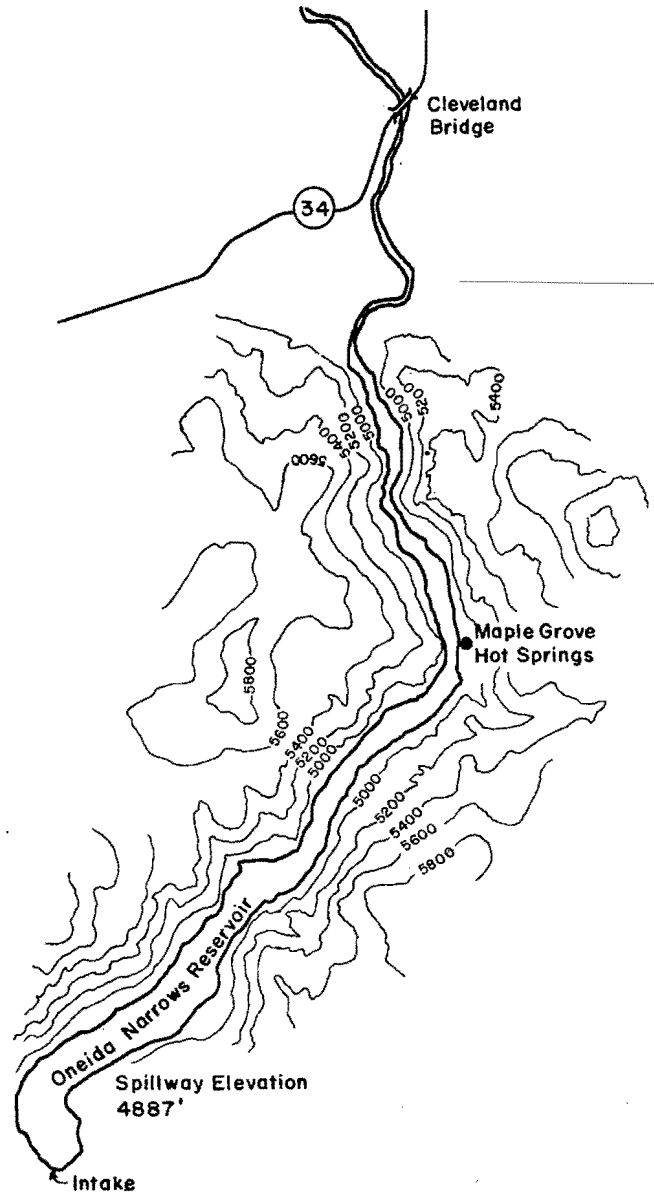


Figure 4.2. Oneida Narrows Reservoir, Idaho. For location see rectangle A in Figure 4.1.

- 5) West bank above bridge near Thatcher meetinghouse.
- 6) West bank above bridge at Thatcher.
- 7) Middle of bridge near Cleveland.
- 8) 50 m north of penstock (surface).
- 9) 50 m north of penstock (6 m depth).
- 10) 100 m east of Oneida Dam spillway.
- 11) 100 m north of bend above Oneida Dam.
- 12) 500 m south of bath house at Maple Grove Hot Springs.
- 13) 200 m north of bath house at Maple Grove Hot Springs.
- 14) Bridge 2 km south of Oneida dam tailrace in Oneida Narrows.
- 15) Maple Hot Springs.
- 16) Bridge at Oneida Narrows (west bank and stream center).

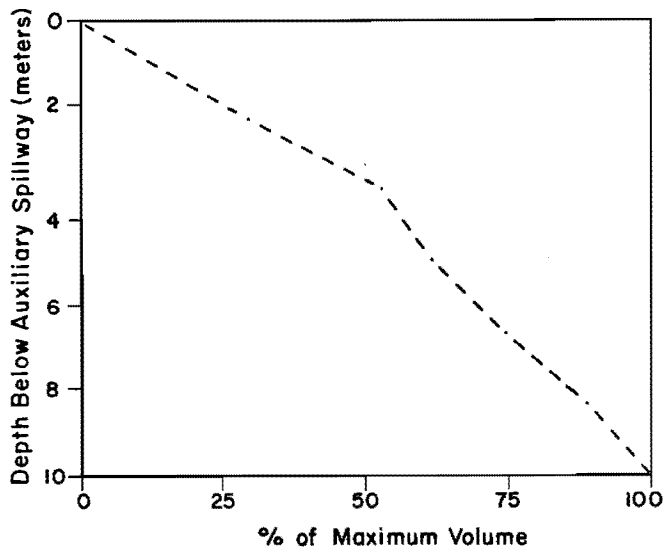


Figure 4.3. Depth volume curve for Oneida Narrows Reservoir.

Samples collected from bankside were taken above bridges to prevent backwater effects around pilings. Samples were collected in acid-washed, polyethylene bottles previously rinsed with the sample. Samples taken from bridges and at depth in the reservoir were collected in either a polystyrene or brass Van Dorn sampler and transferred to polyethylene bottles. Bottles were completely filled, tightly capped to minimize CO₂ exchange with the headspace, and immediately iced. Specific conductance and temperature were measured *in situ* using a YSI Model 33 S-C-T meter previously calibrated in the laboratory. A second synoptic survey on March 10, 1981, sampled specific conductance and temperature only at sites 1 through 7 and below 16, just above the confluence with Mink Creek.

Reservoir sampling. Samples were taken between Cleveland Bridge (7) and the bridge below the Oneida Narrows Reservoir (16) at various sampling locations and depths on April 4, 1980; July 16, 1979; July 15, 1980; August 1, 1980; August 7, 1980; and August 19, 1980. Sampling methods were the same as those described above. Sampling maps are presented in Chapter V.

Sample handling. Samples were returned to the laboratory in an ice chest, and alkalinity, TDS, and turbidity were measured on raw water samples. An aliquot was filtered through 0.45 μ m millipore filters for subsequent analysis for calcium and total hardness, sodium and potassium, silica, and chloride. Raw water determinations and filtration and hardness titrations were done within 18 hours of sample collection. Analytical methodology is described below.

Sediment samples. Sediment samples were collected from approximately 400 m south of Maple Grove Hot Springs and 100 m north of the Oneida Narrows Reservoir tailrace on July 16, 1979, using a "thunderstick," an acetone-filled metal wedge which freezes the sediment to its side, whereupon it can be removed intact (e.g. Stocker 1972). The sediment samples were cleared for examination for diatom frustules using the method described by Patrick and Reimer (1966), in which a sample is digested with hot H₂SO₄, oxidized with potassium dichromate, and washed with distilled water. The cleared sample was then mounted on a glass slide in Hyrax under a cover slip. Sediments to be used in the microcosms were collected from the main pool of the reservoir using an Eckman Dredge.

Soil samples. Soil samples were collected from Gentile Valley in February of 1980 to examine the effects of suspended plastic material on salinity. Samples were collected from open erosion faces that obviously contributed sediment to the Bear River above Oneida Reservoir. Although the samples were not classified formally, they included a clay, a silt, and a sand, as judged from gross physical texture.

Laboratory Studies

The overall goal of the laboratory studies was to provide empirical evidence for the operation of the four mechanisms that could result in salinity removal as outlined in Chapter III. By controlling various environmental factors which influenced these mechanisms, we hoped to be able to isolate individual mechanisms and to study some of the controlling factors. These studies generally attempted to gain initial insights into the possibilities for the various mechanisms, and were not intended to "duplicate" a particular reservoir. There were five basic experiments.

Experiment I. Aphotic coagulation/precipitation. To see whether coagulation or precipitation may be important in the absence of photosynthesis, water was collected from the Bear River at Cleveland Bridge (station 6, Figure 5.1) and from the east bank of the main pool of Oneida Narrows Reservoir (near the penstock) on February 25, 1980. The water was mixed in equal volumes and placed in an acid washed polypropylene carboy on the following day and incubated in the dark in a temperature controlled laboratory. Samples were periodically withdrawn for analysis. One aliquot was not filtered and analyzed for temperature, pH, specific conductance (EC), and dissolved oxygen (DO). The second aliquot was filtered through a Whatman GFC glass fiber filter and analyzed for pH, EC, total dissolved solids (TDS), suspended solids (SS; method 208D, APHA 1975), and silica. The final aliquot was filtered through a Nucleopore polycarbonate membrane filter (0.2 μ m pore diameter) and analyzed for pH, EC, TDS, and silica. Analytical methods are described below.

Experiment II. Effects of photosynthesis. In order to investigate the effects of photosynthesis on salinity removal we attempted to examine water chemistry changes resulting from no photosynthesis (dark) and enhanced photosynthesis (nutrient amended) in 3 phase microcosms relative to a light, untreated control. Water and sediment were collected from Oneida Narrows Reservoir on April 4, 1980. Water samples were collected from the surface, and sediment samples were collected from the littoral zone near the penstock. Nine microcosms (Figure 4.4) were filled with the sampled water and sediments on April 8. Sediment was homoge-

nized and evenly distributed among the microcosms up to the top of the blacklined basal sections, and 5.8 l of water were evenly distributed into the microcosms. The use of such triphasic, semicontinuous microcosms has been thoroughly described by Reynolds et al. (1975), although in this experiment, the microcosms were incubated with an open headspace.

After allowing approximately two weeks for stabilization, the study was begun on May 11. Microcosms 1, 6, and 11 were placed in the dark adjacent to the other microcosms. Microcosms 3, 8, and 9 were spiked with 5

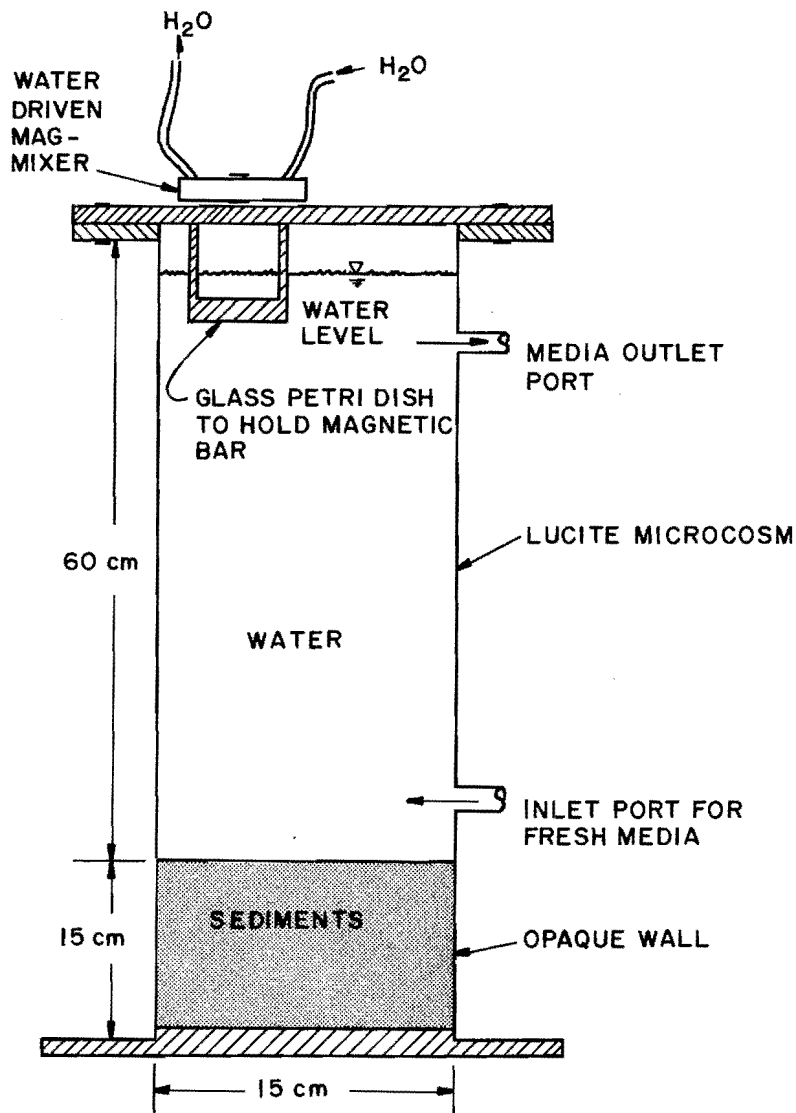


Figure 4.4. Schematic diagram of three phase microcosm.

mg/l $\text{KNO}_3\text{-N}$, which was determined to be the growth limiting nutrient (Table 4.1). Microcosms 3, 7, 8, 9, 10, 11, and 12 were held under conditions of constant light (2000 lux measured at the top of the microcosms). The magnetic stirrers were started, and the microcosms were incubated through May 24. Samples (700 mls from each microcosm) were taken on May 11, 12, 15, 17, 20, 22, and 24. May 11 samples were taken before the microcosms were treated and the stirrers started. The samples were drawn from the lower tap on the microcosms and the microcosms were filled from the top to bring the volume back to 5.8 liters. The reservoir water used to refill the microcosms was held at 6.7°C in the cold room. This "reserve" water was sampled for analysis on alternating sampling dates.

Chlorophyll a was measured by various methods for this study. On May 2 chlorophyll a was measured for the respective microcosms using filtration, extraction with 90 percent acetone for 24 hours, and measurement of the extract on a spectrophotometer. Chlorophyll a was measured on May 11, 12, 15, 17, 20, and 22 by extraction of 10 ml of sample with 90 ml of acetone for 24 hours. The samples were then read on a Turner Model 420 Fluorometer. Because background fluorescence of the water obscured fluorescence of the chlorophyll a, 100 ml samples from May 24 were filtered through GFC filters, the filters were extracted with 90 percent acetone for 24 hours, and the extract was read on the fluorometer as before. Samples were filtered through $0.45\ \mu\text{m}$ millipore filters, and the filters were preserved in methanol for zooplankton counts. Ten ml samples were taken for phytoplankton counts and were preserved with formaldehyde.

At each sample period, the following analyses were done by Standard Methods (APHA 1975): dissolved oxygen, specific conductance, pH, alkalinity, silica, and chloride. A probe and a YSI DO meter were calibrated before each use and were used to measure DO within the microcosms. Samples were titrated to pH 4.6 to determine alkalinity. Total dissolved solids were measured from 100 ml samples and were only done on May 24. Samples were also taken for atomic absorption and emission analysis for Ca^{++} , Mg^{++} , Na^+ , K^+ , and Fe^{+++} . The replacement (reserve) water was held in two carboys. The first carboy was used up with the May 17 refill, and the second carboy was used for the remainder of the study. Chemical analyses indicated no significant differences between the water in the two carboys.

Following this experiment, on June 13, the microcosms were sampled for EC, TDS, pH, alkalinity, and suspended chlorophyll a (EPA 1973). Also, the sides of the microcosms were thoroughly scraped with a rubber policeman, and the dry weight of the attached Aufwuchs community biomass was measured by drying at 105°C and combustion of organic matter at 550°C .

Table 4.1. Results of five-day bioassays of microcosm water spiked with nitrate (10 mg $\text{NO}_3\text{-N/L}$) and phosphate (10 mg $\text{PO}_4\text{-P/L}$); results are means of duplicate analyses.

Treatment	Chlorophyll α ($\mu\text{g/l}$)
Control	110
Nitrate	400
Phosphate	71

Experiment III. Mixing of upstream waters. To see whether mixing of turbid, upstream water with less turbid reservoir water contributed to coagulation or stimulation of photosynthesis the following experiment was conducted. On June 16, 1980, the microcosms from Experiment II (which had been subsequently emptied and the surface cm of sediment removed) were filled with water collected from the east center of the main pool of the reservoir on June 14. All microcosms were incubated under constant fluorescent light (2000 lux) and allowed to equilibrate for 8 days. Beginning on June 24, the microcosms were analyzed every 1-3 days for calcium and total hardness, pH, alkalinity, TDS, sodium, potassium, chloride, sulfate, and silica. Not all of the parameters were measured on each sampling date due to the constraints of the work schedule. Following withdrawal of each 700 ml sampling aliquot from the top port of the microcosm, a 700 μl volume of reserve water from the original sampling date (stored in 4 walk-in cold rooms at 4°C) was added to the bottom port to make up the original volume.

Beginning on July 18, three of the microcosms (1, 9, and 11) began to receive 700 ml aliquots of water from a carboy collected at the Cleveland Bridge on July 14. Microcosms 6, 7, and 8 continued to receive Oneida Narrows Reservoir water from the original June 14 sampling date. The remaining three microcosms were discontinued (the microcosms receiving the various treatments were chosen using a random number table). Samples were periodically drawn from the six microcosms and the two reserve water carboys for analysis as described in the previous paragraph. Although turbidity analyses should reveal changes in plankton biomass, no biological data were gathered.

Experiment IV. Coagulation/mixing with saline spring water. The objectives of this experiment were 1) to investigate the relationship between submicron particle size distribution and water chemistry and 2) to investigate the effects of mixing Maple Grove hot springs water with water from the Oneida Narrows Reservoir. Water samples were collected at various stations and depths (see

location map, Figure 5.7) on August 7, 1980. Samples were returned to the laboratory and an aliquot of Maple Grove hot spring water was subsequently mixed in a 1:7 ratio with water from station 2, upstream from the hot spring influent. Samples were incubated under ambient conditions in the laboratory (~16 hours light, 8 hours dark, ~21°C) in acid washed polypropylene 3.8 l bottles. Samples were withdrawn on July 7 (immediately after mixing), from microcosms 8, 11, 14, filtered through Millipore 0.45 µm membrane filters, and aliquots were analyzed for calcium and magnesium (EDTA titration), sodium and potassium. TOC and Si were measured on July 7, 11, and 14, and July 8, respectively. The filtrates were also analyzed for submicron particle size distribution using a Coulter Electronics Nannosizer (T.M.), but there was an insufficient mass of particles (< 1 mg/l) to produce a reading on the instrument at any sampling date. TDS (single analyses), alkalinity, and pH were runs of aliquots of each sample at every date.

Experiment V. Heterogeneous precipitation. To test the effects of clay inputs to the reservoir on heterogeneous precipitation

(coprecipitation) three soils were collected above Oneida Narrows Reservoir from erosional areas typical of those that could contribute sediment to the Bear River. A sediment sample was also taken from the Bear River above Cleveland Bridge. Subsamples of each of the three soils and the sediment were mixed with a synthetic Bear River water made up to resemble the composition of the water, as determined on February 25, except for spiking with CaCl₂ to give calcium hardnesses of 150, 200, 250, and 300 mg/l as CaCO₃. Two sets of samples, one representing 0.5 g sediment/l and one representing 1.0 g/l under field moisture conditions, together with control flasks filled with artificial river water alone, were incubated with each water type on a shaker table in the dark at 18°C for 36 hours. Following the incubation, aliquots were withdrawn, filtered through Whatman GFC filters, and analyzed for pH, TDS (in triplicate), and calcium ion (atomic absorption spectrophotometry: AA).

Analytical methods

Methods used in analyzing field and laboratory samples are summarized in Table 4.2.

Table 4.2. Methods for water analyses.

Analytical Parameters	Detection level	Method
TDS mg/l	1 mg/l	Gravimetric; SM p. 92
TSS mg/l	1 mg/l	Gravimetric; SM p. 94
Turbidity	0.05 NTU	Nephelometric; SM p. 132
Specific Conductance	1 µmho/cm @ 25°C	Conductivity; SM p. 71
pH	0.1 pH units	pH Electrode; SM p. 460
Total Hardness	1 mg/l; as CaCO ₃	EDTA Titrimetric; SM p. 202
Calcium (Ca) Dissolved mg/l	1 mg/l	EDTA Titrimetric; SM p. 189
Magnesium (mg) Dissolved mg/l	0.1 mg/l	Calc. from Tot. Hard
Potassium (K) Dissolved mg/l	0.1 mg/l	Flame Photometric; SM p. 234
Sodium (Na) Dissolved mg/l	1.0 mg/l	Flame Photometric; SM p. 250
Alkalinity	1 mg/l	Titrimetric, SM p. 278
Bicarbonate (HCO ₃) mg/l	1 mg/l	Calc. from Alkalinity
Carbonate (CO ₃) mg/l	1 mg/l	Calc. from Alkalinity
Chloride (Cl) Dissolved mg/l	0.1 mg/l	Ferricyanide (automated); SM p. 613
Sulfate (SO ₄) mg/l	1.0 mg/l	Methylthymol Blue (automated); SM p. 628
Total Organic Carbon mg/l	1 mg/l	Combustion Infrared; SM p. 532
Silica (Si) Dissolved mg/l	0.5 mg/l	Molybdosilicate; SM p. 487

SM - Standard Methods for Examination of Water and Wastewater, 14th Ed., (APHA 1975).

CHAPTER V

SALINITY REMOVAL IN ONEIDA NARROWS RESERVOIR

The field portion of this investigation was conducted at Oneida Narrows Reservoir because there was preliminary evidence that salinity was lower in the reach below the reservoir than above (Hill et al. 1973) and because of its proximity to the laboratory. Experiments were directed toward mass balance and equilibrium modeling of water chemistry above, below, and within the reservoir in order to search for supersaturation of carbonate species, for patterns of element removal, and for in situ evidence of coagulation or biodeposition of elements in the sediments. In addition to reexamining the data gathered by Hill et al. (1973), samples were gathered sporadically between the summers of 1979 and 1980. Sampling and analytical methods have been described in Chapter IV.

Evidence for Ion Removal Based on Changes in Chemical Concentrations

Bear River Study

Initial evidence that salinity removal may have been occurring in Oneida Narrows Reservoir was based on data collected by Hill et al. (1973, Appendix F.) Paired-t statistics (HP 1977) were calculated for constituents of interest for samples taken at the same date (usually 2 hours apart) at Alexander, Idaho, and the Oneida Dam tail-race. The results of this analysis, presented in Table 5.1, indicated that TDS concentrations showed significant ($\alpha=0.05$) decreases downstream, but that sodium and chloride, and to a lesser extent, calcium, exhibited significant increases. Sulfate also increased and alkalinity decreased downstream, but the differences were not significant.

Qualitative examination of the data initially suggests in situ dissolution or allochthonous inputs of sodium, potassium, and calcium balanced by chloride and sulfate ions, together with the subsequent precipitation of calcium carbonate. However, a mass balance of ions (Table 5.1) indicates the increase in sulfate (0.06 meq/l) to be insufficient to account for enough calcium going into solution (perhaps from gypsum) to offset the 0.68 meq/l of alkalinity presumed to be lost by calcite precipitation. This leads one to suspect the data for at least one of the chemical species to be in

error. Indeed, addition of the ions in Table 5.1 indicates a discrepancy of 113 mg/l TDS (546 minus 433) for the upstream station and 174 mg/l TDS (522 minus 348) for the downstream station. Inorganic carbon species lost through volatilization or conversion to oxides during the TDS analysis (APHA 1975) may account for some of the discrepancy.

Proceeding on the assumption that the TDS, rather than the constituent ion values, were in error, ion ratios of each ion to chloride were calculated. If one assumes that chloride ion concentration is not altered by biogeochemical processes, but only by concentration or dilution of the water mass by evaporation or mixing with a new water mass (Liss 1976), a change in such ratios often suggests the operation of biogeochemical processes in aquatic systems. Again paired-t tests were run on upstream versus downstream ratios, using the data of Hill et al. (1973). The results (Table 5.2) failed to indicate a statistically significant change in any single ion relative to chloride, although a reduction in the TDS/chloride ratio was significant at the $\alpha = 0.05$ level. These data thus indicated a need for further study, both within the Oneida Narrows Reservoir itself and also along the stream reach between Alexander and the headwaters of the reservoir, in order to gain a better understanding of temporal and spatial changes in ion concentrations within the study area.

It should be borne in mind that the only way to conclusively demonstrate salinity removal is through a mass balance, as described in Chapter II. Establishing the required hydrologic gaging network was beyond the scope of this project. Thus the objective of the field studies described below was to suggest the potential for salinity removal to occur in the reservoir or the upstream river reach and the most likely spatial and temporal pattern of such removal, if it were indeed occurring.

Bear River Synoptic Study

One problem with the data from the earlier study was that they did not distinguish between processes occurring in the stream reach above Oneida Narrows Reservoir and those occurring within the reservoir itself. Several springs flow into the river

Table 5.1. Comparison of paired samples taken upstream (Alexander) and downstream (Oneida Narrows Reservoir tailrace) several hours apart (data from Hill et al. 1973, Appendix F).

	TDS	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ⁼	ALK
Upstream								
Concentration	433	74	25	26	3.1	29	49	279
mg/l (+ 1 S.D.)	(+119)	(+30)	(+20)	(+9)	(+1.1)	(+10)	(+13)	(+72)
Downstream								
Concentration	348	75	25	31	4.2	36	52	245
mg/l (+ 1 S.D.)	(+114)	(+22)	(+12)	(+9)	(+2.1)	(+14)	(+20)	(+82)
Percent change	-20	+1	0	+19	+35	+24	+6	-12
Change in meq/l	-	+0.05	0	+0.22	+0.03	+0.20	+0.06	-0.68
t-statistic	1.9*	1.8*	0.5	-4.4*	-2.3*	-2.5*	-0.6	1.1
(d.f.)	(14)	(13)	(13)	(12)	(12)	(13)	(12)	(14)

*Significant at $\alpha = 0.05$

Table 5.2. Comparison of ion:chloride ratios of samples taken several hours apart at Alexander, Idaho, and at the Oneida Narrows Reservoir tailrace (data from Hill et al. 1973, Appendix F).

	Ratio						
	Ca ⁺⁺ /Cl ⁻	Mg ⁺⁺ /Cl ⁻	Na ⁺ /Cl ⁻	K ⁺ /Cl ⁻	SO ₄ ⁼ /Cl ⁻	ALK/Cl ⁻	TDS/Cl ⁻
Alexander	2.6	0.76	0.86	0.10	1.7	9.2	15
Oneida Reservoir	2.7	0.84	0.94	0.12	1.7	8.2	11
t-statistic (d.f.)	0.47 (12)	0.62 (12)	-0.46 (10)	-0.87 (11)	0.14 (10)	-1.17 (12)	3.6 (11)*

*Significant at $\alpha = 0.05$

from the lava flow near Alexander (Figure 4) and Rupp and Adams (1981) have recently demonstrated that calcium carbonate precipitation is promoted in stream reaches by periphyton communities growing in northern Utah streams. Thus several locations upstream from Oneida Narrows Reservoir offer the potential for salinity removal to occur. Therefore, a synoptic sampling of the entire river reach between Alexander and the bridge crossing the Bear River in the Oneida Narrows, several kilometers below the reservoir, was undertaken on July 26, 1980. Concentrations of the various constituents are depicted in Figure 5.1. The complete data are tabulated in Appendix A, Table A3. Results of a second confirmatory study measuring temperature and conductivity only are depicted in Figure 5.2.

Comparison of upstream with downstream samples (Soda Point versus a station below the Oneida Dam tailrace) indicates the same general patterns as the previous study. Sodium, chloride, and potassium increase, while TDS and alkalinity show small decreases. On the July 26 date, calcium

decreases slightly downstream. Silica, not measured in the previous study, increases from 4.3 mg/l at Soda Point to 5.7 mg/l at the bridge below the narrows.

Examination of the changes in species concentrations between the Soda Point and Oneida Narrows stations indicates a complex pattern of events. A source of saline water apparently enters the river between the Grace power plant (station 3) and the bridge near the Thatcher meetinghouse (station 4). Station 3 is located above the power plant discharge, and is fed upstream by minimal outlets from the Grace diversion dam (station 2) and groundwater inflows, particularly from a number of springs in lower Black Canyon (Figure 4.1). It is somewhat more saline than the power plant discharge, which is delivered through a relatively new (and presumably watertight) penstock from the Grace diversion dam. Thus most of the salinity increase between stations 3 and 4 must come from groundwater, from creeks entering the river from the west (Densmore, Dry, and Smith), or from springfed creeks to the east. These sources apparently deliver

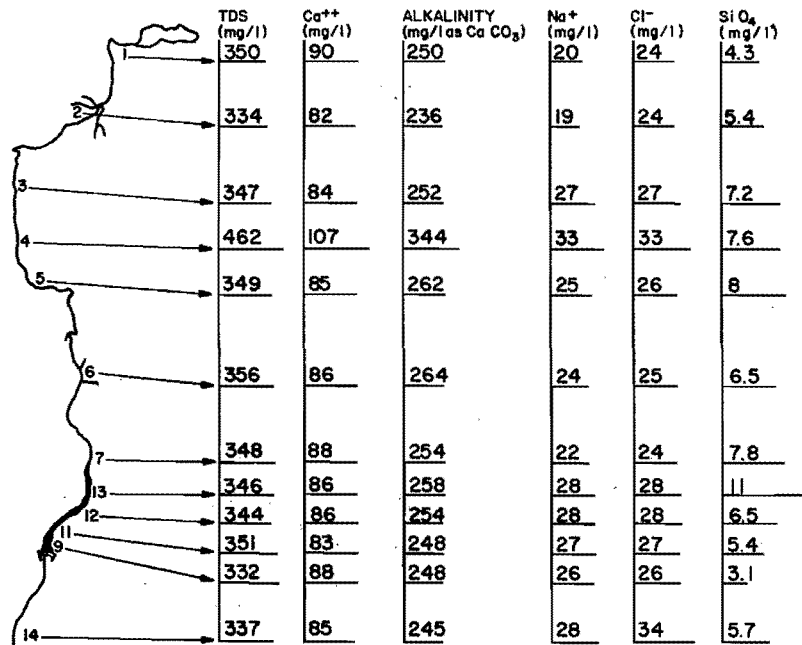


Figure 5.1. Concentrations of various chemical constituents in Bear River on June 26, 1980 (mg/l except for alkalinity which is in mg/l as CaCO₃). Station 8 includes 9a and 9b, station 11 includes 10, and station 14 includes 15 in Table A.3 (Appendix A).

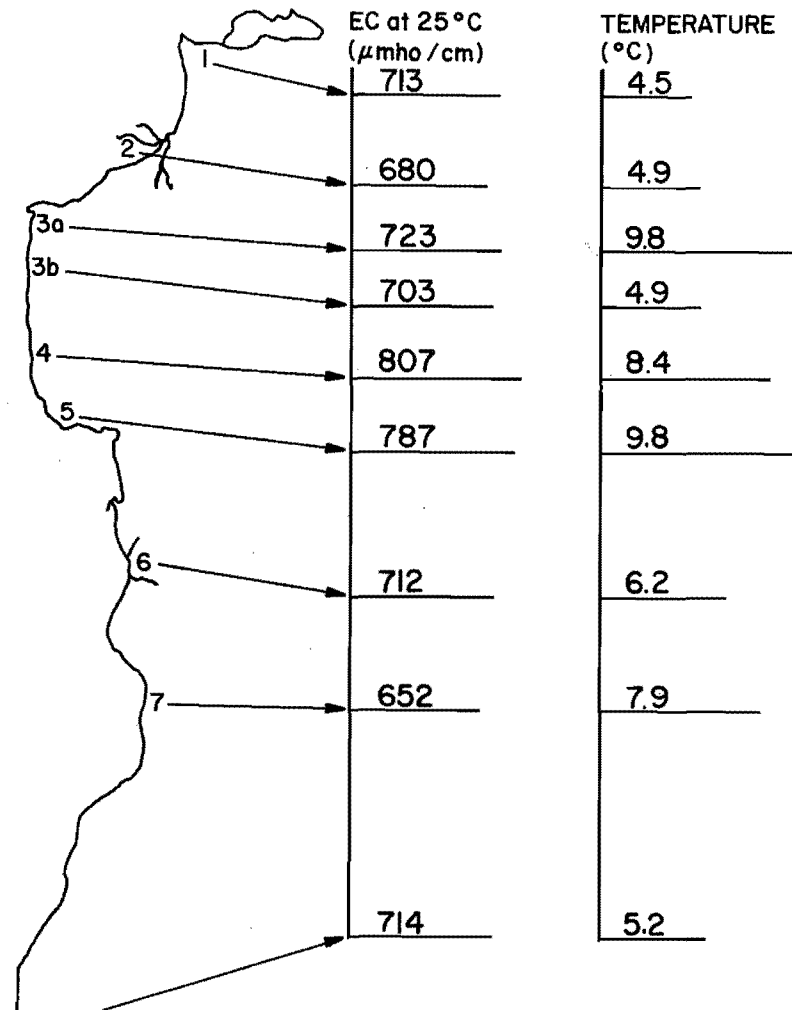


Figure 5.2. Specific conductance and temperature in the Bear River on March 10, 1981.

both calcium carbonate and sodium chloride waters with little silica. Conductivity measurements on March 10, 1981, confirm this spatial pattern, and also indicate a salinity source downstream from the Grace power plant.

The high salinity level at station 4 seems to be reduced to levels typical of those below Soda Point Reservoir by the time it reaches the bridge at Cleveland (station 7). Whether the reduction is caused by biogeochemical processes or by dilution with relatively fresh groundwater is not known. Temperature patterns indicate virtually no stream cooling between stations 4 and 7 on the July date, and stream temperatures decreased in the reach on the March date, which fact tends to suggest little groundwater influence (no snow was present on either date). However, TDS, calcium, alkalinity, sodium, and chloride all decreased by 67-82 percent, indicating either dilution with relatively fresh water or biogeochemical processes simultaneously removing calcium carbonate and sodium chloride, which seems unlikely.

The next change in river chemistry results from the input of hot, saline water from Maple Grove hot springs between stations 12 and 13. There is little evidence for changes in calcium and alkalinity during the synoptic study, the major changes being an increase in sodium, chloride, and alkalinity. These concentrations appear to decrease to slightly above upstream levels by the time the main pool of the reservoir is reached, either through reaction, or complete mixing with the reservoir contents. The fourfold decrease in silica is most noteworthy.

Generally, Ca/Cl ratios and TDS/Cl ratios tend to decrease slightly between stations 1 and 3, to increase between 3 and 7, to decrease again near the hot springs, and to increase again near the reservoir penstock. The stations below the reservoir indicate a slight source of sodium chloride groundwater upstream, but little change in TDS overall. The results of the reservoir study, as well as laboratory studies, with the Maple Grove hot spring water will be discussed below.

A commonly used statistical method of analyzing patterns in diverse, multivariable data bases is cluster analysis (e.g. Boesch 1977). The data collected at the various stream locations in the synoptic study were analyzed using the CLUSTAND package (USU Computer Center) available on the Utah State University Burroughs B6800 computer and the UPGMA (group average) combinatorial method. The variables included were calcium, chloride, TDS, alkalinity, silica, sodium, and potassium (subsequent inclusion of turbidity and total hardness made little difference in ultimate clustering). The resultant dendrogram (Figure 5.3) separates one group of stations (1, 2, and 8), typical

of reservoir water lying just above a diversion, from a second group (3, 5, 6, 7 and 12) being representative of more riverine situations. A third group (4, 13 and 14) appears dominated by inputs of more saline water, although the composition of the saline water seems different (no similarity between stations), owing either to differences in the composition of the newly input water, the receiving water, or perhaps both. The analysis suggests the possibility that main pool reservoir water is somewhat lower in sodium and alkalinity than other water in this reach of the Bear River, although possible biogeochemical mechanisms for removal of sodium bicarbonate (e.g., in Oneida Narrows Reservoir) are not readily apparent.

Initial Oneida Reservoir synoptic study. Samples were collected from six sites above, within, and below the Oneida Narrows Reservoir on July 16, 1979, to look for spatial patterns of ion concentrations that might suggest salinity removal mechanisms operating within the reservoir. The results are presented in Table 5.3. The upstream station (UP) is at the bridge near Cleveland (station 1 in Figure 5.4); stations 2, 3, 4, and 5 are within the reservoir in a downstream direction, and the downstream (DOWN) station is located below the outlet to the tailrace of the power plant. These locations are shown in Figure 5.4.

The most striking feature of the ion concentrations is their homogeneity, both in horizontal and vertical directions. Statistically there is no difference among upstream and downstream stations nor among depths. Although not statistically significant, station 2, near where the river enters the reservoir, appears to have a somewhat lower calcium concentration, a pattern not shared by other ions, including total hardness (as evidenced by the ion ratios in the last two columns). Also, there appears to be a general freshening of water with increasing depth in the pool of the dam above the penstock (station 5). Although all constituents decrease with depth, the ion ratios remain relatively constant, thus suggesting dilution rather than a biogeochemical process. Ion ratios (e.g., calcium:chloride) were calculated but followed no particular pattern and are not shown.

Subsequent reservoir synoptic studies. A sampling program was carried out during the summer of 1980 to determine if the reservoir samples taken as part of the Bear River synoptic study described in the previous section were characteristic of the entire summer. Sampling trips were conducted on July 15 and August 1, 7, and 19, a period during which biogenic precipitation of calcite could be expected to be at its maximum. Selected results of these surveys are presented in Figures 5.5, 5.6, and 5.7. A complete tabulation of the data can be found in Appendix A, Tables A.4, A.5, and A.6.

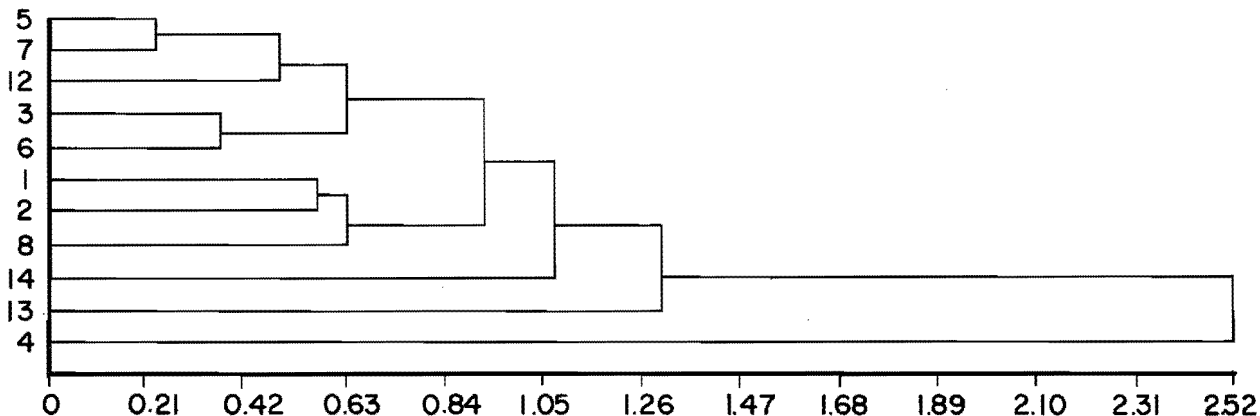


Figure 5.3. Dendrogram representing the results of a cluster analysis of the data collected at stations shown in Figure 5.1 for the variables Ca^{++} , Na^{++} , K^{+} , TDS alkalinity, Cl^{-} , and silica.

Comparison of Figures 5.5, 5.6, and 5.7 reveals a striking similarity of patterns with respect to the various chemical constituents measured. Total dissolved solids increase between stations 1 and 2, and again in response to input from Maple Grove hot springs. The TDS concentration then decreases to approximately the upstream (station 1) value by the time the main pool is reached. Calcium, sodium, and chloride show similar behavior, whereas alkalinity (see also Table A.6) seems to show less change, except on August 7, a date for which the chemical analyses are somewhat suspect. The patterns generally indicate relatively low Ca/Cl and TDS/Cl ratios near the spring inlet, returning to their upstream values in the main pool. Species concentrations at the bridge in the narrows downstream from the reservoir are generally similar to those in the main pool, although calcium was somewhat lower on July 15, and TDS was lower on the August 1 sampling date.

As in the earlier study, neither the temperature nor chemical data indicate more than slight temporary stratification in the downstream reach of the reservoir (see Tables A.4-A.6), thus minimizing the potential for hypolimnetic salinity storage, as in Lake Powell. Unfortunately, biogenically controlled calcite removal from a stable euphotic zone is also not observable. The chemical patterns thus observed suggest general dilution of the Maple hot springs water below (and possibly above) the spring inlet, but there is little evidence to suggest the operation of one or more biogeochemical homeostatic mechanisms operating in Oneida Narrows Reservoir during the period of study.

Thermodynamic Analysis of Carbonate Supersaturation

Another way of viewing the data presented above is in terms of the thermodynamic

stability of the waters sampled with respect to various solid phases. As discussed in Chapter III, homogeneous precipitation of dissolved constituents as calcite (or a related mineral) has frequently been espoused as the most probable mechanism for salinity removal in reservoirs. It should be noted at the outset that the absence of thermodynamic stability does not necessitate precipitation, perhaps because of slow kinetics (e.g., Reynolds 1978), and that the values of thermodynamic parameters are often not known with great precision (e.g. Krauskopf 1979, p. 71). Nonetheless, clear cases of undersaturation preclude precipitation, and temporal patterns in supersaturation ratios may be revealing.

The thermodynamic model used in the analyses was modified from a model created by Stan Peterson in the Soil and Biometeorology Department at Utah State University. The revised model, listed in Appendix B, was written in Microsoft Fortran for a Pixie Microcomputer. It is of the continued fraction type and depends on thermodynamic input data from tabulations by Sadiq and Lindsay (1979), Krauskopf (1978), and Plummer (1975). All equilibrium constants are corrected for temperature by using either empirical relationships (see Table 3.1) or standard free enthalpies of formation together with the van'T Hoff equation (Krauskopf 1978, p. 168-170). After each initial calculation of ion pairs and complexes involving calcium, magnesium, sodium, potassium, sulfate, carbonate and bicarbonate, a mass balance is performed on each of these species, and the calculations reiterate until the free ion concentrations change by less than 0.1 percent from the previous iteration. A charge balance is computed on the free and complexed ions and the error reported. Although many models adjust the charge balance (or proton condition) after each iteration, this was not done in this study inasmuch as complete analyses were seldom

Table 5.3. Constituent concentrations in Oneida Narrows Reservoir on July 16, 1979. Values are in mg/l except calcium and total hardness and alkalinity, which are in mg/l as CaCO₃, and ion ratios which are dimensionless. Station locations are shown in Figure 5.

Station Location and Depth (m)	pH	Total Hardness	Ca Hardness	Alkalinity	Chloride	Sulfate	Total Hardness/Alkalinity	Ca ⁺ Hardness/Alkalinity
UP	8.00	337	233	286	44	61	1.18	0.81
DOWN	8.08	333	234	287	44	63	1.16	0.82
2-S	8.04	338	192	288	45	66	1.21	0.67
2-1	8.06	334	198	286	46	65	1.17	0.69
2-2	8.05	339	192	288	44	66	1.18	0.69
3-5	8.09	337	234	288	45	68	1.17	0.81
3-2.5	8.10	338	224	288	45	64	1.17	0.78
3-3.5	8.13	338	187	287	45	60	1.18	0.65
4-S	8.04	342	219	292	43	63	1.17	0.75
4-5	8.06	339	212	293	45	63	1.16	0.72
4-11	8.08	337	198	294	44	64	1.15	0.67
5-S	8.14	343	213	293	46	67	1.17	0.73
5-2	8.13	338	198	291	44	67	1.16	0.68
5-6	8.12	337	196	294	44	64	1.15	0.67
5-10	8.09	339	199	290	44	64	1.17	0.69
5-14	8.08	330	205	286	42	62	1.15	0.72

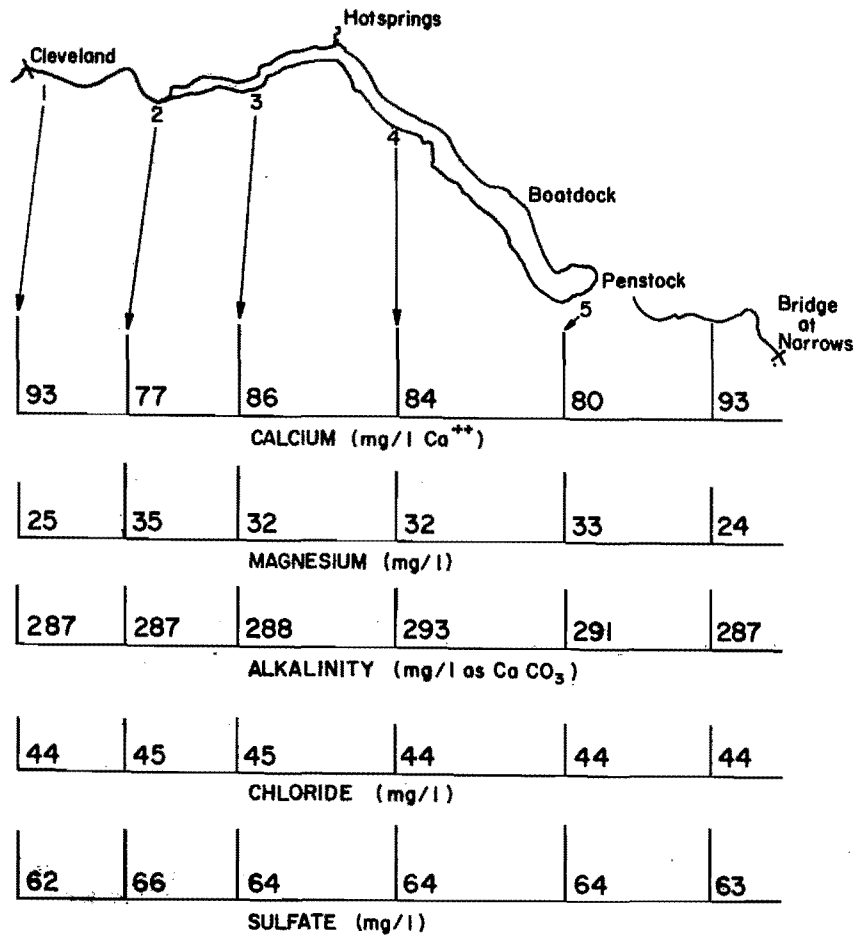


Figure 5.4. Concentrations of chemical constituents in the vicinity of Oneida Narrows Reservoir on June 16, 1979. Concentrations given for stations 2-5 are averaged over depth.

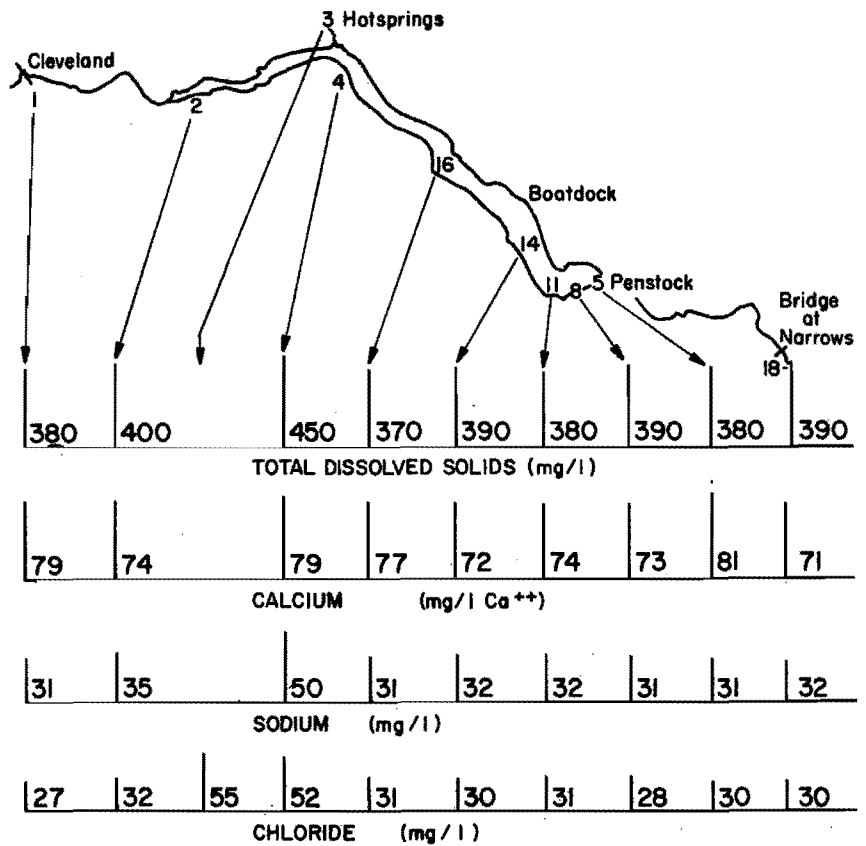


Figure 5.5. Concentrations of chemical constituents in the vicinity of Oneida Narrows Reservoir on July 15, 1980. Stations 5, 8, 11, 14, and 16 are averaged over depth.

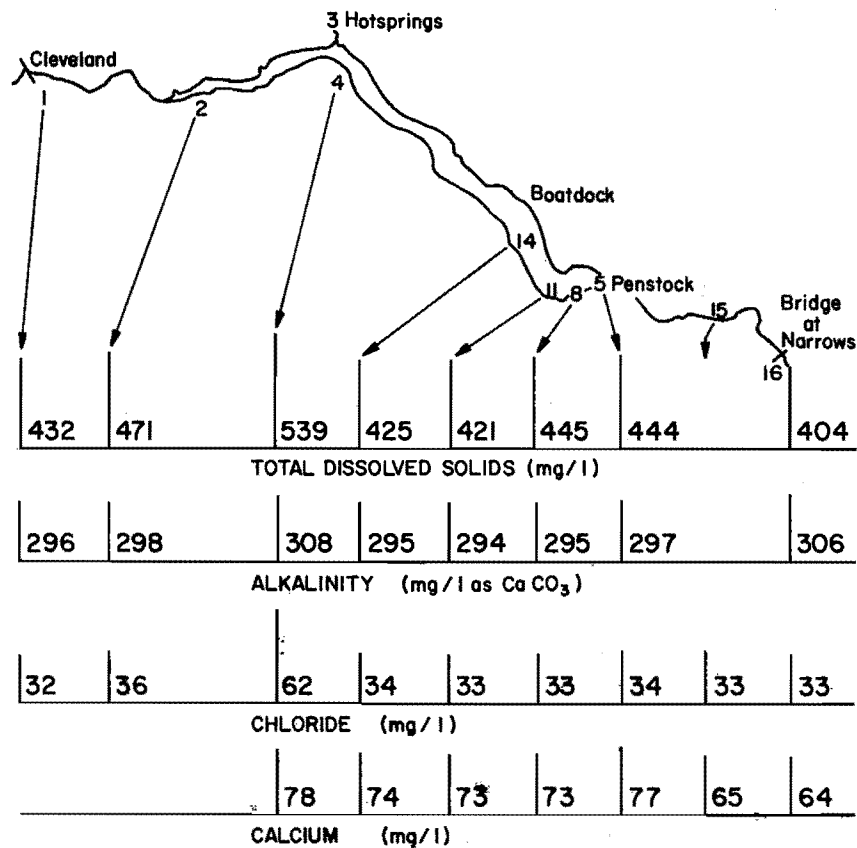


Figure 5.6. Concentrations of chemical constituents in the vicinity of Oneida Narrows Reservoir on August 1, 1980. Stations 5, 8, 11, and 14 are averaged over depth.

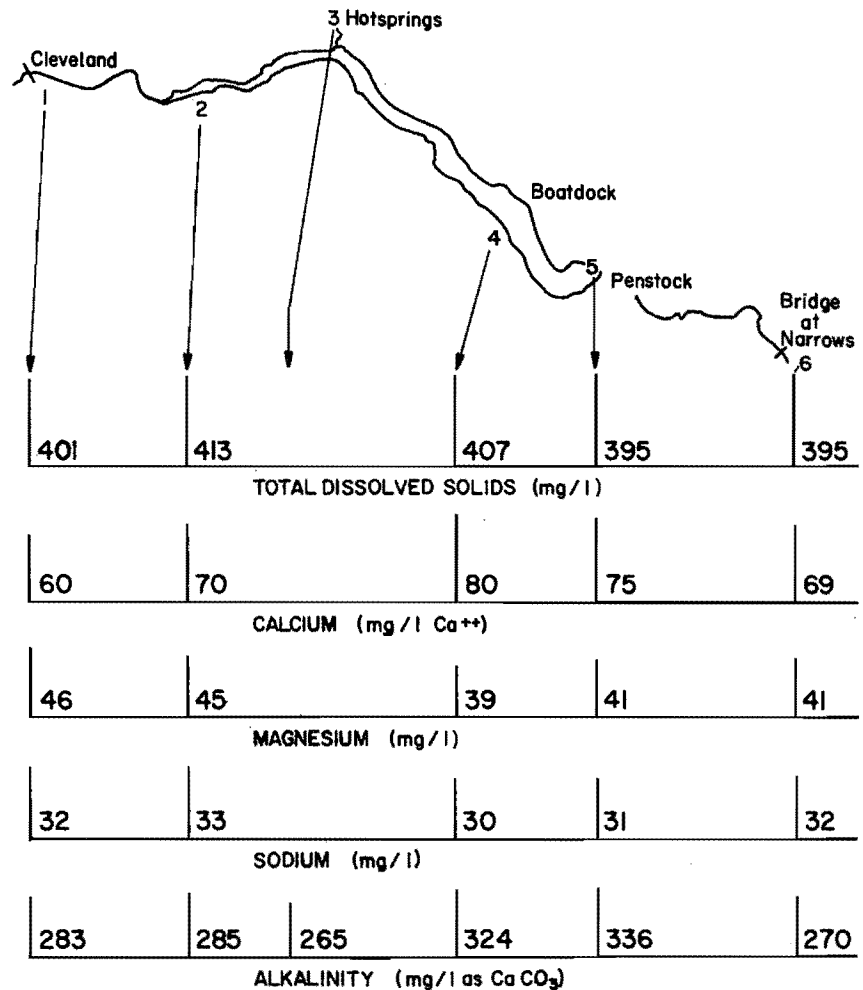


Figure 5.7. Concentrations of chemical constituents in the vicinity of Oneida Narrows Reservoir on August 8, 1980. Stations 4 and 5 are averaged over depth.

available. The error in the charge balance was generally less than 10 percent, usually with anions exceeding cations.

Bear River Study. The first analyses were run on the upstream/downstream data of Hill et al. (1973). The results (Figures 5.8 and 5.9) show striking differences between the water below Soda Point Reservoir and that below the Oneida Narrows Reservoir tailrace. The water below Soda Point Reservoir (Figure 5.8) was quite undersaturated with respect to calcite during the late summer of 1971 and, except for a brief excursion in October, remained so until March of 1972. Thereafter, the water remained slightly supersaturated until July of 1972 (the asterisked data point is of questionable veracity owing to a poor ion balance), whereupon the saturation index, SI (= ion activity product \div K_{sp}) exceeded 1.5 for the remainder of the summer. Conversely, the water below Oneida tailrace (Figure 5.9) was consistently supersaturated (except for February 1972) with respect to calcite. The pattern below the tailrace, which is presumably indicative of lower reservoir chemistry, was one of increasing supersaturation in the fall of 1971, a subsequent decrease during the winter and spring, and increases in July and September of 1972.

The observed patterns appear to be consistent with the hypothesis that phytoplankton blooms occurring in the reservoir during early summer and late fall supersaturate the water primarily by increasing the pH. However, pH is a poor predictor of saturation index ($r^2 = 0.42$ for a regression of SI on antilog pH), and variations in calcium and alkalinity concentrations and temperature confound such a simple interpretation. It is nonetheless clear that calcite precipitation was thermodynamically possible throughout much of the 1971-1972 sampling season in the lower part of the Oneida Reservoir, especially during early fall, and that calcite precipitation was unlikely at the upstream (Soda Point) station, except during late summer and early fall of 1972. The undersaturation during the winter below Soda Point Reservoir may result from sublimnetic input of the CO₂-rich "soda" spring water, from which the reservoir derived its name.

Bear River synoptic study. Supersaturation ratios calculated using the data collected on the July 16, 1980, synoptic study (Figure 5.1) suggest that the undersaturation typical of the station below Soda Point may not continue very far downstream. The only two downstream stations demonstrating undersaturation were the Soda Point station (1) and the bridge near the cheese plant in Gem Valley (4). The latter station was unusual in that it had high concentrations of calcium and alkalinity, but also a low pH. Station 3, characterized by spring water inputs above the Grace power plant, was supersaturated almost fivefold, and relatively high SI values (>2.2) were observed elsewhere downstream and in the reservoir.

Reservoir synoptic studies. Saturation indices were also calculated for samples obtained in three reservoir sampling trips: July 16, 1979, and August 1 and 15, 1980. The results are displayed in Table 5.4. On these sampling dates, the water was generally supersaturated with respect to calcite, except for the bottom waters on August 1, 1980. The chemistry of the reservoir water column on this date (and to a lesser extent on August 7) suggests decreasing supersaturation with depth, owing largely to decreasing pH. This may result from CO₂ and other acidic metabolites diffusing out of the sediments or being produced in the aphotic zone. The calcium profiles (Tables A.5 and A.6, Appendix A) show no evidence of calcium removal from surface waters, however, even though the surface water is generally supersaturated. It is also interesting that the supersaturation is greater at the bridge below the narrows, and less at Cleveland Bridge, than in the surface waters of the reservoir itself.

Summary. The results of the thermodynamic modeling thus indicate that, below the Soda Point sampling station, the Bear River is generally supersaturated with respect to calcite. With supersaturation often increasing downstream, there is little evidence that calcite precipitation is occurring. Hydrogen ion activity, perhaps controlled primarily by algal productivity and the decomposition of organic matter, seems to be the principal control on supersaturation ratios. Although dissolved organic matter may retard calcite precipitation from supersaturated water, polyphenolic organic color, as measured by spectrophotometric absorbance of 420 nm light by filtered samples at pH 8.3 (5 cm path length) was virtually negligible (absorbance < 0.035), thus there is little likelihood of inhibition.

Finally, it should be noted that analyses of two sediment cores taken from the center of the reservoir exhibited a CaCO₃ content of 16 percent, as determined by loss on ignition between 550° and 1000°C. This concentration is in the low range for "carbonate" lakes in the midwest, and would be typical of lakes with a total cation concentration in the range of 2.5-3.5 meq total cations/l (Dean and Gorham 1976), a value markedly lower than the average 7 meq/l characteristic of the waters in Table 5.1. Whether this is indicative of a lower efficiency of precipitation or higher carbonate solubilization in Oneida Narrows Reservoir sediments is not clear, although the saturation profiles described above suggest the latter.

Homogeneous Precipitation of Other Species

As discussed in Chapter III, precipitation of species other than calcite in most freshwaters is usually limited by thermodynamic stability. Very little evidence exists for authigenic precipitation of clay minerals (Jones and Bowser 1978), except in

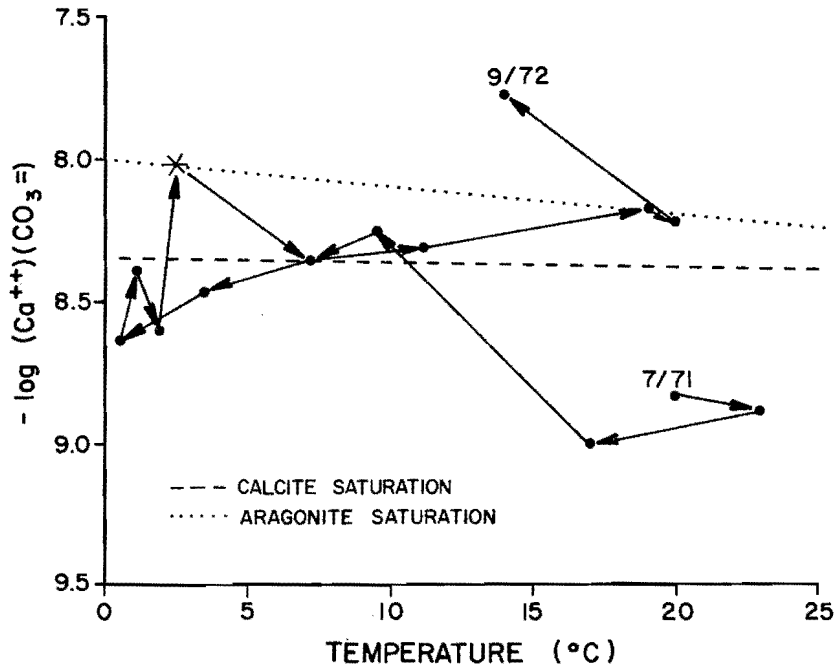


Figure 5.8. Ion activity product of calcium and carbonate at Soda Point between July 8, 1971, and September 9, 1972. Data points correspond to dates in Table A.1. The asterisked data point is of questionable veracity due to a poor ion balance on that date.

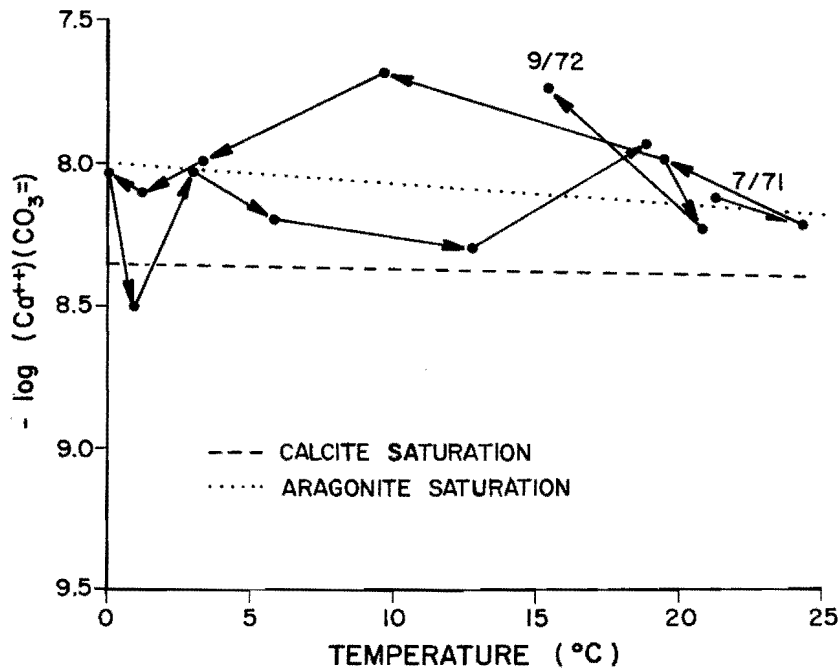


Figure 5.9. Ion activity product of calcium and carbonate below Oneida Narrows Reservoir tailrace between July 8, 1971 and September 9, 1972.

saline evaporites and brines, and the solubility product constants for most carbonates exceed those of calcite (Table 3.2). Saturation ratios for aragonite were also calculated by the computer program described in the previous section. The K_{sp} for aragonite, displayed in Figures 5.8 and 5.9, indicates supersaturation in Oneida Reservoir only during late fall, and on only one late fall date below Soda Point Reservoir. The June 16 Bear River synoptic study indicated supersaturation at all sites that were also saturated with respect to calcite. The Oneida Narrows synoptic studies indicated undersaturation on August 1, 1980, and supersaturation on August 19 ($SI = 1.36 \pm 0.16$). However, the Mg^{++}/Ca^{++} ratios in the Bear River and the reservoir seldom exceed 1.0 and are usually more on the order of 0.25-0.35, indicating that the precipitation of aragonite and magnesian calcites relative to calcite is kinetically not favorable (Müller et al. 1972). It is noted that, while solid phases such as hydroxyapatite may be important in controlling phosphorus solubility, it is unlikely that these phases precipitate stoichiometrically significant quantities of calcium (e.g. Stumm and Morgan 1981).

Other Salinity Removal Mechanisms

Incongruent precipitation. An alternative to homogeneous precipitation of clay minerals is incongruent precipitation, as described in Chapter III. Although reports of water column clay diagenesis are rare, Roche (1975) found that magnesium concentrations in Lake Chad, Africa, were controlled by montmorillonite diagenesis from kaolinite, despite the low (~350 mg/l) TDS. Analysis of silica concentrations on the Bear River synoptic study (e.g. Table A.3, Appendix A), as well as subsequent spot analyses, indi-

cated log silica activities between -5.1 and -4.2 and log $(K^+)/ (H^+)$ ratios between 3.4 and 3.7, thus indicating that kaolinite is stable with respect to montmorillonite (= muscovite, Figure 3.1) in the reservoir. Also, as discussed previously, there is little evidence to suggest potassium or sodium removal based on ion ratio patterns observed during the synoptic studies. There is thus neither thermodynamic nor circumstantial evidence to indicate incongruent precipitation as an important salinity removal mechanism. This conclusion is further supported by laboratory studies to be described in the following chapter.

Coagulation. It was reasoned that if coagulation were occurring in the reservoir, differential size fractionation of suspended matter through the use of different pore size filters would reveal a shift from many smaller (i.e., filterable, APHA 1975) particles to fewer, larger (i.e., nonfilterable) particles. Such size fractionation was carried out on two sets of field samples using 0.22 μm Nucleopore polycarbonate membrane filters, 0.45 μm Millipore membrane filters, and Whatman GFC (~0.7-1.0 μm) glass fiber filters.

The results from the first set of analyses on four samples taken on February 19, 1980, are shown in Table 5.5. Paired sets of samples showed virtually no difference in TDS results, either between 0.22 μm and 0.45 μm membrane filters, or between 0.45 μm membrane filters and ~1 μm GFC filters. Indeed, the filtrates from the smaller pore size filters frequently showed higher TDS concentrations. The somewhat higher values for the 0.45 μm filtrate at two of the three stations may represent dissolution or desorption from clay minerals during

Table 5.4. Saturation indices for calcite in Oneida Narrows Reservoir on three sampling dates.

Station (Figure 5.4)	S.I.			Station (Figure 5.5)
	July 15, 1979	August 1, 1980	August 7, 1980	
UP	1.21	-	1.94	1
DOWN	1.48	6.06	2.73	16
2-S	1.11	-	2.73	14-S
2-1m	1.20	1.00	2.20	14-6m
2-2m	1.13			
3-S	1.51	1.62	2.73	8-S
3-2.5m	1.48	1.43	2.10	8-6
3-3.5m	1.32	1.00	2.32	8-12
4-S	1.27	1.36	2.56	5-Sm
4-5m	-	1.11	2.47	5-6m
4-11m	1.28	0.95	-	5-12m
5-S	1.55	1.28	2.36	11-S
5-2m	-	-	-	
5-6m	1.39	1.15	2.33	11-6m
5-10m	1.29	-	-	
5-14m	1.71	0.96	2.12	11-12m

Table 5.5. Comparison of TDS determined on filtrates of Bear River samples using filters with different pore sizes (GFC = 2 μm , millipore = 0.45 μm , and nucleopore = 0.22 μm).

Date Filtered	Filter Pore Diameter	Station ¹		
		Grace (4)	Thatcher (6)	(Cleveland (7))
2-19-80	2 μm	304 _(8%) ²	484 (3%)	435 (2%)
	0.45 μm	290 (6%)	480 (6%)	438 (3%)
2-20-80	0.45 μm	365 (3%)	475 (2%)	474 (1%)
	0.22 μm	343 (4%)	485 (4%)	445 (2%)

¹Figure 5.1

²Coefficient of variation of 3 replicates

storage, a result suggested by laboratory experiments described in the next chapter.

The second set of samples were collected on the Bear River on June 26, 1980. Total dissolved solids were analyzed on 0.22 μm membrane and GFC filtrates. Analysis of the results (shown in Table A.3, Appendix A) indicated mean values of 350 ± 31 (+ 1 S.D.) mg/l and 346 ± 30 mg/l/TDS for the GFC and membrane filters, respectively. The mean difference of 1 percent was not found to be statistically significant using a paired-t test, and no upstream/downstream pattern of differences was apparent, although stations 6 and 7, above the reservoir (Figure 5.1) had slightly higher differences (~ TDS was 6 percent higher in the GFC filtrate) than the other samples. Although this pattern could suggest coagulation occurring somewhere above the hot spring (near station 13 in Figure 5.1), perhaps as a result of increasing ionic strength, removal by this process would be slight. It is recognized that the analysis outlined above is subject to the caveat that coagulation of a constant input of submicron particles could not be differentiated from a static situation in which no coagulation occurred. However, in the latter case one would expect to find some spatial pattern in the data, assuming that the input of colloidal matter from a heterogeneous environment would be unlikely to be uniform.

Bioassimilation. The two principal mechanisms by which bioassimilation could remove significant quantities of salinity in Oneida Reservoir would be through silica assimilation by diatoms and insect emergence. Unfortunately, no biological information of either type is available for the reservoir. However, an examination of cleared sediment preparations on samples taken near Maple Grove hot springs and from the main pool of the reservoir revealed very few diatom frustules. Most of the frustules present belonged to species (e.g. *Gomphonema*) that exhibit a sessile habit and were prob-

ably contributed largely from upstream reaches. Either silica sedimentation is unimportant or the redissolution rate is sufficiently high to return most of the silica to the water column on an annual basis.

Summary

The results of the field sampling indicate that homogeneous precipitation of calcite is the most likely contributor to any total dissolved solids removal from the Bear River reach between Soda Point Reservoir and the lower Oneida Narrows. Synoptic studies indicate a removal of TDS between Soda Point Reservoir and the Oneida Narrows Reservoir tailrace, being accompanied primarily by a reduction in alkalinity, but no real change in cation concentrations. Although gypsum dissolution accompanied by calcite precipitation could cause such an observation, the stoichiometric increase in sulfate was insufficient to balance the needed input of calcium ions. Synoptic studies indicated that virtually the entire reach below the sampling station at Alexander was supersaturated with respect to calcite. The highest supersaturation values occurred when pH was highest, thus tending to support a photosynthetic, rather than a temperature-controlled process.

Spatial calcite supersaturation patterns within the reservoir itself failed to suggest calcite precipitation. Patterns of decreasing specific ion concentrations downstream from Maple hot springs could indicate an homeostatic biogeochemical mechanism in operation, but could equally as well indicate simple dilution away from the source. Neither incongruous precipitation of clay minerals (including ion exchange), coagulation, nor bioaccumulation appeared to play a significant role in salinity removal in the reservoir or river reach during the period of study.

CHAPTER VI
LABORATORY EXPERIMENTS ON NATURAL SALINITY
REMOVAL PROCESSES

In addition to the field studies described in the previous chapter, several laboratory experiments were designed to test the salinity removal mechanisms hypothesized in Chapter III. While the bench scale approach in no way duplicates the natural environment with respect to irradiation signature, physical mixing, importance of attached (Aufwuchs) communities relative to plankton, and similar characteristics, it does allow a water column mass balance to be constructed, and various physical, chemical, and biological variables to be controlled and independently varied.

The purpose of these experiments was to explore the potential for the various processes under study to occur, together with their most likely causes in the field. Process rates, which are very much a function of solar and geothermal energy inputs, can only realistically be studied using rather expensive and labor intensive in situ studies.

The five experiments described below studied congruent and incongruent precipitation and coagulation processes only. Bioassimilation cannot be meaningfully studied directly in the laboratory because of the difficulty in maintaining a realistic, complex water column with a planktonic population similar in form and function to that occurring in an actual reservoir. However, the three phase microcosms described in Chapter IV probably come as close to representing such a system as is possible in the laboratory, and these were used in experiments in which the presence of a sediment phase and complex biological system was appropriate. The first experiment presented below was an exploratory examination of changes in chemical species content of water held over a 6-day incubation period. The other four examined the effects of: 1) the biological community present, 2) influent water chemistry on biogeochemical processes, 3) saline influent on precipitation and coagulation, and 4) suspended allochthonous and autochthonous inputs of clay minerals and sediments on incongruous precipitation, including ion exchange.

Experiment I. Aphotic Coagulation/
Precipitation

The initial exploratory laboratory study was designed to investigate the incubation of a 1:1 mixture of Bear River water collected at Cleveland Bridge with water collected from the main pool of the Oneida Narrows Reservoir in February 1980. Incubation of triplicate samples in the dark at 15°C for 6 days resulted in the patterns displayed in Figure 6.1. The only secular changes in chemical species involved calcium ion and pH, which generally showed a pattern consistent with calcite precipitation and redissolution according to reaction [3.19]. Total dissolved solids concentration showed a trend similar to calcium ion concentration, although calcite removal (based on the decrease of Ca⁺⁺ ion) would be expected to remove only 40 mg/l TDS instead of the 62 mg/l observed. Dissolved oxygen declined from 8.0 to 6.0 mg/l, indicating that aerobic conditions persisted throughout the experiment.

There was virtually no difference in the TDS concentration measured by filtration through GFC (~1 μm pore size) versus membrane (0.2 μ) filters, indicating little potential for coagulation, at least in the >0.1 μm particle size range. Analysis of the various ions shown in Figure 6.1 in the 0.2 μm membrane filtrates showed virtually identical concentrations to those in the GFC filtrates, further indicating the absence of coagulation in the 0.2-1 μm size range. Inasmuch as the Bear River water was quite turbid at the time of collection (day 0 suspended solids = 88 mg/l), the absence of a secular trend in Na⁺, K⁺, or Mg⁺⁺ ion concentrations tends to indicate the absence of significant heterogeneous (e.g. ion exchange) reactions during the course of the incubation.

Experiment II. Effects of Photosynthesis

The initial laboratory microcosm study was performed to investigate the effects of photosynthesis on Oneida Narrows Reservoir water and to test the utility of three-phase microcosms in general. Details of the

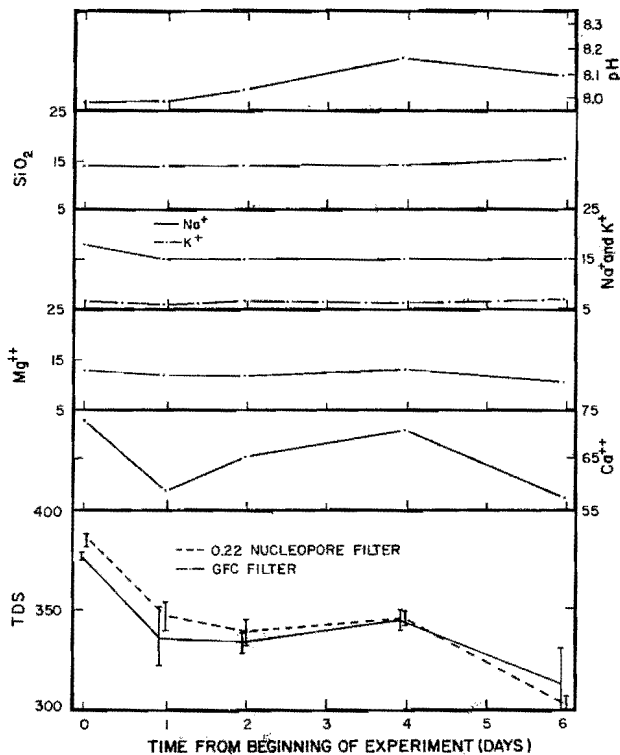


Figure 6.1. Changes in concentrations of chemical species resulting in a mixture of Bear River waters at 15°C for 6 days. All values are for GFC filtrates except where noted, for TDS, and pH, which is for bulk water. All values are in mg/l except pH. Bars in bottom frame represent range of triplicate values.

experimental methodology have been presented in Chapter IV, but we shall recapitulate some important points that pertain to the interpretation of data. The microcosms and their operation are particularly well described by Reynolds et al. (1975).

The microcosms contain a sediment phase that allows for removal or input of dissolved ions as controlled by interfacial processes (e.g. Berner 1980) and also provide some degree of chemical buffering. Water is replaced at 2 or 3 day intervals, which resupplies essential nutrients and removes bioactive (both stimulatory and inhibitory) metabolites. Such semicontinuous operation has been shown to approximately simulate chemostatic behavior without the requirements for an extensive pumping system (Reynolds et al. 1975). The microcosms are fully mixed using magnetic stirrers.

Replacement water in these experiments was collected from the appropriate field source and stored in polyethylene carboys in a refrigerated walk-in (5°C) cooler. Although it was initially feared that this water might change chemically with time, periodic analyses indicated no secular changes in water chemistry during storage. Under these circumstances (which may well not hold with other waters) the use of actual water, with its particular complex suite of dissolved organic and inorganic species, is far superior to the use of a laboratory recipe, which may not contain ions that enhance or interfere with reaction kinetics (e.g. Reynolds 1978). Although these microcosms can be operated with a closed headspace for gas measurement, they were not in this case in order to prevent supersaturation with oxygen during the incubations.

A preincubation of nine replicate microcosms for approximately 20 days indicated a pattern of relatively stable major ion concentrations and electrical conductivity (EC). Afterwards, the experiment was begun by moving three microcosms to a dark chamber, and spiking three of the microcosms left in the light with 10 mg/l nitrate-N, which was shown to be the growth limiting nutrient to *Selenastrum* in a preliminary bioassay (see Table 4.1). The extensive amount of data collected during this experiment is listed in Table A.6 in Appendix A. In the following sections, we will highlight the behavior of some ions of interest.

As a prelude to discussing individual ion behavior, some general trends are noted. The dark microcosms behaved much differently than the light microcosms, generally exhibiting trends of increasing ion concentrations (as measured by electrical conductivity), despite the fact that the sediment-water interface never became anaerobic. Of the two groups of light microcosms, there was little difference between the nitrogen-spiked and control group. This may have been the result of silica, rather than nitrogen, limitation of the Aufwuchs community comprising the lion's share of the biomass in the microcosms. One of the spiked microcosms behaved rather unusually, and it is considered separately below.

Initially trends were graphed for each constituent in each microcosm and examined to indicate availability of the various ions for chemical and biological reactions. Data were aggregated only when justified by the similarity of response in a number of the microcosms. The danger of doing otherwise will become apparent in the following paragraphs. Changes may result not only from biogeochemical processes, but also from dilution with the replacement water. Thus absolute biogeochemical reaction rates cannot be simply deduced from changes in species concentrations. The mass balances (which are not susceptible to such problems in interpretation), together with some statistical treatment of the data, will follow

the discussions of individual constituent behavior.

Dissolved oxygen. During preincubation (days -20 to 0) the dissolved oxygen concentration (DO) was able to rise to 12 to 16 mg/l because of the long period (14 days) between water replacement (Figure 6.2). At the beginning of the experiment, however, the DO level fell to approximately 5 mg/l in the light microcosms on day 1, followed by an unremarkable increase to 6-7 mg/l for the remainder of the experiment. In the dark microcosms, the DO concentration dropped to 3 mg/l during the first day of the incubation where it remained.

The failure of the light microcosms to maintain oxygen saturation (\approx 8-9 mg/l) despite constant illumination and a continuous accumulation of periphyton on the walls of the microcosms is somewhat per-

plexing. The combined biochemical (BOD) and sediment (SOD) oxygen demands in the dark microcosms apparently were insufficiently high to exceed the reaeration rate, inasmuch as a low level of DO was maintained throughout the experiments. Thus the slight undersaturation in the light microcosms must indicate some relatively stable balance between photosynthesis, autochthonous SOD, and the BOD of both the biological community and the influent water.

Hydrogen ion. An increasing trend in pH levels was observed in all of the light microcosms (Figure 6.2) beginning on the first day of preincubation (pH = 8.0-8.2) and climbing gradually through the last day of observation (pH = 9.0-9.7). There was no apparent difference in the nitrogen-amended and control groups. The dark microcosms showed identical changes to the light microcosms during the preincubation under constant

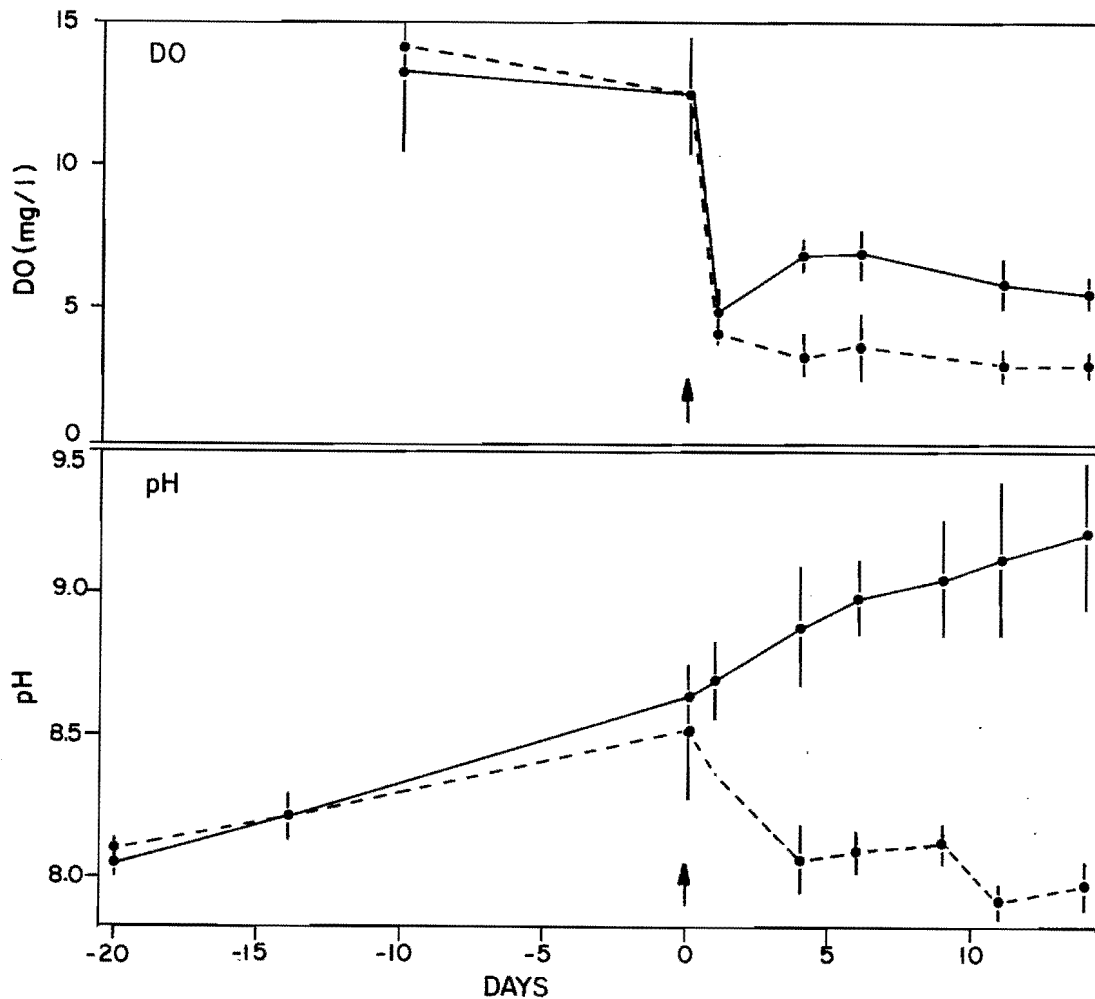


Figure 6.2. Changes in dissolved oxygen (DO) and pH before and during incubation of Oneida Narrows Reservoir water in the light (-) or dark (--) in semicontinuous, 3-phase microcosms.

light, but decreased back to pH 8.0-8.1 by the last day of the experiment.

Calcium. Calcium concentration patterns showed three distinct patterns during the incubations. Five of the six light microcosms followed one pattern and the sixth a distinctly different one. The light microcosms were thus grouped into Group I (five similar light microcosms), Group II (one unusual light microcosm) and Group III (three dark microcosms). Unless otherwise noted, there were no significant differences between the nitrogen-amended and unamended light microcosms in Group I.

Calcium concentrations in all the microcosms ranged from 75 to 83 mg/l on day -14 of the preincubation and diverged somewhat (65-96 mg/l) by the beginning of the experiment (Table A.6), although high and low values were randomly distributed among the three groups. Groups I and II showed a secular decline in calcium concentrations during the experiment (Figure 6.3), with Group II showing a much smaller decline than Group I. The dark microcosms showed only a slight decrease in calcium concentration.

Magnesium. Magnesium concentrations exhibited changes similar to those for calcium ion (Figure 6.3). Secular decreases occurred in Groups I and II, with Group II showing a much smaller change than Group I. Proportional changes were much smaller than in the case of calcium. There was virtually no change in the Group III microcosms.

Alkalinity. In Group I, alkalinity exhibited a slow decrease during preincubation (Table A.6), followed by a more precipitous decline during the experiment (Figure 6.3). The microcosms in Group II and Group III exhibited virtually no change.

Specific conductance. The specific conductance patterns (Figure 6.4) are complex. In Group I, EC drops and then increases during preincubation (Table A.6), and then drops significantly during the experiment. Group II is similar, except that there is no secular trend during the experiment, while Group III shows a significant increase in EC throughout the experiment, despite the aerobic sediment water interface.

Silica. Changes in silica concentrations during the experiment suggest the reason for the similar behavior of the nitrogen-amended and unamended microcosms. Silica concentrations ranged from 12 to 15 mg/l at the beginning of the preincubation and decreased almost linearly until the experiment started (Figure 6.5). In all but one of the Group I light microcosms (shown separately), silica concentrations decreased to below 2 mg/l, despite the periodic addition of replacement water containing 19 mg/l of silica. This suggests that most of the microcosms may have been silica, instead of or in addition to, nitrogen limited. In the

dark microcosms, silica increased toward the 19 mg/l level present in the replacement water. Subsequent analysis will indicate that little or no silica was released from the sediments.

Other ions. No trends were observed for chloride, sodium or potassium, and no distinct patterns were observed that distinguished one treatment from the others. Although sulfate was not monitored regularly, preincubation concentrations between days 20 and 14 did show a slight (not statistically significant at $\alpha = 0.05$) increase. Total dissolved solids, although also not monitored, were measured on the last day (13) of the experiment. Group I averaged 337 ± 13 mg/l; Group II, 455 mg/l, Group III, 460 ± 18 mg/l, and the reserve water exhibited a TDS of 470 mg/l. Thus only the Group I light microcosms showed a significant decrease in TDS below the replacement water.

Biological changes. The observation that the Aufwuchs community far outstripped the plankton in standing crop led to a de-emphasis of plankton monitoring during the course of the experiment. Unfortunately, samples for later examination were improperly stored, and thus many were lost or ruined. Nonetheless, spot checking of a score of the samples that were well preserved led to the following generalization. At day 0 of the incubation, the light microcosms were sparsely populated with coccoid green algae, Pediastrum, Navicula, and other smaller diatoms. The unamended microcosms developed small populations dominated by the diatom, Synedra, and also developed populations of the rotifer, Monostyla, together with some Trichocerca. The amended microcosms developed relatively larger (although still small in absolute terms, i.e. <100/ml) populations dominated by Synedra, and with far fewer rotifers. Tabellaria and Melosira species were occasionally present. Zooplankton data are only reliable for day 10 of the preincubation and ranged from 100-400 organisms/l, except for microcosm 8, which had 930/l. It is interesting that this microcosm later showed the greatest populations of Synedra during days 4-6 of the incubation. Cladocerans dominated the net plankton.

Following the last day of the study, the Aufwuchs community was harvested and examined for composition and dry weight. The unamended microcosms were codominated by Phormidium and Lyngbya, two species of filamentous bluegreen algae. The amended microcosms were dominated by Lyngbya and Chroococcus, a colonial bluegreen alga. The ash free dry weight was somewhat higher in the unamended microcosms (0.94 g versus 0.64 g), as was the accumulated ash weight (1.8 g versus 1.5 g). The amended microcosms, however, displayed a healthier Aufwuchs community, the community in the unamended microcosms appearing somewhat chlorotic. Planktonic chlorophyll a was similar in both groups, averaging less than 3 $\mu\text{g/l}$.

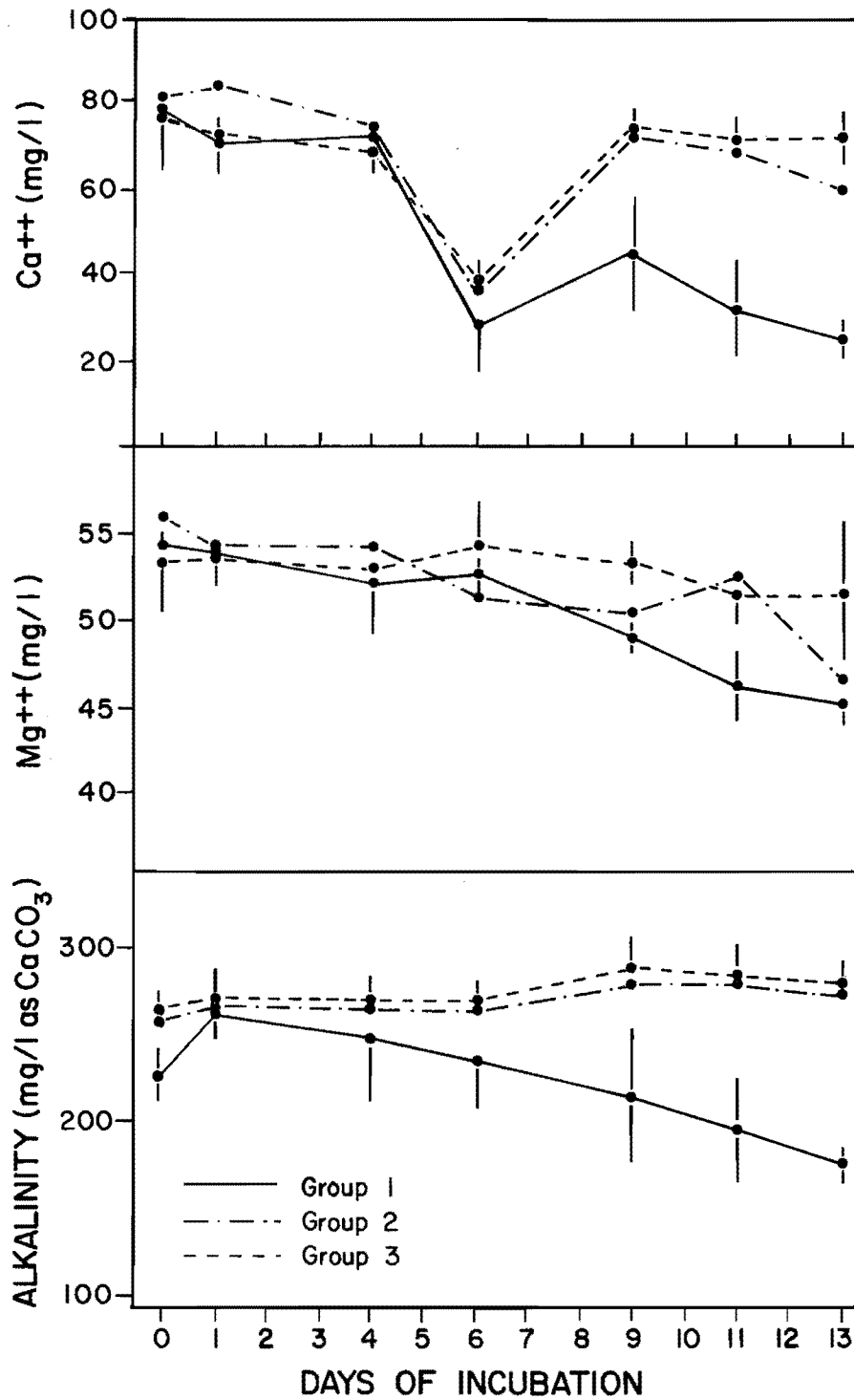


Figure 6.3. Changes in calcium, magnesium, and alkalinity in Oneida Narrows Reservoir water during incubation in light (Groups I and II) and dark (Group III) in semi-continuous 3-phase microcosms.

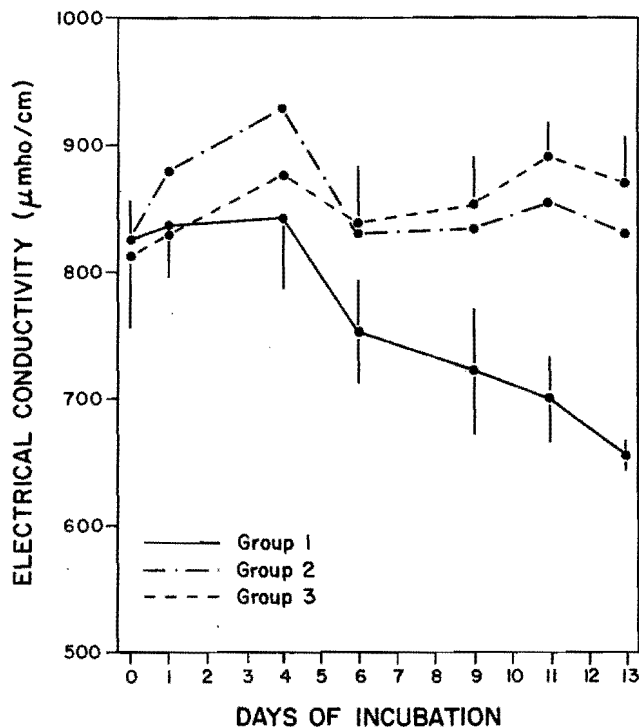


Figure 6.4. Changes in electrical conductivity occurring during incubation of Oneida Narrows Reservoir water in light (Groups I and II) and dark (Group III) 3-phase semicontinuous microcosms.

Mass balance analyses. Results of mass balance analysis on the microcosms indicate that attached algal communities (Aufwuchs) are capable of reducing the total dissolved solids in Bear River water, principally by the mechanism of calcium carbonate precipitation. In the absence of photosynthesis, salinity may actually increase somewhat, although this effect is likely to be small, provided the water column remains oxygenated.

Table 6.1 summarizes the overall effect of the incubations. In each group, the beginning value is the average of the first two days (0 and 1) of data. This averaging was done to decrease any error that might have arisen from random sampling or analytical error on the first day (day 0). This value was corrected for the periodic replacements of microcosm water with reserve water, which dilutes the sample either with solute or solvent depending on the relative concentrations of the constituent of interest. Finally, the average of the final two days of observation (11 and 13) is subtracted from the adjusted initial value to estimate the change in concentration over the incubation period.

Virtually all of the constituents investigated decreased between the beginning

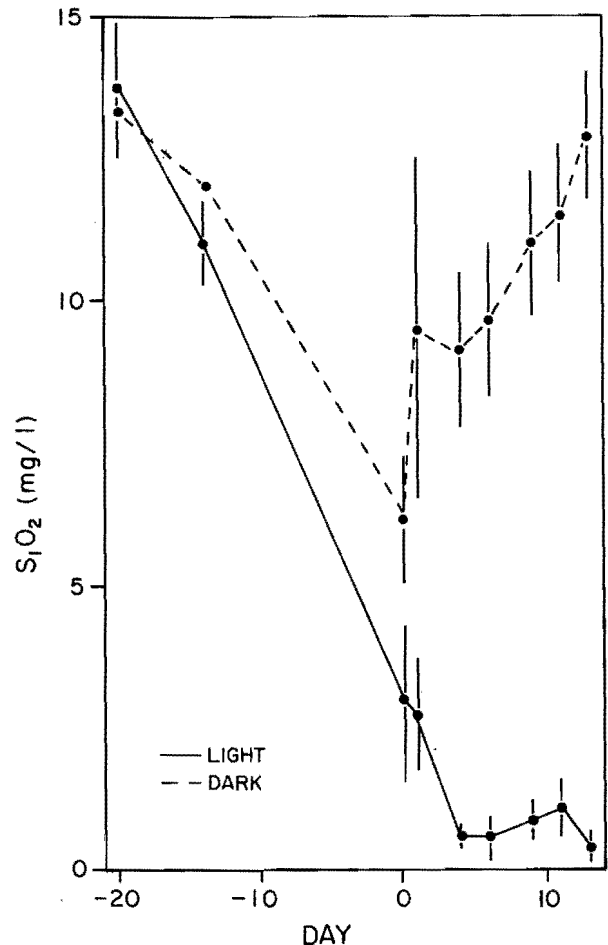


Figure 6.5. Changes in silica concentration in Oneida Narrows Reservoir water incubated in light and dark semicontinuous, 3-phase microcosms.

and end of the experiment, with the greatest changes occurring in the lighted Group I microcosms (Table 6.1). The greatest changes were in silica, hydrogen ion, and calcium concentrations, with alkalinity and magnesium concentrations being smaller. The changes in the dark microcosms generally were not statistically significant, except for conductivity, which increased, and calcium, which decreased. The Group I microcosms showed highly significant decreases in all constituents, including hydrogen ion.

The large changes in pH, alkalinity, and calcium ion are reflected in the relatively small changes observed in calcite saturation index (SI), which remained in the (average) range of 5-6. Most of the Group I microcosms showed an elevation of the saturation index on day 4 or 9, before returning to a relatively lower value. Microcosm 10 (Group I) showed a particularly high peak (SI = 22.8) on day 9 before returning to 5.9 on day 13. The Group II microcosm increased gradually to an

Table 6.1. Changes in concentrations, adjusted for dilution of selected constituents over the course of incubation under light (Groups I and II) or dark (Group III) conditions for 11 days. Asterisked values are significant at $\alpha = 0.01$ level.

Constituent	Δ Concentration	Percent Change	Group
Conductivity (μ mhos/cm)	-153	-18 ^{*b}	I
	+1	0	II
	+54	+7 [*]	III
pH ^a	+0.77	+9 (-83) [*]	I
	+0.84	+10 (-86) [*]	II
	-0.18	-2 (+52)	III
Alkalinity (mg/l as CaCO ₃)	-98	-35 [*]	I
	-7	-3	II
	-5	-2	III
Silica (mg/l)	-9	-88 [*]	I
	-10	-92 [*]	II
	-1	-7	III
Calcium (mg/l)	-56	-68 [*]	I
	-22	-26 [*]	II
	-13	-16 [*]	III
Magnesium (mg/l)	-7	-14 [*]	I
	-4	-8	II
	-1	-2	III
Calcite Saturation ^b Index (IAP/K _{sp})	-0.7	-13	I
	+8.8	+244	II
	-2.1	-66	III

^a Values in parameters calculated as $\Delta(H^+)$

^b Excluding #10 which had an unusually high index on day 11; inclusion would result in +0.9 (+18%)

SI of 12.3, where it remained. The Group III microcosms fell to and remained near saturation by day 4.

Closer examination of the salinity removal process indicates the operation of calcite precipitation, enhanced perhaps by another process removing hardness. Figure 6.6 indicates the removal of 1.08 meq/l of calcium for each meq of alkalinity, which is not statistically different ($\alpha = 0.05$, $H_0: b_{1.1} = b_{1.0}$) than the expected stoichiometric ratio of 1:1. Superimposed on this alkalinity-related removal is a loss of 0.65 meq of calcium which is not accompanied by alkalinity removal, amounting to approximately 25 percent of the calcium removed in the light microcosms. Similar analysis of the magnesium removal gave a slope of 0.25 meq Mg/meq alkalinity, with a y intercept of 0.12 meq ($r^2 = 0.78$, $b = 0$ at $\alpha = 0.01$). These analyses suggest that magnesium may be coprecipitated with calcium carbonate, although such a conclusion would suggest that the slope of the regression line in Figure 6.6 is too high by 0.33 meq Ca/meq alkalinity.

Examination of the data from the individual microcosms indicates a clear decreasing trend from day to day, and likewise

the standard curves for calcium and magnesium analysis failed to indicate any bias between dates. Thus the trends appear in no way artifactual. However, in the case of magnesium, the change in mean concentration between the beginning and end of the experiments (Table 6.1), although statistically significant, represents a loss of only 6 mg/l against a background of 50-55 mg/l, which is in the range of instrumental error for this analysis. Therefore, the decrease in magnesium must be regarded with some caution. It may be worthwhile noting that linear regression of calcium against magnesium loss yielded a correlation coefficient (r^2) of only 0.74, which may indicate the absence of very strong coupling between the removal mechanisms.

Removal of calcium and magnesium ion in the absence of carbonate precipitation could occur by bioassimilation in conjunction with H^+ ion excretion to maintain charge balance or through clay mineral diagenesis or ion exchange. In the first case, the ash free dry weight of the Aufwuchs (~1 g/microcosm) could only account for 4 mg of noncarbonate calcium and 3 mg of the magnesium (Wetzel 1975, p. 641, after Vallentyne), which is less than 2 percent and 7 percent of the mass

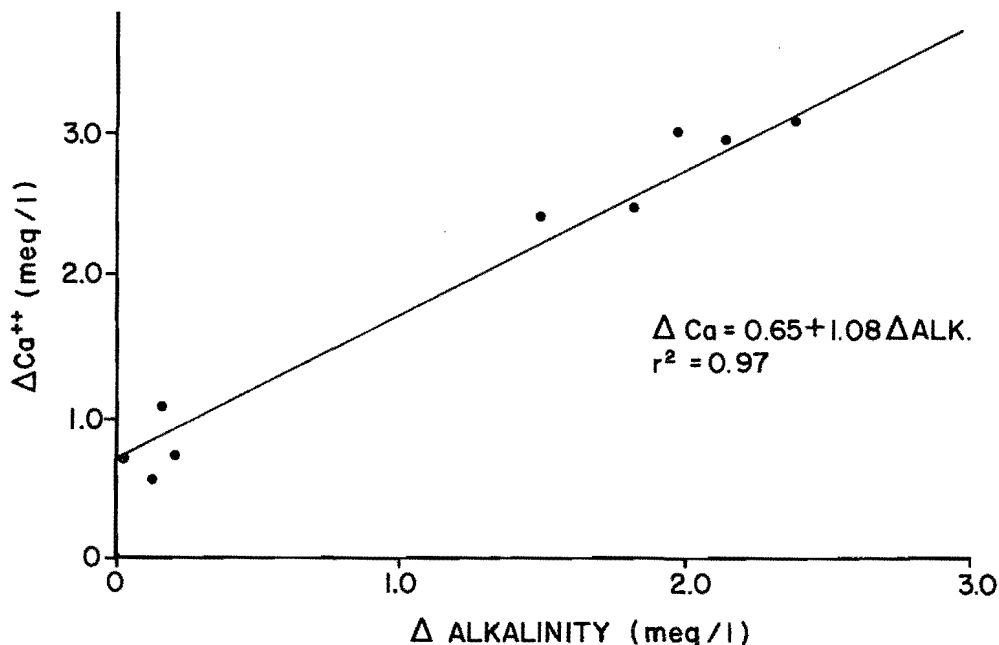
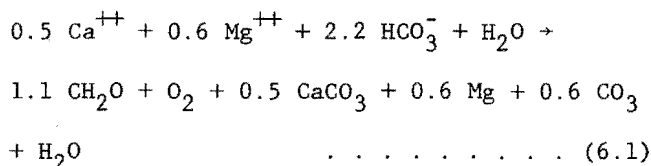


Figure 6.6. Relationship between calcium and alkalinity removal in individual microcosms between the beginning (days 0 and 1) and end days (11 and 13) of incubation. Changes are corrected for dilution with replacement water. Groups II and III are nearer the origin.

lost from the light microcosms of calcium and magnesium, respectively. Alternatively loss of 13 mg/l (= 0.65 meq) Ca^{++} by ion exchange would entail the input to the medium of 15 mg/l of Na^+ or 25 mg of K^+ , or would decrease the pH by 5 units (or some combination of the above). The possibilities of a Na^+ increase of 15 mg/l against a background of approximately 40 mg/l cannot be categorically ruled out, but does not appear to be supported by the data. The potassium concentration decreased, if anything, and H^+ clearly cannot be responsible for much of the exchangeable ion. Aluminium could account for a fraction of the exchange but was not measured. Formation of significant amounts of new silicate phases is not supported by the mass balance in the dark microcosms (Table 6.1). Thus the calcium and magnesium removal not related to alkalinity changes, if real, are minor and not elucidated by the experimental results.

One final mass balance calculation proves instructive, although enigmatic, especially because it is in agreement with field data collected by Megard (1968). The mean loss of calcium in the light microcosms (216 mg Ca^{++}) may be compared with the mean organic carbon accumulation of 379 mg in the Aufwuchs (50 percent of the ash free dry weight) to give a Ca^{++} /organic C ratio of 0.17. This can be compared with the expected value of 0.45 which can be derived from the stoichiometry which holds for a water in which all of the hardness derives from carbonate minerals:



It is interesting that Megard found ratios of Ca/organic C ranging from 0.1 to 0.4 in four Minnesota lakes, which were also less than the predicted stoichiometric ratio (~0.5). Two factors which could alter the stoichiometry in Equation 6.1 include a third alkalinity source (e.g. NaHCO_3 , sodalite) and the possibility that some of the precipitated calcium may be colloidal (e.g. Kelts and Hsu 1978) and thus be analyzed with the dissolved ions.

Kinetic analyses. Analysis of the data for kinetic relationships between constituent removal rates and concentrations failed to yield statistically useful models. Plots of calcium, magnesium, and alkalinity removal against calcium, magnesium, and carbonate concentrations, the calcite supersaturation index or $(\text{Ca}^{++})(\text{CO}_3^-) - K_{sp}$ calcite, indicated that high constituent concentrations or supersaturation led to high removal rates and vice versa. However, within the subset of light or dark microcosms, there were no clear relationships between rates and concentrations, either at timesteps of 1-3 days or over the entire experiment, on a microcosm by microcosm basis.

This behavior may have resulted from the fact that the kinetic constants in crystal growth equations such as Equations 3.21 and 3.22 are not constant during the experiment, but change as precipitation and crystal growth and aging proceeds. Nonetheless, plots of both calcium and carbonate removal versus $(Ca^{++})(CO_3) - K_{sp}$ fit linear models much better than power functions for all but two of the light microcosms, indicating the unlikelihood of kinetic inhibition (e.g. Reynolds 1978). Unobserved excursions of constituent concentrations away from the endpoints of the averaging period, together with random sampling and analytical error, may also have obscured such kinetic relationships as were observed in carefully controlled, two-phase apparatus used by Reynolds (1978). However, complexities introduced by early diagenetic reactions, and concentration gradients in the surficial sediments cannot be ruled out.

Synopsis. The combined data strongly support the hypothesis that precipitation of calcite (and perhaps magnesian calcite) occurs through the agency of an increase in pH brought about by photosynthesis. The slight precipitation in the dark microcosms, if real, may be the result of establishment of chemical equilibrium in a (relatively) closed, nonbiological system. Failure of microcosm 9 (Group II) to precipitate calcium and magnesium at the same rate as the other light microcosms remains enigmatic owing to the lack of comparative biological data. However, the fact that the relatively low Aufwuchs biomass in that microcosm probably indicates low productivity agrees with the photosynthesis hypothesis. There was no conclusive evidence of removal of cations by processes other than carbonate precipitation.

Experiment III. Mixing of Upstream Water

As discussed in Chapter III, the solubility of calcite is a function of many factors which can vary between water masses (e.g., Wigley and Plummer 1976). The third experiment was designed to assess the effect of the Bear River water flowing into the Oneida Narrows Reservoir on calcite precipitation. The experiment began by reestablishing the microcosms used in the previous experiment with fresh reservoir water and allowing them to equilibrate for one week. Spot checking at that time resulted in selection of six of the nine microcosms that were chemically the most similar for use in the experiment. One group, A (1, 7, and 11) received periodic replacement, as described in the previous experiment, with Bear River water collected at Cleveland Bridge. The remaining group, B (6, 8, and 9), received replacements of reservoir water collected in the main pool. All of the microcosms were kept under continuous light, and the reserve water was stored in a cold room.

Results of mass balance analyses for several constituents of interest are presented in Table 6.2. The raw data are tabulated in Table A.8 in Appendix A. The Bear River water contained somewhat higher concentrations of all the constituents than did the microcosms (Table A.8) or the reservoir replacement water; and as Table 6.2 indicates, absolute removal of most constituents was higher in the microcosms receiving the river water. The differences between TDS concentrations and calcium concentrations at the beginning and end of the experiments were statistically significant using a t-test on the two means, but there was no significant differences between removal in the two carboys. The pattern of data, however, indicates that another experiment of this type may be fruitful.

Comparison of this experiment with Experiment II reveals both similarities and differences. Calcite precipitation is apparently again the salinity removal mechanism. Saturation indices during the experiment were in the range of 2.2 to 3.4, indicating that precipitation was thermodynamically possible. Although the fraction of calcium removed in this experiment was smaller than that in Experiment II, the duration of the present experiment was only 4 days, relative to 13 for Experiment II. In this experiment, the Aufwuchs community was visibly less well developed, although the microcosms were again capable of maintaining the silica levels below 2 mg/l, despite the 5 mg/l concentrations in the replacement water. Removal of small amounts of magnesium was suggested again in Experiment IV, although the removal was well within analytical error.

Experiment IV. Effects of Saline Influent on Precipitation and Coagulation

The potential for precipitation or coagulation as a result of changing ionic strength and composition has been pointed out in Chapter III. The input of saline water

Table 6.2. Changes in selected constituents in microcosms initially containing Oneida Narrows Reservoir water receiving daily replacement of 12 percent Bear River water versus 12 percent reservoir water (control).

Constituent	Group I Bear River		Group II Reservoir	
	mg/l	%	mg/l	%
TDS	-32	-11*	-26	-10*
Ca ⁺⁺	-10	-20*	- 5	14
Mg ⁺⁺	- 1	- 4	- 2	10
Na ⁺	- 1	- 4	0	0
Si ⁺	-0.5	-32	-0.7	-42

*Significant at $\alpha = 0.05$, d.f. = 4.

from Maple Grove hot springs (e.c. = 3.1 mmho/cm) to the Oneida Narrows Reservoir provided an opportunity to test such a hypothesis, which may also pertain to reservoir reaches along the Colorado River that receive inputs of saline spring water. In this experiment, water from various parts of the reservoir were incubated in polyethylene containers (capped, no sediment phases) on a laboratory countertop, and one upstream sample was mixed with spring water. The chemistry and submicron particle size distribution in the containers was monitored for 7 days.

The original intent of this experiment was to correlate chemical changes with changes, either in colloid size or concentration, as the experiment progressed. The results of size fractionation using the Coulter Electronics Nannosizer, however, indicated that the submicrometer particle concentration in all of the incubated waters was consistently lower than 1 mg/l (the minimum level of detection of the instrument), even immediately after mixing. The results of this experiment thus suggest that coagulation cannot be responsible for significant salinity removal under the summer conditions characteristic of Oneida Narrows Reservoir at the time of sampling. However, the results should not be extrapolated to turbid spring meltwater runoff without further studies.

Despite the failure of the Nannosizer to yield quantitative results, water chemistry was nonetheless monitored for 7 days in order to detect the occurrence of any other biogeochemical processes occurring in the absence of a sediment phase. Chemical changes in the unmixed waters are depicted in Figure 6.7 and 6.8, and those occurring in the hot springs/reservoir mixture are shown in Figure 6.9. Individual data are recorded in Table A.9 of Appendix A.

All of the incubations except Number 1 (Cleveland Bridge), showed sharp decreases in calcium during the first day of incubation, but alkalinity generally increased slightly during the incubations. The average net change in calcium concentration during the incubations (day 7 minus day 0) was 25 ± 8 mg/l (~ 33%) with the mixed sample almost exactly at the mean value (24 mg/l). Net loss of alkalinity during the same period was 31 ± 65 mg/l as CaCO_3 , assuming the two high alkalinity values on day 0 (4b and 5b, shown in Table A.9 but not in Figure 6.7) are not artifacts. It is interesting that the extent of calcium removal, 33 percent, compares favorably with the 44 percent removal over 9 days of incubation in the Group I microcosms of the previous experiment. Of the remaining chemical parameters measured, sodium increased from 31 ± 2 to 41 ± 1 mg/l, pH increased from 8.0 to 8.3 units, and magnesium, potassium, and dissolved organic carbon (~6 mg/l) showed no change in the unmixed microcosms. The saline spiked microcosm showed an increase in sodium

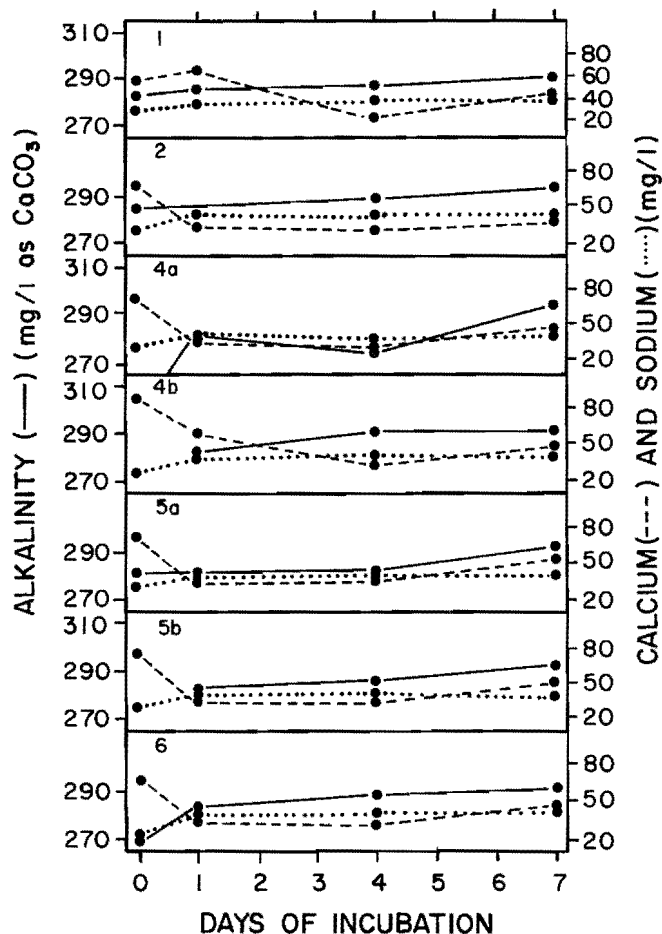


Figure 6.7. Changes in alkalinity, calcium, and sodium concentrations during incubation of Oneida Narrows Reservoir water under ambient laboratory conditions in the absence of a sediment phase. Sampling stations correspond to Figure 5.7.

of 10 mg/l (78 to 88), and virtually no change in the other parameters.

Assuming a loss of 25 ± 8 mg/l calcium, calcite precipitation should result in 62 ± 0 mg/l removal in alkalinity, which is clearly much higher than the observed change. Adsorption onto suspended particulates is the only other apparent mechanism that could remove dissolved species. Ion exchange with sodium should cause an increase in the mean sodium concentration of 29 ± 9 mg/l, which is approximately three times higher than the observed change. These results thus suggest some combination of calcite precipitation, ion exchange with sodium, and perhaps a third mechanism, in addition to inherent sampling and analytical errors.

A significant point is the positive 19 mg/l change in TDS in the unmixed samples

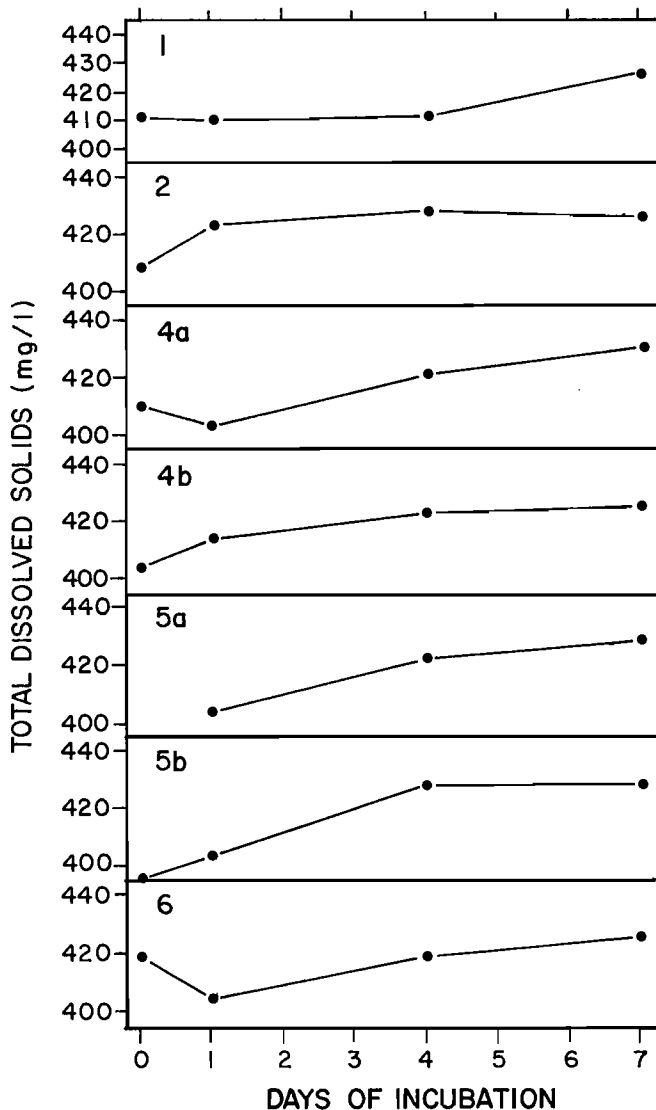


Figure 6.8. Changes in total dissolved solids during incubation of Oneida Narrows Reservoir water under ambient laboratory conditions in the absence of a sediment phase. Sampling stations correspond to Figure 5.7.

(significantly at $\alpha = 0.01$, paired $t = 5.38$, $df = 5$), despite the apparent decreases in other constituent concentrations. These results suggest that the decrease in calcium and perhaps alkalinity may be overestimated, or that some unmeasured ion (e.g. sulfate) was released from suspended particulate matter, inasmuch as the trend in TDS concentrations displayed in Figure 6.8 does not suggest the operation of analytical or sampling error on a particular date. Replacement of a relatively volatile anion (e.g. bicarbonate) by a less volatile one (e.g. sulfate) is another possibility. At

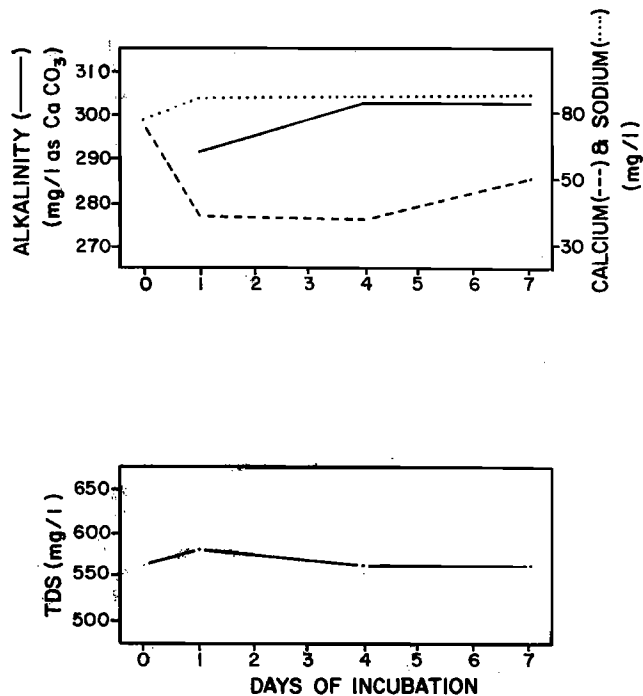


Figure 6.9. Changes in chemical concentrations during incubation of a 1:7 mixture of Maple Grove hot springs water with Oneida Narrows Reservoir water under ambient laboratory conditions in the absence of a sediment phase.

any rate, the change represents only 2 percent of the initial TDS value. No change in TDS was observed in the sample receiving the spring water (Figure 6.9).

Experiment V. Heterogeneous Precipitation

The purpose of this experiment was to assess the extent to which heterogeneous (incongruous) precipitation and ion exchange processes might contribute to or remove salinity from Oneida Narrows Reservoir water. Essentially, the design called for incubating two concentrations of three soils and a river sediment sample on a shaker table in the dark in four media of increasing ionic strength (synthetic Bear River water spiked to give increasing calcium concentrations). The hypothesis tested was that increasing soil loading would lead to increasing dissolution (release), uptake, or exchange, while increasing initial ionic content would cause a decrease in salinity for a given treatment by decreasing the concentration gradient between the ion surface and the bulk aqueous phase. Kinetic versions of such a model have been applied successfully by Nezafati (1981) and Jurinak and Wagenet (1981) to describe salinity interactions between particulates and river water.

The results of the experiment indicated that the initial calcium concentration of the incubation medium was the most important of the three independent variables tested in describing the behavior of TDS in the experimental systems. Figure 6.10 displays the combined results of the 0.5 g and 1.0 g soil/l incubations, which were not significantly different from each other. Raw data are presented in Table A.10 of Appendix A. Three-way analysis of variance using the ANOVA routine of SPSS (Nie et al. 1975) was run on the test results, treating all three independent variables (calcium concentration, soil concentration, and soil type) as non-metric factors, and employing the sum of squares of the three-variable interaction to produce the residual error term (i.e. SPSS Option 4). The dependent variable was the average difference in TDS between triplicate determinations on each experimental flask and a corresponding single control flask of the same calcium concentration but without sediment. The TDS in one control flask (150 mg/l Ca^{++} hardness) was adjusted upward from 487 to 515 mg/l to put it on a TDS/ Ca^{++} hardness concentration curve (Figure 6.11) that fit both the remaining three control data points and also the expected relationship between the initial TDS concentration and the calcium chloride spike used to increase the salinity.

The results of the ANOVA are shown in Table 6.3. A highly significant interaction ($\alpha = 0.001$) between initial calcium concentration and the ultimate TDS concentration was the only statistically significant relationship in the analysis. There were no significant interactions between the independent factors, and the entire model accounted for 71 percent (r^2) of the variation in TDS (of which 67 percent, ETA^2 , was accounted for by the calcium concentration). As pointed out above, there were no statistically significant effects of either sediment type or initial sediment concentration on net TDS accumulation or release.

Counterintuitively, however, the effect of increasing calcium concentration on the TDS was to cause salinity removal at the lower concentrations and salinity increases at higher concentrations (Figure 6.10 and 6.11). Such a phenomenon could only be caused by the indifferent ion effect, because any increase in calcium ion concentration should force its removal from the liquid phase, either through ion exchange or precipitation. The latter probability is unlikely, in that the measured calcium concentrations in the control flasks corresponded to the expected concentrations, except in the 300 mg/l control, which showed an analytical concentration of only 282 mg/l. Because the TDS/calcium ratio was "correct" in this control flask (Figure 6.11), however, the calcium value is not likely to be in error (i.e., the analytical concentration does not equal the true concentration), but it is impossible to separate the possibility that

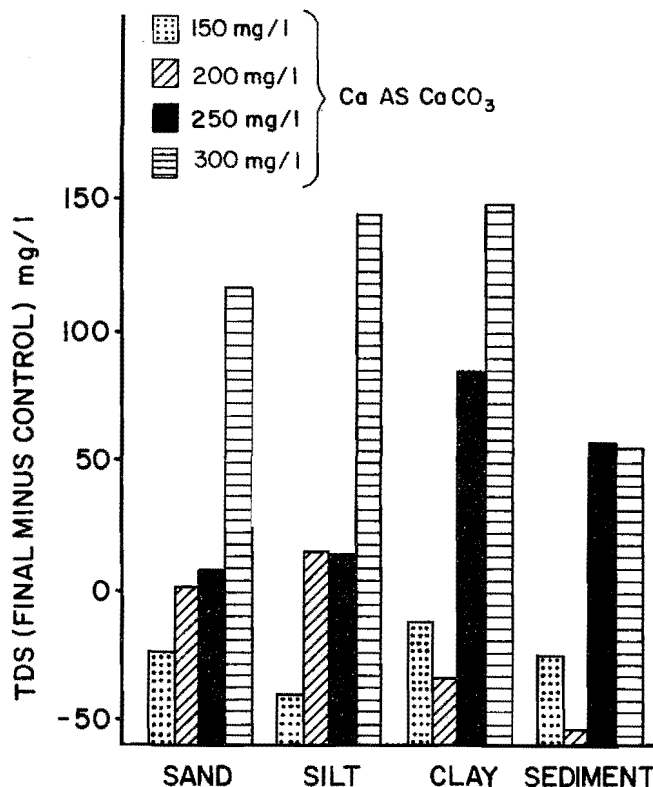


Figure 6.10. Change in TDS 48 hours after addition of various Bear River watershed soils to synthetic Oneida Reservoir water containing different concentrations of Ca^{++} (expressed as mg/l CaCO_3). Both 0.5 and 1.0 g additions have been combined.

some precipitation occurred from that of an error made in preparing the media.

If the increasing TDS concentrations were the result of calcium ion exchange, increasing calcium ion concentration could lead to an increase in TDS, provided that the counter ions have a larger equivalent mass than calcium (e.g. $\text{Na}^+ = 23$ mg/meq, $\text{k}^+ = 39$ mg/meq versus 20 mg/meq for Ca^{++}). However, a TDS change of 115 mg/l \times 0.07 l = 8.2 meq, such as occurred in the 300 mg Ca^{++} /l spike, would entail a cation exchange capacity of $(8.2 \div (23-20)) = 2.7$ meq per 0.5 g of soil which is far too high for even an expandable lattice clay (~ 100 meq/100 g). Also, ANOVA analyses of calcium, sodium, magnesium, potassium, and pH failed to show a significant effect of initial calcium concentration on the parameter concentration following incubation. The only remaining possibility that appears likely is that increasing the ionic strength alone increases the solubility of some unmeasured constituent (e.g. aluminum, silica, organic matter, etc.) which leads to the observed increase in TDS. Additional work is needed to clarify the role or existence of such a mechanism.

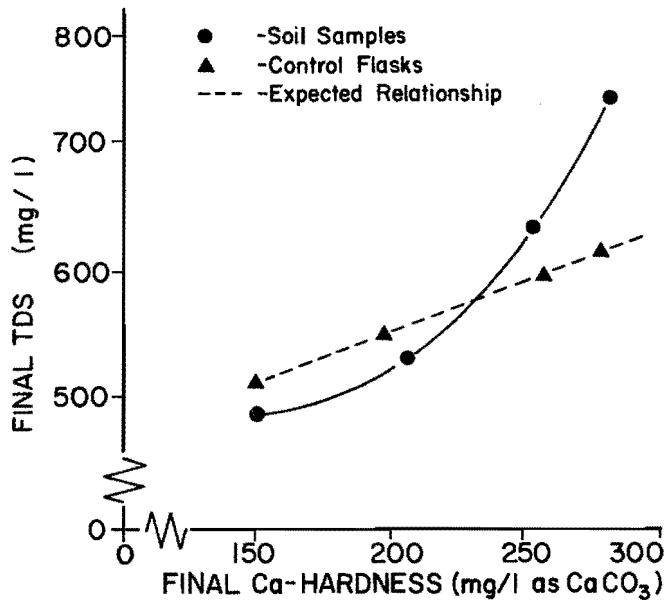


Figure 6.11. Final TDS and calcium hardness concentrations in experimental flasks containing various amounts and types of soil and in soil-free control flasks incubated with various initial concentrations of calcium ion. The dotted line indicates the expected relationship in the absence of biogeochemical interactions affecting calcium and TDS differentially.

Perhaps the most significant result of this experiment was that, at calcium concentrations typical of Bear River or Oneida Narrows Reservoir water suspended, particulates could act only as a minor source or sink for salinity. The curve in Figure 6.11 indicates a calcium concentration of approximately 90 mg/l as Ca⁺⁺ as the line of demarcation between contribution and removal. At lower calcium values (150 and 200 mg/l as CaCO₃), removals of approximately 3-5 percent are indicated, whereas at 250 mg/l as CaCO₃ (100 mg/l as Ca⁺⁺, which is typical of late summer values), a contribution of 7 percent is indicated. Clearly the results of such a process, if controlled by water hardness alone, are not highly significant in the Upper Bear River, and would be more

likely to contribute salinity, rather than remove it, in the harder waters downstream.

It is worth noting that, although the differences were not statistically significant, the various soil samples tested showed unusual patterns, and two interaction terms between amounts of sediment in the flask and initial calcium concentrations were statistically significant at the $\alpha = 0.05$ level. The differences in pH between soil types was also highly significant. In spite of the statistical relationships, however, most constituent differences were within the range of precision of the analytical technique. The conclusion in this case is that, although one cannot reject the hypothesis that two treatments give different results, the explanation for these complexities may well lie more with the day-to-day vagaries of the chemical analyses than with the actual biogeochemistry. Very careful experimental design, sampling, and analytical quality control will likely be necessary to truly unravel such apparently complex chemical behavior.

Summary

The results of the laboratory experiments indicate the calcium carbonate precipitation brought about by photosynthesis is the most likely salinity removal mechanisms in Oneida Narrows Reservoir, and that heterogeneous precipitation or ion exchange of hardness-causing ions may be of secondarily (and likely minor) importance. Slight magnesium removal may occur through coprecipitation as magnesian calcite, or may result from an incongruous precipitation process. Coagulation, either through biological mechanisms or saline groundwater inputs, does not appear to be detectable in the river/reservoir system studied. Biological assimilation could only be studied in Aufwuchs communities, and in these the actual assimilation of hardness-causing ions could only account for a small fraction of the amount removed from the water column.

In general, the extent of salinity removal, relative to the original concentrations in the systems studied, was minor. Neither precise stoichiometric nor kinetic models with good predictive power could be derived from the experiments, owing to the number of uncontrolled variables changing over sampling periods that were far apart, relative to the rate of reactions. Nonetheless, trends were clear, and no thermodynamic rules were violated.

Table 6.3. Results of multiple ANOVA analysis of changes in TDS concentration relative to controls following incubation with different amounts of soils and sediments from the Bear River watershed in synthetic river water of varying initial calcium hardness.

ANALYSIS OF VARIANCE*				
Source of Variation	DF	Mean Square	F	Signif of F
TDS by Conc Amt Type Calcium Hardness Amount of Soil Soil Type				
Main effects	7	15529.281	10.089	0.001
Conc	3	34073.281	22.137	0.000
Amt	1	318.781	0.207	0.660
Type	3	2055.448	1.335	0.323
2-Way Interactions	15	2021.098	1.313	0.348
Conc Amt	3	765.531	0.497	0.693
Conc Type	9	2217.142	1.440	0.298
Amt Type	3	2688.531	1.747	0.227
Explained	22	6319.156	4.106	0.017
Residual	9	1539.170		
Total	31	4931.418		

Multiple $r^2 = 0.711$

*SPSS ANOVA routine, Option 4 (Nie et al. 1975).

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Increasing salinity in the Lower Colorado River Basin promises to cost almost a half-million dollars annually for each milligram per liter increment and promises to pose problems with international treaty commitments in the near future. Exploitation of naturally occurring salinity removal processes have been suggested in developing lower cost management options to substitute, in part, for more expensive structural measures. The purpose of this study was to review the evidence for natural salinity removal processes in western reservoirs and to conduct laboratory and *in situ* investigations of their controlling factors. The field investigations were accomplished by using Oneida Narrows Reservoir, in southeastern Idaho, as a model system.

Investigations of chemical changes occurring as a result of impoundment have been conducted for decades, but salinity removal has not often been systematically examined in such studies. Typically such studies have indicated that the most likely range of gross salinity removal is between 0 and 10 percent of the annual input load. They further suggest that salinity removal mechanisms such as calcium carbonate precipitation often only partially offset salt loading from the reservoir sediment, the net result being a gross increase in salinity downstream. Overall, however, the vagaries of sampling to determine water column salt storage and the failure to account for bank storage, together with often necessarily unfounded assumptions and unnecessarily unclear calculations, cast doubt as to the validity of these conclusions. There is little doubt that calcium carbonate precipitation occurs, but its quantitative effect is not clear from past studies. If a generalization can be made from the results of the previous studies, it would be that calcium carbonate precipitation is more important in the newer Colorado River mainstem reservoirs (Flaming Gorge and Lake Powell) than in the older Lake Mead. Other ions, except possibly silica, do not appear to be removed.

Examination of the biogeochemical literature indicates that the four types of processes most likely to contribute significantly to natural salinity removal in reservoirs are homogeneous precipitation; coprecipitation processes that include clay diagenesis and ion exchange reactions which

replace lighter counter ions with heavier ones; coagulation, including biocoagulation; and bioassimilation followed by sedimentation or emigration. Calcite precipitation, driven either by photosynthetically induced increases in pH or by increasing temperature, has been amply demonstrated in natural lakes, although the stoichiometry does not always correspond to that predicted. Homogeneous precipitation of other carbonates and authigenic precipitation of clay minerals do not appear to be important in relatively fresh waters.

Of the remaining processes, less is known. Past research indicates that incongruous clay mineral diagenesis is restricted to sediment environments, except in high magnesium or particularly saline waters. Coagulation, either as a result of the input of saline spring water or through the trapping effect of bacterial fibrillar colloids, has not been thoroughly investigated in fresh waters. Bioassimilation may be important in controlling chemicals incorporated into refractory hard parts, but emigration is unlikely to be of sufficient magnitude to represent an important chemical sink in saline waters.

In order to test hypotheses relating to the occurrence and relative importance of these mechanisms, a combined field and laboratory study was conducted. In order to facilitate frequent site visits, Oneida Narrows Reservoir on the Bear River in southeastern Idaho was chosen as the study site. Results of field studies indicated a potential for calcite precipitation, based on thermodynamic supersaturation, almost everywhere below Soda Point in the Bear River during the summer. The supersaturation was principally the result of the relatively high pH acting in concert with high summertime water temperatures.

Although mass balances could not be done, significantly lower total dissolved solids and alkalinity at the most downstream, relative to upstream stations indicated the possibility of calcite precipitation *in situ*. It is not clear whether precipitation occurs instream by periphyton or in the reservoir by phytoplankton or both. The absence of changes in calcium concentration and the increasing sulfate concentrations indicate potential gypsum dissolution, although the

stoichiometry is not exactly correct. There is evidence for the input of saline spring water, both in Gem Valley and also from Maple Grove hot springs. Although these springs cause the concentrations of sodium and chloride to increase, there is insufficient information on spring discharge to determine whether some fraction of these ions are removed *in situ*. The chemical effects of input of Maple Grove hot springs water to the Oneida Narrows Reservoir is not apparent several hundred yards downstream, but it is not known whether this is merely the result of simple dilution of a relatively small input. Thermodynamic analyses, differential filtration experiments, and sediment analyses fail to support the operation of incongruous precipitation processes, coagulation, or biogenic silica deposition.

Laboratory studies included experiments designed to demonstrate the possibilities of aphotic, heterogeneous precipitation, photosynthetically driven calcite precipitation, and precipitation or coagulation resulting from changes in ionic strength resulting from saline spring inputs. Two-phase flask incubations or three-phase laboratory microcosms were used, depending on the appropriateness of a sediment phase. Incubation of water in two separate experiments demonstrated the apparent absence of coagulation in response to changing ionic strength, and further indicated the absence of a significant concentration (> 1 mg/l) of submicron particles, at least during the summer.

Results of an extensive three phase laboratory microcosm experiment indicated the likelihood of biogenically driven calcite precipitation, accompanied perhaps by some magnesium coprecipitation. Five of six microcosms exposed to continuous light showed stoichiometric removal of calcium and carbonate. One light microcosm showed lower Aufwuchs biomass and correspondingly lower calcite precipitation. The light microcosms showed secular increases in pH which increased calcite supersaturation which was subsequently relieved by precipitation. Dark microcosms showed a slight, albeit significant, loss of calcium to the sediments, returning the supersaturation index to near unity. The results of these experiments indicate little evidence for inhibition of efficient calcite precipitation kinetics by organics, but the importance of such inhibition in Aufwuchs communities was not addressed. There was no evidence for removal of other ions except for silica which was presumably assimilated by diatoms in the Aufwuchs assemblage. The net result was a 25 percent decrease in TDS in the light microcosms.

Results of a second microcosm experiment also indicated the operation of calcite precipitation, removing approximately 10 percent of the TDS input over 4 days under continuous light. Although there was a suggestion that addition of Bear River water

to the microcosms, rather than reservoir water, may somewhat enhance calcium removal, the results were not statistically significant. The effect that occurred was perhaps caused by addition of a limiting nutrient that stimulated phytoplankton growth. It is interesting to note that, despite higher concentrations of most ions in the Bear River water, microcosms receiving Bear River replacement water tended toward the same final concentrations of calcium, magnesium, and silicon as did those receiving reservoir water. Such results suggest (but do not prove) the operation of biogeochemical homeostatic processes *in situ*, which is somewhat borne out by the reservoir synoptic studies. A final experiment (IV) conducted without a sediment phase, also hinted at calcite precipitation as the only operant salinity removal mechanism, and also pointed to the lack of importance of saline spring water in enhancing or retarding precipitation processes.

The final experiment (V) described here revealed the complexity, and often counter-intuitive behavior, of salinity with respect to particulates. In synthetic Bear River water, low calcium concentrations in the water led to suspended soils and sediments removing salinity, whereas at higher concentrations these particulates acted as a salinity source. In both cases, the relative impacts were minor (< 10%), but these experiments suggest caution in designing particle-salinity exchange experiments with respect to choice of ions used and measurement procedures.

In summary, the results of all the experiments conducted, *in situ* studies, and literature reviewed suggest that some natural salinity removal occurs in western reservoirs as a result of calcium carbonate precipitation. Smaller amounts of silica and magnesium may be removed through coprecipitation. In general it has not been established that the magnitude of salinity removal by natural processes in reservoirs is large, although it can be argued that even minor amounts of removal are valuable to downstream users. The potential for management of natural salinity processes, and some potential environmental impacts, will be considered, prior to suggesting some avenues for further research.

Caveats Regarding Managing Calcite Precipitation as a Salinity Removal Process

As pointed out in Chapter II, even a small reduction in salinity has been predicted to save \$448 million (1980 dollars) in downstream damages annually per mg/l removed above Imperial Dam (Kleinman and Brown 1980). This calculation is subject to caveats that 1) without mitigation the salinity at Imperial Dam will reach 1225 mg/l; 2) municipi-

pal costs exhibit linear increments of \$240,500 per mg/l (1976 dollars) over the 800-1400 mg/l range of salinity; and 3) that agricultural costs can be directly related to TDS and exhibit an indirect cost multiplier of 5.32 (Kleinman and Brown 1980). While the foregoing analysis of economic impacts of salinity in the Colorado is likely the best possible given the available data, the savings resulting from the differential removal of calcium ion must be interpreted with some caution.

As to damage to materials, corrosion is the normal response to increasing concentrations of monovalent cations and magnesium and the nonalkaline anions, while carbonate hardness is associated with scaling of pipes, boilers, water mains, and so on. Because municipal costs are based on replacement of corroded or scaled fixtures, the removal of calcium (relative to sodium) may increase or decrease the \$240,500 per mg/l cost, depending on the relative damage of scaling versus corrosion, which was not considered in the analysis.

If water treatment were upgraded to avoid damages, however, natural calcium removal would be much less valuable than sodium removal if damages from the two effects are otherwise assumed to be equal. While hardness and carbonate alkalinity can be removed through conventional lime-soda softening, sodium, chloride, and sulfate must be removed through more expensive desalination procedures such as reverse osmosis. Thus although reduction of salinity involves the same thermodynamic cost per mole of solute removed (usually measured using the corresponding change in vapor pressure of the solution), some removal processes require higher quality energy and more intensive (and thus expensive) technology.

Agricultural damages present thornier problems. The value of irrigation water depends not only on its salinity, but also on the ratio of sodium to divalent cations. Because sodium causes alkalization and loss of tilth of clayey soils, reduction of salinity through removal of divalent ions alone, without a corresponding decrease in sodium, will increase the exchangeable sodium percentage and thus harm the soil structure. The sodium absorption ratio, SAR (USDA 1954) has long been used in the U.S. to quantify this phenomenon. The ratio:

$$SAR = \frac{\text{meq/l Na}^+}{\sqrt{\frac{\text{meq/l Ca}^{++} + \text{Mg}^{++}}{2}}} \dots \dots \dots (7.1)$$

should not exceed 6 in the range of salinity resulting in an electrical conductivity of 750 μ mho/cm. Reynolds and Johnson (1974) report values of approximately 4 meq/l for sodium and calcium, and 2 meq/l for magnesium in Lake Powell in summer. If half of the

calcium were removed by precipitation (representing a decrease in 100 mg/l salinity), the SAR would be increased from 2.3 to 2.8, a value still well within the low salinity range. Similarly, the calcite precipitation occurring in the Group I microcosms increased the SAR only from 0.9 to 1.2. Nonetheless, removal of calcium relative to magnesium will produce a poorer quality irrigation water, despite its lower salinity, in that more must be applied in order to enjoy the same benefit when leaching to reclaim saline soil. For the sake of argument, if we assume that removing calcium alone results in no benefits, then the savings are reduced 30 percent (agricultural losses plus indirect effects) to \$313,400 (1980) per mg/l (cf. Kleinman and Brown 1980, p. 18-19). Nonetheless, the savings per mg/l remain substantial.

Assuming then that calcium carbonate removal is desirable the method by which it is to be removed requires some thought. Temperature and pH appear to be the factors which most strongly affect the saturation index of calcite. Table 7.1 indicates the results of methodically varying temperature, pH, and various ions of interest which either contribute to or compete for calcium and carbonate ions. Temperature acts to force the inorganic carbon equilibrium toward carbonate, and less substantially to decrease the calcite solubility product, while pH also contributes to the former process. Calcium and alkalinity of course provide the constituent ions of calcite, while magnesium competes for carbonate through ion pairing. Sulfate and chloride primarily interfere with precipitation through the diverse ion effect, although their impact is relatively slight.

The analysis in Table 7.1 suggests that promising methods of calcite removal include maintaining a high pH through encouraging photosynthesis, and maintaining a high surface temperature through release of flows from deep within the reservoir. This last technique, however, would significantly increase water loss from evaporation.

Encouragement of algal growth and high pH will likely lead to dominance by nuisance bluegreen algae (Shapiro 1973), and the resultant organic loading to the hypolimnion may cause anoxia. Conventional wisdom presently holds that such anoxia leads to solubilization and release of additional phosphorus, thus exacerbating and perpetuating eutrophic conditions in the reservoir (Mortimer 1971, Imboden 1974). Of course this also results in the discharge of cold, anoxic water from deep in the reservoir, which must be mechanically aerated if it is to support a cold water fishery in the tailwater. Clearly such side effects need to be carefully weighed (or ameliorated) against the benefits of in situ water softening.

The results of the study by Reynolds (1978) suggest an innovative possibility with

Table 7.1. Effect of varying physical and chemical parameters of Oneida Narrows Reservoir water on the calcite saturation index as determined by equilibrium modeling (Appendix B). The underlined value was held constant when evaluating the remaining variables.

Parameter	Value	Calcite Saturation Index*
Temperature	0 C	1.32
	5	1.65
	10	2.05
	15	2.55
	20	3.22
	<u>25</u>	3.89
pH	7.5	0.52
	7.7	0.82
	7.9	1.29
	8.1	2.04
	8.3	3.22
	<u>8.5</u>	5.07
Calcium	59 mg Ca/l	2.67
	84	3.22
	<u>109</u>	3.63
Alkalinity	176 mg/l as CaCO ₃	2.28
	252	3.22
	<u>328</u>	4.14
Magnesium	6.6 mg/l	3.63
	16.6	3.22
	<u>26.6</u>	2.90
Sulfate	16 mg/l	3.25
	40	3.22
	<u>64</u>	3.19
Chloride	10.2 mg/l	3.23
	25.6	3.22
	<u>64</u>	3.21

*Jacobsen and Langmuir (1974)

less drastic secondary impacts. Reduction of the input of polyphenolic organic molecules through nonpoint source management practices that reduce forest floor leaching could remove an important natural inhibitor to precipitation of the supersaturated calcite and promote a rapid spiral crystal growth mechanism. The relative merit of reducing the amount of dilution water transporting the organic compounds, or alternatively treating or diluting it during periods critical to calcite precipitation, would have to be weighed against the value of the salinity removal to downstream users.

One remaining problem involves the fate of the calcite precipitated in the epilimnion of the reservoir. Calcite crystals settling into a dark, CO₂ rich, undersaturated hypolimnion may redissolve to some extent and

be released downstream through the deep discharge. Such a mechanism operates at a much grander scale in the ocean (e.g., Edmund 1974). Although this problem is exacerbated in cold, saline, anoxic waters, which favor slow settling rates and carbonate dissolution, Kelts and Hsü (1978) found that only 10 percent of the calcite typically dissolves during settling through the 120 m hypolimnion of Lake Zurich in Switzerland.

A potentially very valuable tool for assessment of enhancement (or amelioration) of natural salinity removal processes is construction of a biogeochemical model linked to a finite element hydraulic reservoir model that would apportion and mix waters of different temperature, salinity, and chemical composition among the various depth zones of a reservoir according to density and momentum. A phytoplankton model could then be used to drive surficial pH changes, and sinking, ion exchange, coagulation, and kinetic/equilibrium models used to predict chemical changes in the resultant water masses. The compilations by Canale (1975), Chadderton and Shane (1978) and Scavia and Robertson (1979) suggest that such modeling efforts are within reach of the present state of the limnological art.

Suggestions for Further Research

Further research should revolve around three complementary goals: 1) assessment of process rates and mass balance *in situ* in systems of interest; 2) controlled laboratory studies, again using local water, sediments, etc., to formulate kinetic expressions; and 3) construction of multidisciplinary, physical-biogeochemical reservoir and river models that integrate the effects of various individual processes. A list, by no means complete, of specific topics should include:

I. Assessment:

1. Measuring water column storage in the system of interest of constituent ions.
2. Measuring bank storage and migration rates and directions of salts dissolved in bank storage waters.
3. Measuring sedimentation rates of biogeochemical constituents such as diatom tests and autochthonous calcite crystals.
4. Measuring supersaturation throughout the season *in situ* using carbonate saturoimeters.
5. Collecting and correlating daily (diel) primary production and calcite precipitation rates.
6. Determining the content of ion exchange sites on suspended particulates as they move

longitudinally and vertically through river/reservoir systems.

II. Laboratory studies:

1. Conduct radiocarbon tracer studies to determine why carbonate/organic carbon stoichiometry often falls below the predicted level.
2. Examine the exchange of ions, particularly calcium magnesium, alkalinity, and sulfate between surficial sediments and overlying water in microcosms (the gypsum dissolution/calcite precipitation model is particularly interesting).
3. Examine the effect on calcite precipitation on consumer controlled (three-component) versus producer controlled (two-component) microcosms.

III. Modeling:

1. Construct and verify a hydraulic-biogeochemical reservoir model. It should include the following components:
 - A. Hydraulic model (driven by density and momentum).
 - B. Equilibrium/kinetic model (driven by constituent activities).
 - C. Phytoplankton model (driven by isolation, extinction

coefficient, and a limiting nutrient).

- D. Heterogeneous equilibrium/kinetic model (driven by solid-solution concentration gradients of counter ions and coagulation models).

A general observation that is particularly important with respect to all of these research suggestions is the need for special care and expertise at all levels of investigation. Chemical analyses must be done immediately and with special attention to calibration and quality control, and the time intervals over which changes are to be measured may range from minutes to hours. The sensitivity of the calcite saturation index to changes in pH and temperature indicate the need for much caution. Field meters should be carefully calibrated, and both alkalinity and acidity should be titrated in the field as soon as possible following collection.

Regarding mass balance calculations and the chemical analyses upon which they are based, one should bear in mind that a reduction of 10 mg/l of salinity in the Lower Colorado River may save \$5 million annually. However, demonstrating a 10 mg/l decrease against a background of 700 mg/l requires the utmost care in analysis and replication. Although one cannot solve the problem of demonstrating a secular trend of this magnitude against the "noise" level characteristic of natural environments, such demonstrations may be possible during short duration laboratory or in situ studies. We feel that the time is at hand for such careful work.

REFERENCES

- Ackerman, W., G. White, and E. Worthington [eds.]. 1973. Man-made lakes: their problems and environmental effects. Am. Geophys. Union, Washington, D.C.
- Anderson, E., and A. Pritchard. 1960. Circulation and evaporation. In: W. Smith et al. [eds.]. Comprehensive survey of sedimentation in Lake Mead, 1948-1949. U.S. Geol. Surv. Prof. Paper 295, pp. 125-148. Washington, D.C.
- APHA. 1975. Standard methods for the analysis of water and wastewater, 14th Ed. New York.
- Berner, R. 1975. The role of magnesium in the crystal growth of calcite and aragonite from seawater. *Geochim. Cosmochim. Acta* 39: 489-504.
- Berner, R. 1980. Early diagenesis. Princeton Univ. Press, Princeton, N.J.
- Bitton, G., and R. Mitchell. 1974. Effect of colloids on the survival of bacteriophages in water. *Water Res.* 8:227-229.
- Boesch, D. F. 1977. Application of numerical classification in ecological investigations of water pollution. EPA-600/3-77-033. Washington, D.C.
- Bolke, E. L. 1979. Dissolved oxygen depletion and other effects of storing water in Flaming Gorge Reservoir, Wyoming and Utah. USGS Water Supply Paper 2058. Washington, D.C.
- Bolke, E., and K. Waddell. 1975. Chemical quality and temperature of water in Flaming Gorge Reservoir, Wyoming and Utah, and the effect of the reservoir on the Green River. U.S. Geol. Surv. Water Supply Paper 2039-A. Washington, D.C.
- Bowen, G. 1980. Biogeochemistry of the elements. Academic, New York.
- Brunskill, G. 1969. Fayetteville Green Lake. New York. II. Precipitation and sedimentation of calcite in a meromictic lake with laminated sediments. *Limnol. Oceanogr.* 14:830-847.
- Canale, R. P. [ed.]. 1976. Modeling biochemical processes in aquatic ecosystems. Ann Arbor Science, Ann Arbor, Mich.
- Chadderton, R., and R. Shane. 1978. A model of pH determining parameters in impoundments. *Water Resources Res.* 14:1357-1369.
- CRC. 1976. Handbook of chemistry and physics. 57th Edition. CRC Press, Cleveland.
- Dean, W. E., and E. Gorham. 1976. Major chemical and mineral components of profundal surface sediments in Minnesota lakes. *Limnol. Oceanogr.* 21:259-284.
- DOI. 1981. Quality of water: Colorado River Basin. Proc. Rept. No. 10, U. S. Department of Interior, Washington, D.C.
- Duffer, W. R., and C. Harlin. 1971. Changes in water quality resulting from impoundment. 16080 GGH 08/71. U. S. Environmental Protection Agency. Washington, D. C.
- Edmund, J. 1974. On the dissolution of carbonate and silicate in the deep ocean. *Deep Sea Res.* 21:455-480.
- Edzwald, J., J. Upchurch, and C. O'Melia. 1974. Coagulation in estuaries. *Environ. Sci. Technol.* 8:58-63.
- Eisenreich, S. 1981. Atmospheric inputs of pollutants to natural waters. Ann Arbor Science, New York.
- Emerson, S. 1975. Chemically induced CO₂ gas exchange in a eutrophic lake: A general model. *Limnol. Oceanogr.* 20:743-753.
- Emerson, S., and G. Widmer. 1978. Early diagenesis in anaerobic lake sediments. II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. *Geochim. Cosmochim. Acta.* 42:1307-1316.
- EPA. 1973. Biological field and laboratory methods for measuring the quality of surface waters and effluents. EPA 670/4-73-001. U. S. EPA, Washington, D. C.
- EPA. 1979. Methods for chemical analysis of water and wastes. EPA-625/6-79-003a. EMSL, U.S. EPA, Cincinnati.
- Ferrante, J., and J. Parker. 1977. Transport of diatom frustules by copepod

- fecal pellets to the sediments of Lake Michigan. *Limnol. Oceanogr.* 22:92-98.
- Folk, R. 1974. The natural history of crystalline calcium carbonate: effect of magnesium content and salinity. *J. Sed. Petrol.* 44:40-53.
- Frey, D. 1974. Paleolimnology. *Mitt. Int. Ver. Limnol.* 20:95-123.
- Garrels, R., and C. Christ. 1965. Solutions, minerals, and equilibria. Harper and Row, New York.
- Garrels, R., and F. Mackenzie. 1967. Origin of the chemical compositions of some springs and lakes. In: W. Stumm [ed.] *Equilibrium Concepts in Natural Water Chemistry.* ACS Symp. Ser. No. 67. Washington, D. C. pp. 222-242.
- Garrels, R., M. Thompson, and R. Siever. 1960. Stability of some carbonates at 25°C and one atmosphere total Pressure. *Am. Jour. Sci.* 258:402-418.
- Gunnison, Douglas, and Martin Alexander. 1975. Resistance and susceptibility of algae to decomposition by natural microbial communities. *Limnol. Oceanogr.* 20:64-70.
- Hahn, H., F. Kaser, and R. Klute. 1980. Modeling particulate transport in impounded rivers. In: M. Kavanaugh and J. Leckie [eds.]. *Particulates in Water.* Adv. Chem. Ser. 189:213-232. Am. Chem. Soc., Washington, D.C.
- Hannan, H. 1979. Chemical modifications in reservoir-regulated streams. In: R. Ward and S. Stanford [eds.]. *The Ecology of Regulated Streams.* Plenum, New York. pp. 75-94.
- Hannan, H., and L. Broz. 1976. The influence of a deep storage and an underground reservoir on the physicochemical limnology of a permanent central Texas river. *Hydrobiologia* 51:43-63.
- Hannan, H., I. Fuchs, and D. Whitenberg. 1979. Spatial and temporal patterns of temperature, alkalinity, dissolved oxygen, and conductivity in an oligomesotrophic deep-storage reservoir in Central Texas. *Hydrobiologia* 66:209-221.
- Hannan, H., and W. Young. 1974. The influence of a deep-storage reservoir on the physico-chemical limnology of a central Texas river. *Hydrobiologia* 44:177-207.
- Harned, H., and S. Scholes, Jr. 1941. The ionization constant of HCO_3^- from 0 to 50°. *Am. Chem. Soc. Jour.* 63:1706-1709.
- Hasset, J., and J. Jurinak. 1971. Effect of ion pair formation on calcium and magnesium ion activities in aqueous carbonate solutions. *Soil Sci.* 111:91-94.
- Haws, F., and T. Hughes. 1973. Hydrologic inventory of the Bear River study unit. PRWG40-8. Utah Water Res. Lab., Logan.
- Hem, J., and C. Lind. 1974. Kaolinite synthesis at 25°C. *Science* 184:1171-1173.
- Hendrick, J. 1973. Technique for modeling reservoir salinity. *Hydrol. Pap.* 62. Colorado State University, Fort Collins.
- Hill, R., E. Israelsen, J. Riley. 1973. Computer simulation of the hydrologic and salinity flow systems within the Bear River basin. PRWG104-1. Utah Water Research Lab., Logan, Utah.
- Howard, C. 1960. Chemistry of the water. In: W. Smith et al. [eds.]. *Comprehensive survey of sedimentation in Lake Mead, 1948-1949.* U.S. Geol. Surv. Prof. Paper 295. Washington, D.C. pp. 115-124.
- HP. 1977. HP-19C/HP-29C solutions-statistics. Hewlett-Packard, Houston.
- Hutchinson, G. 1975. A treatise on limnology. V.3. *Limnological botany.* John Wiley, New York.
- Imboden, D. 1974. Phosphorus model of lake eutrophication. *Limnol. Oceanogr.* 19:297-304.
- Ingle, S., J. Keniston, and D. Schults. 1980. REDEQL.EPAK. EPA-600/ 3-80-049. U.S. EPA, Corvallis, Or.
- Ingle, S., M. Schuldt, and D. Schults. 1978. A user's guide for REDEQL.EPA. EPA 600/3-78-024. U.S. EPA, Corvallis, OR.
- Iorns, W., C. Hembree, and G. Oakland. 1965. Water resources of the Upper Colorado River Basin. Technical Report, Prof. Paper 441. U. S. Geol. Surv., Washington, D. C.
- Jacobsen, R., and D. Langmuir. 1974. Dissociation constants of calcite and CaHCO_3^+ from 0°-50°C. *Geochim. Cosmochim. Acta* 38:308-318.
- Jenne, E. 1977. Trace element sorption by sediments and soil-sites and processes. In: W. Chappell and K. Peterson [eds.]. *Molybdenum in the environment.* Marcel Dekker, New York. pp. 425-553.
- Jones, B. F., and C. J. Bowser. 1978. The mineralogy and related chemistry of lake sediments. In: A. Lerman [ed.]. *Lakes Chemistry Geology Physics.* Springer-Verlag. pp. 179-235.
- Kavanaugh, M., and J. Leckie. 1980. Particulates in water. *Adv. Chem. Ser.* 189. Am. Chem. Soc., Washington, D. C.

- Kelts, K., and K. J. Hsu. 1978. Freshwater carbonate sedimentation. In: A Lerman [ed.]. *Lakes Chemistry Geology Physics*. Springer-Verlag. pp. 295-324.
- Kindle, E. 1929. A comparative study of different types of thermal stratification in lakes and their influence on the formation of marl. *J. Geol.* 37:150-157.
- Kittrick, J. 1970. Precipitation of kaolinite at 25°C and 1 atm. *Clays Clay Min.* 18:261-267.
- Kleinman, A., and F. Brown. 1980. Colorado River salinity economic impacts on agricultural, municipal, and industrial users. Bureau of Rec., U. S. Dept. of Interior, Washington, D. C.
- Kramer, J. 1967. Equilibrium models and composition of the Great Lakes. In: W. Stumm [ed.]. *Equilibrium concepts in natural water systems*. Adv. Chem. Ser. 67, pp. 243-254. Am. Chemical Soc., Washington, D. C.
- Krauskopf, K. 1978. *Introduction to geochemistry*. 2nd ed. McGraw-Hill, New York.
- Liss, P. S. 1976. Conservative and non-conservative behavior of dissolved constituents during estuarine mixing. In: J. Burton and P. Liss [eds.]. *Estuarine Chemistry*. Academic Press. pp. 93-130.
- Marshall, K. 1971. Sorptive interactions between soil particles and microorganisms. In: A. McLaren and J. Skujins [eds.]. *Soil Biochemistry*. Vol. 2. Marcel-Dekker, New York.
- Massalski, A., and G. Leppard. 1979a. Survey of some Canadian lakes for the presence of ultrastructurally discrete particles in the colloidal size range. *J. Fish. Res. Bd. Can.* 36:906-921.
- Massalski, A., and G. Leppard. 1979b. Morphological examination of J. Fis. Res. Bd. Can. 8:922-938.
- Mayer, L. 1977. The effect of Lake Powell on dissolved silica cycling in the Colorado River. Lake Powell Research Project Bull. 42. NSF-RANN. Washington, D.C.
- Megard, R. 1968. Planktonic photosynthesis and the environment of calcium carbonate deposition in lakes. Interim. Rept. No. 2. *Limnological Res. Cent.*, Univ. of Minnesota, Minneapolis.
- Menzie, C. 1980. Potential significance of insects in the removal of contaminants from aquatic systems. *Wat. Air Soil Poll.* 13: 473-479.
- Merritt, D. H., and N. M. Johnson. 1977. Advective circulation in Lake Powell, Utah-Arizona. *Lake Powell Res. Proj. Bull.* 61. NSF-RANN, Washington, D. C.
- Mortimer, C. 1971. Chemical exchanges between sediments and water in the Great Lakes - speculations on possible regulatory mechanisms. *Limnol. Oceanogr.* 16:387-404.
- Müller, G., and U. Foerstner. 1973. Recent iron ore formation in Lake Malawi, Africa. *Mineral. Deposita.* 8:278-290.
- Müller, G., G. Irion, and U. Foerstner. 1972. Formation and diagenesis of inorganic Ca-Mg carbonates in the lacustrine environment. *Naturwissenschaften* 59:158-169.
- Nancollas, G., and M. Reddy. 1971. The crystallization of calcium carbonate. II. Calcite growth mechanism. *J. Colloid Interface Sci.* 37:824-830.
- Narayanan, R., S. Padungchai, and A. Bishop. 1979. Economic evaluation of the salinity impacts from energy development: the case of the Upper Colorado River Basin. UWRL/P-79/07. Utah Water Research Laboratory, Logan.
- Nezafati, H. 1981. Salt release from suspended sediment as a source of Colorado River salinity. Ph.D. Dissertation, College of Engineering, Utah State University, Logan.
- Nie, N., C. Hull, J. Jenkins, K. Steinbrenner, and D. Bent. 1975. *Statistical package for the social sciences*. McGraw-Hill, New York.
- Obeng, L. 1969. *Man-made lakes: the Accra symposium*. Ghana Univ. Press, Accra.
- O'Melia, C. 1980. Small particles in water. *Environ. Sci. Technol.* 14:1052-1060.
- Otsuki, A., and R. Wetzel. 1973. Interaction of yellow organic acids with calcium carbonate in freshwater. *Limnol. Oceanogr.* 18: 490-493.
- Otsuki, A., and R. G. Wetzel. 1974. Calcium and total alkalinity budgets and calcium carbonate precipitation in a small hard-water lake. *Arch. Hydrobiol.* 73:14-31.
- Pagenkopf, G. 1978. *Introduction to natural water chemistry*. Marcel Dekker, New York.
- Parker, J., and D. Edgington. 1976. Concentration of diatom frustules in Lake Michigan sediment cores. *Limnol. Oceanogr.* 21:887-893.
- Patrick, R., and C. Reimer. 1966. *The diatoms of the United States*. Vol. 1. Monogr. 13. Philadelphia Acad. Nat. Sci., Philadelphia.

- Peterson, S. R., J. J. Jurinak, and R. J. Wagenet. 1981. Salt release from suspended sediment - a simulation model. Research Report 62, Utah Agricultural Experiment Station, Utah State University, Logan, Utah.
- Plummer, L. 1975. Mixing of sea water with calcium carbonate ground water. *Geol. Soc. Amer. Memoir* 142:219-235.
- Postma, H. 1967. Sediment transport and sedimentation in the estuarine environment. In: *Estuaries* (G. H. Lauff, ed.). AAAS, Washington, D. C. pp. 158179.
- Reddy, M. 1975. Kinetics of calcium carbonate formation. *Verh. Internat. Verein. Limnol.* 19:429-438.
- Reynolds, J., E. Middlebrooks, D. Porcella, and W. Grenney. 1975. Comparison of semi-continuous and continuous flow bioassays. E. Middlebrooks et al. [eds.]. *Biostimulation and nutrient assessment*. PRWG168-1. Utah Water Res. Lab, Logan. pp. 241-266.
- Reynolds, R. C. 1978. Polyphenol inhibition of calcite precipitation in Lake Powell. *Limnol. Oceanogr.* 23:585-597.
- Reynolds, R., and N. Johnson. 1974. Major element geochemistry of Lake Powell. *Lake Powell Res. Proj. Bull.* 5. NSF-RANN, Washington, D.C.
- Roche, M.-A. 1975. Geochemistry and natural ionic and isotopic tracing; two complementary ways to study the natural salinity regime of the hydrological system of Lake Chad. *J. Hydrology* 26:153-171.
- Rupp, G., and V. Adams. 1981. Calcium carbonate precipitation as influenced by stream primary production. UWRL/Q-81/01, Utah Water Res. Lab, Utah State Univ.
- Sadiq, M., and W. Lindsay. 1979. Selected standard free energies of formation for use in soil science. In: W. Lindsay [ed.]. *Chemical equilibria in soils*. John Wiley, New York. pp. 385-422.
- Scavia, D., and A. Robertson. 1979. Perspectives on lake ecosystem modeling. Ann Arbor Science, Ann Arbor, MI.
- Shainberg, I., and W. Kemper. 1967. Ion exchange equilibria on montmorillonite. *Soil Sci.* 103:4-15.
- Shapiro, J. 1973. Blue-green algae: why they become dominant. *Science* 179:382-384.
- Sheldon, R. 1972. Size separation of marine seston by membrane and glass fiber filters. *Limnol. Oceanogr.* 17:494-498.
- Smith, W., C. Vetter, and G. Cummings. 1960. Comprehensive survey of sedimentation in Lake Mead, 1948-949. U.S. Geol. Surv. Prof. Paper 295, Washington, D. C.
- Sneath, P., and R. Sokal. 1973. *Numerical taxonomy*. Freeman: San Francisco. 573 p.
- Soltero, R., and J. Wright. 1975. Primary production studies on a new reservoir; Bighorn Lake-Yellowtail Dam, Montana, USA. *Freshwater Biol.* 5:407-421.
- Soltero, R. A., J. C. Wright, and A. A. Harpestad. 1973. Effects of impoundment on the water quality of the Bighorn River. *Water Res.* 7:343-354.
- Soltero, R., J. Wright, and A. Harpestad. 1974. The physical limnology of Bighorn Lake-Yellowtail Dam, Montana: Internal density currents. *Northwest Sci.* 48:107-124.
- Sorensen, D., T. Hughes, C. Israelsen, A. Huber, E. Israelsen, M. Mandavia, and L. Baker. 1976. Inventory related to water quality objectives. Bear River Basin Type IV study, Idaho-Utah-Wyoming. Utah Water Research Lab., Logan.
- Sorokin, J. 1969. On the trophic role of chemosynthesis and bacterial biosynthesis in water bodies. In: C. Goldman [ed.]. *Primary productivity in aquatic environments*. Univ. of Calif. Press, Berkeley. pp. 187-208.
- Steeman Nielsen, E., and J. Kristiansen. 1949. Carbonic anhydrase in submersed autotrophic plants. *Physiologia Pl.* 2:325-331.
- Stocker, Z. 1972. A freezing core method for describing the vertical distribution of sediments in a streambed. *Limnol. Oceanogr.* 17:136-139.
- Stoffers, P., and R. Fischbeck. 1974. Monohydrocalcite in the sediments of Lake Kivo (East Africa). *Sedimentology* 21:163-170.
- Strong, A., and B. Eadie. 1978. Satellite observations of calcium carbonate precipitation in the Great Lakes. *Limnol. Oceanogr.* 23:877-887.
- Stumm, W. E., and J. J. Morgan. 1981. *Aquatic chemistry*. 2nd ed. Wiley Interscience.
- Sutherland, J. 1970. Silica mineral stability and mineral equilibria in the Great Lakes. *Environ. Sci. Technol.* 4:826-833.
- Symons, J. 1969. Water quality behavior in reservoirs - a compilation of published

- research papers. U.S. Dept. of Health, Education, and Welfare: Washington, D.C.
- Temple, T. 1980. The Colorado - America's hardest working river. EPA Journal 6:44-48.
- Truesdell, A., and B. Jones. 1974. WATEQ, a computer program for calculating chemical equilibria of natural waters. J. Res. U.S. Geol. Surv. 2:233-248.
- USDA. 1954. Diagnosis and improvement of saline and alkali soils. Agr. Handbook No. 60. U. S. Salinity Laboratory.
- USDI. 1977. Quality of water: Colorado River Basin Progress Rept. No. 8. U. S. Dept. of Interior, Washington, D. C.
- USDI. 1981. Quality of water: Colorado River Basin. Progress Rept. No. 10. U. S. Dept. of Interior. Washington, D.C.
- USGS. 1979. Water resources data for Utah. Water year 1978. Water Data Rept. UT-78-1. U. S. Geol. Surv., Washington, D. C.
- USPHS. 1965. Symposium on streamflow regulation for quality control. 99-WP-30. U. S. Public Health Service, Washington, D. C.
- USU. 1975. Colorado River regional assessment study. Utah Water Research Lab., Logan, Utah.
- Ward, R., and S. Stanford. 1979. The ecology of regulated streams. Plenum, New York.
- Wetzel, R. 1975. Limnology. Saunders, New York.
- Wiecherst, H., P. Sturrock, and G. Marais. 1975. Calcium carbonate crystallization kinetics. Water Res. 9:835-845.
- Wigley, T., and L. Plummer. 1976. Mixing of carbonate waters. Geochim. et Cosmochim. Acta. 40:989-995.
- Wiklander, L. 1964. Chemistry of the soil. In: F. Bear [ed]. Soil Science, 2nd ed. Reinhold, New York.
- Yariv, S., and H. Cross. 1979. Geochemistry of colloid systems. Springer-Verlag.
- Zen, E. 1972. Gibbs free energy, enthalpy, and entropy of ten rock-forming minerals: calculations, discrepancies, implications. Am. Mineral. 57:524-553.

APPENDIX A. DATA

Table A.1. Chemical concentrations in Bear River below Soda Point Reservoir (at Alexander) from Hill et al. (1973).

Date	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	pH	Temp (C)
July 8, 1971	60	56.6	14.6	3.7	332	52	37	7.5	-
Aug. 4	62	41	29.2	3.9	312	72	23	7.4	23
Sept. 9	58	60	21.2	3.9	333	60	39	7.4	17
Oct. 7	106	3.7	32	2.6	330	-	32.5	7.9	9.5
Nov. 12	99	15.3	33	3.0	304	-	33	7.9	3.5
Dec. 10	112	0	30	2.5	152	50	35	8.0	0.5
Jan. 15, 1972	112	20.5	37	3.5	320	52	34	8.0	1.2
Feb. 9	89.6	21.5	32	3.5	256	44	37	7.9	1.9
Mar. 9	144.8	2.0	28	4.4	286	44	5	8.3	2.5
April 17	100	23.9	23	3.0	278	46	3.5	8.0	7.2
May 15	32	18.5	11	1.5	92	30	15.5	8.7	11.2
June 14	96.8	0	8	1.0	376	26	22	8.2	17
July 18	62.4	35.2	34	3.0	256	48	27.9	8.2	19.1
Aug. 14	48.8	42	36	3.6	275	45	34.3	8.0	20
Sept. 9	64	34.8	-	-	297	66	30.9	8.2	14

Table A.2. Chemical concentrations in Bear River below UPLC tailrace at Oneida, data from Hill et al. (1973).

Date	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	pH	Temp (C)
July 8, 1971	63	38.7	15	5.9	220	75	52	8.3	21.3
Aug. 4	59	39.0	36	6.1	350	84	61	8.0	24.4
Sept. 9	60	36.1	33	8.9	322	90	48	8.3	19.5
Oct. 7	100	1.5	38	4.0	320	-	43	8.5	9.7
Nov. 12	95	12.3	37	3.5	284	-	37	8.4	3.3
Dec. 10	94	13.4	35	3.6	244	56	39.5	8.4	1.1
Jan. 15, 1972	102.4	19.0	37	3.5	300	45	40	8.4	0.0
Feb. 9	91.2	22.4	37	4.4	268	40	41.5	8.0	0.9
Mar. 9	109.6	18.5	33	4.4	270	44	20	8.4	3.0
April 17	44.8	39.0	-	-	228	27	-	8.5	6.8
May 15	42.4	10.3	15	2.0	104	37	17.5	8.5	12.8
June 14	68	19.0	20	3.0	214	32	10	8.4	18.9
July 18	65.2	32.1	34	0.4	242	44	28.6	8.4	12.4
Aug. 14	59.2	38.2	38	4.4	281	42	34.3	8.1	20.8
Sept. 9	67.2	33	-	-	291	62	36.7	8.6	15.4

Table A.3. Data collected on Bear River synoptic survey, June 26, 1980. Stations shown in Figure 5.1.

Station-Depth (S = surface)	TDS (GFC) mg/l	TDS (0.22 μ) mg/l	Field Conduc- tivity mho/cm (25°)	Temp °C	Hard- ness mg/l CaCO ₃	Ca ⁺⁺ mg/l	Dissolved Na mg/l	Dissolved K mg/l	Alka- linity mg/l as CaCO ₃	Chloride mg/l	Silica SiO ₄ mg/l	Sulfate mg/l	pH
1-S	350	34.8	570	18.5	280	90.3	20	3	250	23.8	4.31	36	7.73
2-S	334	33.3	544	19.3	269	81.9	19	3	236	24.2	5.43	29	8.18
3-S	347	36.4	591	18.0	284	84.0	27	3	250	27.0	7.21	39	8.54
4-S	462	45.3	749	19.4	373	107.1	33	6	344	32.4	7.62	-	7.33
5-S	349	35.3	574	19.9	301	85.1	25	4	262	25.6	8.03	34	8.12
6-S	356	33.4	560	19.6	284	86.1	24	3	264	24.7	6.46	46	8.22
7-S	348	32.8	554	20.1	292	88.2	22	4	254	24.3	7.83	31	8.15
8-S	335	32.6	-	-	286	84.0	24	4	244	26.1	2.73	31	8.37
9-S	332	34.1	615	19.7	284	87.2	25	4	246	27.0	3.02	31	8.23
9-6 m	341	34.8	571	19.7	280	92.4	26	4	248	27.4	3.89	38	8.20
10-S	323	33.8	588	20.5	282	84.0	28	4	252	25.6	2.32	40	8.30
11-S	351	32.5	583	20.5	282	83.0	27	4	248	27.4	5.43	33	8.14
12-S	344	34.1	565	20.0	288	86.1	28	4	254	28.3	6.50	33	8.18
13-S	346	34.1	575	22.0	280	86.1	28	4	258	28.3	11.00	46	8.18
14-S (bank)	339	34.5	-	-	280	84.0	28	4	247	27.9	6.09	-	8.01
14-S (center)	337	32.7	-	-	286	87.2	26	4	242	26.1	5.34	31	8.12
Hot Spring	1806	1780	3077	52°C	350	124	525	72	400	620	24.8	230	7.65

Table A.4. Data collected on Oneida Narrows Reservoir synoptic study on July 15, 1980. Stations shown in Figure 5.5.

Station - Depth S = Surface	Log #	TDS mg/l	Field Conductivity ($\mu\text{mho/cm @ } 25^\circ\text{C}$)	Temperature $^\circ\text{C}$	Total Hardness mg/l as CaCO_3	Ca^{++} Hardness mg/l Ca^{++}	Na mg/l	K mg/l	Chloride mg/l
1 - S	1	380	633	21.6	288	78.5	31	3	26.5
2 - S	2	297	660	22.0	292	73.6	35	4	32.0
Hot Springs	3	1821	3146	50.0	328	98.1	515	69	54.7
4	4	448	758	27.8	284	78.5	50	6	52.0
5 - 13 m	5	390	629	21.1	292	73.6	29	4	29.0
5 - 6 m	6	379	629	21.1	284	73.6	33	4	29.9
5 - S	7	378	632	22.5	288	81.8	33	4	29.9
8	8	403	661	20.4	284	76.9	32	4	29.0
8	9	388	649	21.2	284	72.8	31	4	29.9
8 - S	10	386	638	22.0	280	72.8	31	4	28.2
11	11	381	659	21.3	284	75.2	31	4	30.7
11	12	385	640	21.1	292	76.0	33	4	30.7
11 - S	13	380	640	22.7	292	74.4	32	4	30.7
14	14	385	630	21.8	284	70.3	32	4	29.9
14 - S	15	391	650	22.7	280	72.0	31	4	29.9
16	16	378	624	21.5	284	83.4	31	4	31.6
16 - S	17	368	641	21.8	282	70.3	30	4	30.7
18	18	390	626	21.4	284	71.1	32	4	29.9

Table A.5. Data collected on Oneida Narrows Reservoir synoptic study on August 1, 1980. Sampling stations are shown in Figure 5.6.

Station - Depth S = Surface	Log #	TDS mg/l	Field Conductivity ($\mu\text{mho/cm @ } 25^\circ\text{C}$)	Temperature $^\circ\text{C}$	pH	Alkalinity	Chloride mg/l Cl^-
1 - S	1	432	667	20.0	8.04	296	31.6
2 - S	2	471	726	19.8	7.64	298	35.9
Hot Springs	3	1859	3088	50.0	7.50	420	55.9
4 - S	4	539	893	24.0	7.76	308	61.5
5 -	5	460	724	22.0	7.79	297	33.7
5 -	6	414	721	22.5	7.89	296	35.0
5 - S	7	458	727	22.5	7.91	296	34.2
8 -	8	452	706	23.5	7.81	295	31.6
8 -	9	441	633	22.0	7.98	296	31.6
8 - S	10	453	621	22.5	8.03	294	34.2
11	11	416	615	23.0	7.91	290	31.6
11 -	12	411	621	22.5	7.80	296	31.6
11 - S	13	435	616	22.5	7.88	295	34.2
14 -	14	426	704	24.0	7.90	295	34.2
14 - S	15a	424	695	24.0	7.70	294	31.6/34.2
15	15b	-	695	25.0	-	-	33.3
16	16	404	580	25.0	8.55	306	33.3

Table A.6. Data collected on Oneida Narrows Reservoir synoptic study on August 19, 1980.

Station - Depth S = Surface	Log #	Field Conductivity $\mu\text{mho/cm @ } 25^\circ\text{C}$	Temperature $^\circ\text{C}$	pH	Alkalinity mg/l as CaCO_3
1 - S	1	725	13.8	8.22	294
2 - S	2	760	14.0	8.24	294
5 - 12 m	3	725	17.0	8.34	296
5 - 6 m	4	761	17.0	8.33	291
5 - S	5	764	17.5	8.28	293
8 - 12 m	6	730	17.8	8.29	291
8 - 6 m	7	748	17.8	8.30	293
8 - S	8	779	18.0	8.30	288
11 - 12 m	9	764	17.5	8.31	290
11 - 6 m	10	764	17.5	8.30	293
11 - S	11	785	18.0	8.29	296
14 - 6 m	12	764	17.5	8.40	288
14 - S	13	794	17.5	8.29	294
16 - S	14	712	17.8	8.38	292

Table A. 7. Concentrations of various constituents in Experiment II. All data are in mg/l except conductivity ($\mu\text{mhos/cm}$), alkalinity (mg/l as CaCO_3), Fe and Chlorophyll a ($\mu\text{g/l}$), and temperature ($^{\circ}\text{C}$).

COSM NO	DAY	DISS OXYGEN	CONDUCTIVITY	PH	TOTAL ALK	SI	CL	CHL <u>a</u>	CA	MG	NA	K	FE	TEMP
1	0	13.2	840.	8.79	262.	7.4	47.3	9.0	89.	50.	59.	9.	409.	19.5
3	0	11.0	820.	8.58	261.	3.7	47.8	9.9	71.	54.	50.	9.	19.	19.5
6	0	12.0	750.	8.35	257.	5.4	38.5	9.0	65.	55.	42.	8.	81.	18.0
7	0	12.0	850	8.69	261.	5.5	44.7	9.9	96.	55.	43.	8.	38.	19.5
8	0	11.0	850.	8.51	269.	4.5	43.7	9.9	83.	54.	46.	9.	15.	19.5
9	0	11.0	825.	8.55	257.	3.1	42.6	12.0	81.	56.	42.	9.	68.	19.5
10	0	11.6	840.	8.54	255.	2.8	46.2	7.2	82.	54.	44.	9.	25.	19.5
11	0	9.5	850.	8.42	269.	5.7	45.7	9.9	75.	55.	36.	9.	11.	19.5
12	0	16.0	770.	8.95	248.	.9	45.2	9.0	67.	54.	41.	9.	8140.	19.5
1	1	4.3	870.	8.48	261.	8.5	45.8	6.3	77.	51.	46.	9.	25.	17.0
3	1	4.8	880.	8.73	270.	3.6	46.7	6.3	80.	54.	42.	16.	217.	18.0
6	1	3.9	810.	8.36	254.	6.9	45.4	9.0	71.	55.	34.	9.	42.	17.0
7	1	4.5	790.	8.76	264.	5.1	45.6	6.3	75.	55.	40.	9.	233.	18.0
8	1	4.4	880.	8.69	272.	3.3	44.2	9.9	78.	55.	46.	15.	17.	18.0
9	1	5.5	880.	8.51	263.	3.2	45.8	8.1	83.	54.	47.	16.	44.	18.0
10	1	5.0	850.	8.55	260.	2.7	45.8	9.0	69.	52.	41.	9.	11.	18.0
11	1	4.0	810.	8.25	280.	13.0	37.1	9.9	72.	55.	34.	9.	20.	17.0
12	1	4.4	780.	8.95	243.	1.1	45.8	8.1	59.	54.	38.	8.	12.	18.0
1	4	2.6	940.	8.06	274.	10.7	46.2	14.0	72.	56.	46.	7.	151.	21.0
3	4	6.9	870.	9.11	268.	.7	44.7	32.0	100.	57.	44.	14.	328.	23.0
6	4	3.6	840.	8.00	255.	8.4	39.6	13.0	61.	50.	35.	7.	25.	21.0
7	4	5.9	835.	8.92	260.	4.1	41.6	15.0	70.	51.	38.	7.	11.	23.0
8	4	7.4	865.	9.04	266.	.6	41.6	15.0	72.	50.	37.	15.	11.	23.0
9	4	7.0	930.	8.80	263.	.7	46.2	15.0	72.	54.	40.	15.	11.	22.0
10	4	7.0	885.	8.98	264.	.8	48.8	62.0	72.	52.	46.	8.	45.	22.0
11	4	3.8	850.	8.11	271.	8.4	35.4	15.0	71.	52.	31.	7.	46.	21.0
12	4	6.8	750.	8.51	187.	.6	44.7	15.0	43.	49.	37.	7.	93.	23.0
1	6	2.5	887.	8.04	273.	11.1	47.8	15.0	33.	57.	42.	6.	57.	20.0
3	6	7.3	757.	9.13	232.	.3	45.7	16.0	25.	53.	38.	9.	11.	22.5
6	6	4.0	810.	8.09	255.	8.6	40.6	11.0	29.	52.	31.	6.	12.	20.0
7	6	6.0	745.	8.84	240.	4.3	43.2	15.0	26.	53.	34.	6.	11.	22.0
8	6	7.5	760.	9.02	233.	.3	42.6	17.0	26.	52.	34.	9.	11.	23.0
9	6	7.6	830.	8.90	263.	.7	47.3	17.0	35.	51.	37.	9.	11.	22.0
10	6	6.3	810.	9.14	265.	.7	46.7	22.0	42.	53.	37.	6.	71.	22.0
11	6	4.7	820	8.16	271.	9.2	36.0	15.0	42.	53.	29.	5.	11.	20.0
12	6	6.5	690.	8.90	195.	1.2	43.2	18.0	15.	51.	32.	5.	11.	22.0
1	9	0.0	895.	8.12	291.	12.8	46.2	15.0	69.	54.	37.	7.	11.	20.0
3	9	0.0	710.	9.19	191.	.5	45.2	14.0	30.	48.	32.	10.	15.	22.0
6	9	0.0	820.	8.10	268.	10.2	39.0	14.0	72.	52.	28.	6.	11.	20.0
7	9	0.0	730.	8.77	216.	4.0	43.2	14.0	46.	49.	33.	6.	11.	22.0
8	9	0.0	730.	8.98	197.	.6	42.1	15.0	38.	49.	30.	10.	14.	22.0
9	9	0.0	835.	8.99	275.	.8	44.7	15.0	69.	50.	35.	12.	12.	22.0
10	9	0.0	785.	9.36	274.	1.2	47.3	16.0	70.	50.	34.	6.	1470.	22.0
11	9	0.0	840.	8.17	294.	10.1	36.0	14.0	73.	53.	27.	6.	11.	20.0
12	9	0.0	650.	9.00	186.	1.2	42.6	16.0	34.	47.	30.	6.	11.	22.0
1	11	2.5	920.	8.06	288.	12.9	45.6	18.0	70.	51.	44.	5.	11.	20.5
3	11	6.1	675.	9.39	169.	.6	44.1	17.0	21.	42.	37.	8.	22.	23.0
6	11	3.0	870.	7.83	268.	10.7	39.5	14.0	60.	49.	41.	5.	11.	20.5
7	11	6.2	685.	8.79	192.	3.8	42.6	14.0	30.	45.	42.	5.	11.	23.0
8	11	5.6	715.	9.09	183.	.9	42.1	18.0	24.	47.	43.	7.	11.	23.0
9	11	5.5	855.	9.06	277.	1.2	43.6	17.0	66.	52.	48.	7.	11.	23.0
10	11	7.0	750.	9.40	239.	1.2	47.7	20.0	44.	49.	51.	5.	11.	23.0
11	11	3.5	880.	8.03	283.	10.8	33.8	17.0	68.	53.	40.	5.	11.	20.5
12	11	5.0	675.	9.02	183.	2.0	42.6	20.0	25.	46.	34.	3.	11.	23.0
1	13	2.6	910.	8.00	277.	14.2	45.1	.4	72.	55.	51.	5.	11.	19.0
3	13	6.1	645.	9.62	162.	0.0	44.1	.3	19.	44.	42.	6.	11.	21.0
6	13	3.2	845.	7.91	268.	12.1	39.5	.3	66.	52.	38.	4.	12.	19.0
7	13	5.0	655.	8.93	175.	3.5	42.1	.3	23.	27.	41.	4.	11.	21.0
8	13	5.5	665.	9.20	175.	.2	42.1	.8	26.	44.	45.	6.	11.	21.0
9	13	5.5	830.	9.13	270.	.6	43.1	.6	60.	46.	48.	6.	11.	20.5
10	13	6.4	655.	9.35	171.	.3	46.7	.6	22.	43.	48.	4.	11.	21.0
11	13	3.3	855.	8.06	281.	12.5	34.9	.2	71.	47.	39.	5.	70.	19.0
12	13	5.1	655.	9.05	180.	.6	41.5	.7	27.	46.	42.	4.	11.	21.0

Table A.8. Concentration of chemical constituents in microcosms during upstream/downstream experiment.

	TDS (mg/l)	Conductivity (μ mho/cm @ 25°C)	pH	Ca ⁺⁺ (mg/l)	Na ⁺⁺ (mg/l)	K ⁺ (mg/l)	Alkalinity (mg/l as CaCO ₃)	Silica (mg/l)	Turbidity (NTU)	Sulfate (mg/l)	Total Hardness (mg/l as CaCO ₃)
<u>7-2-80</u>											
Microcosm											
1		545									
3		486									
6		518									
7		453									
8		479									
9		515									
10		489									
11		525									
12		520									
<u>7-14-80</u>											
Microcosm											
1		400	8.6	42.1							
3		412	8.7	34.8							
6		402	8.6	40.5							
7		391	8.7	49.4							
8		428	8.8	43.7							
9		432	8.7	41.3							
10		468	8.6	47.8							
11		434	8.7	38.9							
12		488	8.6	51.8							
<u>7-17-80</u>											
Microcosm											
1			8.7	36			168			30	
3			8.8	35			-			32	
6			8.7	43			160			28	
7			8.7	38			190			33	
8			8.7	36			180			29	
9			8.7	35			172			31	
10			8.6	44			-			29	
11			8.7	39			168			31	
12			8.5	47			-			-	

Table A.9. Concentration of chemical constituents in microcosms during Experiment III.

	TDS (mg/l)	pH	Ca ⁺⁺ (mg/l)	Na ⁺⁺ (mg/l)	K ⁺ (mg/l)	Alkalinity (mg/l as CaCO ₃)	Silica (mg/l)	Turbidity (NTU)	Sulfate (mg/l)	Total Hardness (mg/l) as CaCO ₃
<u>7-21-80</u>										
Microcosm										
1	247	8.71	34	26	5		.91	12		194
6	233	8.70	30	24	4		.68	10		174
7	258	8.66	42	25	5		.16	17		194
8	254	8.54	45	24	5		1.66	12.5		186
9	258	8.72	34	24	5		.44	9		190
11	243	8.54	36	23	4		.59	11		194
Upstream	325	8.13	66	23	3		4.71	18.5		242
Downstream	363	8.38	79	27	3		4.61	7.5		279
<u>7-22-80</u>										
Microcosm										
1	240		36	25	5	173	1.38	9.5		182
6	220		32	25	4	164	.65	12		171
7	246		41	24	5	188	.29	14.5		198
8	222		38	23	5	187	2.10	10		184
9	226		37	24	5	175	.56	11.5		179
11	231		39	22	4	174	1.24	9.0		179
<u>7-23-80</u>										
Microcosm										
1	246	8.74	39	25	4	151	1.63			183
6	228	8.65	39	23	4	145	.72			178
7	248	8.57	47	23	5	167	.41			199
8	252	8.57	47	23	5	161	2.08			189
9	236	8.58	36	24	5	155	.32			185
11	240	8.59	47	23	4	169	1.09			187
Upstream	289	8.10	64	21	4	-	5.02			242
Downstream	340	8.22	78	26	3	-	4.84			269
<u>7-26-80</u>										
Microcosm										
1	238		36	24	4	179	-	9		182
6	223		41	22	4	170	-	12		170
7	255		43	22	5	199	-	12		200
8	247		40	23	5	195	-	12		192
9	243		38	24	5	185	-	10		188
11	247		41	24	4	190	-	8		192
Upstream	307		61	21	4	244	1.52	26		240
Downstream	347		71	26	4	277	.98	49		270

Table A.9. Continued.

	TDS (mg/l)	Conductivity (μ mho/cm @ 25°C)	pH	Ca ⁺⁺ (mg/l)	Na ⁺⁺ (mg/l)	K ⁺ (mg/l)	Alkalinity (mg/l as CaCO ₃)	Silica (mg/l)	Turbidity (NTU)	Sulfate (mg/l)	Total Hardness (mg/l as CaCO ₃)
<u>7-21-80</u>											
Microcosm											
1	25	400	8.71	34	26	5		.91	12		194
6	23	417	8.70	30	24	4		.68	10		174
7	26	459	8.66	42	25	5		.16	17		194
8	25	442	8.54	45	24	5		1.66	12.5		186
9	26	428	8.72	34	24	5		.44	9		190
11	24	432	8.54	36	23	4		.59	11		194
Upstream	33	585	8.13	66	23	3		4.71	18.5		242
Downstream	36	585	8.38	79	27	3		4.61	7.5		279
<u>7-22-80</u>											
Microcosm											
1	25	462		36	25	5	173	1.38	9.5		182
6	23	440		32	22	4	164	.65	12		171
7	25	479		41	24	5	188	.29	14.5		198
8	23	445		38	23	5	187	2.10	10		184
9	23	455		37	24	5	175	.56	11.5		179
11	24	462		39	22	4	174	1.24	9.0		179
<u>7-23-80</u>											
Microcosm											
1	25	467	8.74	39	25	4	151	1.63			183
6	23	440	8.65	39	23	4	145	.72			178
7	25	482	8.57	47	23	5	167	.41			199
8	25	462	8.57	47	23	5	161	2.08			189
9	24	438	8.58	36	24	5	155	.32			185
11	24	453	8.59	47	23	4	169	1.09			187
Upstream	29	550	8.10	64	21	4	-	5.02			242
Downstream	34	610	8.22	78	26	3	-	4.84			269
<u>7-26-80</u>											
Microcosm											
1	24	437		36	24	4	179	-	9		182
6	23	420		41	22	4	170	-	12		170
7	26	431		43	22	5	199	-	12		200
8	25	429		40	23	5	195	-	12		192
9	24	445		38	24	5	185	-	10		188
11	25	457		41	24	4	190	-	8		192
Upstream	31	530		61	21	4	244	1.52	26		240
Downstream	35	610		71	26	4	277	.98	49		270

Table A.10. Chemical data for coagulation experiment. All values in mg/l except alkalinity (mg/l as CaCO₃) and pH. Sample numbers correspond to the stations (a = 6 m depth, b = surface), c is a 7:1 dilution of sample 2 with water from Maple Grove hot springs (Experiment IV).

Date	TDS	Ca	Mg	Na	K	Alkalinity	Si	TOC	pH
8-7-80									
Sample 1	401	60	46	32	4	283		6.1	7.89
2	413	70	45	33	5	285		5.9	7.91
4a	410	72	40	32	4	256		6.9	8.20
4b	404	89	38	27	4	391		6.3	8.30
5a	-	74	41	32	5	281		6.6	8.08
5b	395	75	41	30	4	391		11.9	7.78
6	417	69	41	32	5	270		6.3	8.07
c	564	74	44	78	11			5.9	9.98
8-8-80									
Sample 1	400	65	48	39	4	285		6.3	8.19
2	423	33	44	42	5	371		5.2	8.06
4a	404	40	45	39	5	278		6.0	7.98
4b	414	58	43	38	5	282		5.9	8.05
5a	408	35	44	40	5	282		6.2	8.00
5b	404	35	43	40	5	282		7.2	8.06
6	404	34	42	38	5	282		6.9	8.29
c	579	34	46	88	12	292		5.4	8.16
8-11-80									
Sample 1	401	26	47	38	4	287	10.2		8.18
2	429	30	48	42	5	288	11.9		8.03
4a	422	32	43	39	5	275	11.0		8.07
4b	417	33	42	39	5	290	10.8		8.11
5a	422	33	43	40	5	286	12.5		8.09
5b	428	36	43	40	5	285	10.1		8.07
6	418	31	42	39	4	288	10.1		8.29
c	565	32	44	87	11	303	14.3		8.08
8-14-80									
Sample 1	427	44	50	41	5	289		5.5	8.39
2	426	38	48	44	5	293		5.4	8.33
4a	431	47	45	42	5	293		6.1	8.25
4b	420	50	43	40	5	290		6.6	8.28
5a	429	58	44	42	5	290		5.9	8.30
5b	427	50	43	41	5	293		6.7	8.28
6	425	49	43	40	5	291		6.8	8.48
c	563	50	46	88	12	302		5.6	8.44

Table A.11. Final concentrations of constituents in control and experimental flasks following incubation with soil samples (Experiment V).

Treatment	pH	TDS	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺
150 mg/l as CaCO ₃ - control	8.09	487	152	33	27	6
0.5 g sand	8.09	490	149	34	24	6
0.5 g silt	8.17	499	141	33	23	2
0.5 g clay	8.27	518	142	34	23	5
0.5 g sediment	8.16	489	146	34	21	5
1 g sand	8.16	489	144	35	21	5
1 g silt	8.29	450	152	35	20	5
1 g clay	8.31	488	167	35	27	5
1 g sediment	8.25	494	147	36	29	6
200 mg/l as CaCO ₃ - control	8.03	552	200	36	23	5
0.5 g sand	8.14	568	212	37	28	5
0.5 g silt	8.07	578	222	36	23	5
0.5 g clay	8.15	500	197	37	22	5
0.5 g sediment	8.30	477	201	36	22	6
1 g sand	8.05	533	209	37	20	5
1 g silt	8.08	554	239	36	22	5
1 g clay	8.25	534	255	37	32	6
1 g sediment	8.15	517	220	36	22	5
250 mg/l as CaCO ₃ - control	8.08	593	261	35	23	5
0.5 g sand	8.18	612	277	35	23	5
0.5 g silt	8.15	628	270	35	27	6
0.5 g clay	8.20	644	253	35	23	6
0.5 g sediment	8.11	623	252	35	23	6
1 g sand	8.08	588	235	36	20	6
1 g silt	8.13	583	257	35	24	6
1 g clay	8.13	709	266	35	23	6
1 g sediment	8.26	675	255	35	23	6
300 mg/l as CaCO ₃ - control	8.08	610	282	35	25	9
0.5 g sand	8.14	720	302	35	26	6
0.5 g silt	8.07	731	301	34	31	6
0.5 g clay	8.20	802	311	35	26	6
0.5 g sediment	8.21	590	306	35	23	6
1 g sand	8.08	731	273	36	24	6
1 g silt	8.21	777	267	35	24	6
1 g clay	8.25	712	274	34	26	6
1 g sediment	8.30	736	270	34	24	6

Soil added as wet weight to dry weight of 0.5 or 1.0 g/l 70 ml/beaker for TDS, 103°C overnight, 3 reps/TDS.

APPENDIX B. CHEMICAL EQUILIBRIUM PROGRAM USED TO CALCULATE SUPERSATURATION OF CARBONATE SOLID PHASES GIVEN ANALYTICAL CONCENTRATIONS OF CONSTITUENT IONS AND TEMPERATURE. SEE CHAPTER V FOR DETAILS OF CONSTRUCTION AND SOURCES OF THERMODYNAMIC DATA.

```

C   CALCULATE ACTIVITY COEFFICIENTS USING DAVIES APPROXIMATION OF THE
C   DEBYE-HUCKEL FORMULA. ION PAIRS HAVE A VALUE OF 1.
      DIMENSION FNAM(3)
C   THIS VERSION USED IN THE REPORT
      REAL KD1, KD2, KD3, KD4, KD5, KD6, KD7, KD8, KD9, KD10, KD11, KD12, IAP, KW, K
      *, KD13, KD14
      EQUIVALENCE (ACT1, ACHCO3, ACNA, ACK, ACNSO4, ACHSO4, ACKSO4, ACCHC3,
      +ACCL, ACCAOH, ACMGOH, ACMHO3, ACNCO3), (ACT2, ACCA, ACMG, ACSO4, ACCO3),
      +(ACT7, ACCS4O, ACMC3O, ACCC3O,
      +ACMS4O),
      +(ACT4, ACS1)
C   SETS PARTIAL PRESSURE OF CARBON DIOXIDE
      PCO2=.000276
      TNASO4=0.
      THSO4=0.
      THCO3=0.
      TCO3=0.
      TCAOH=0.
      TMGOH=0.
      TMHCO3=0.
      TNACCO3=0.
      THCO3N=0.
      TNASO4=0.
      THSO4=0.
      TCHCO3=0.
      TCAOH=0.
      TMGOH=0.
      TMHCO3=0.
      TNACCO3=0.
      WRITE(3, 134)
134 FORMAT(' READY B WITH DATA, THEN TYPE 11 CHAR FILE NAME' /
      *' ..... '// ')
      READ(1, 135)FNAM
135 FORMAT(3A4)
      3 FORMAT(1X, 3A4)
      WRITE(3, 3)FNAM
C   INPUT DATA & CHECK DATA
      WRITE(3, 125)
125 FORMAT(1X, 'WILL CARBONATES BE', /, '      1. -GIVEN?
      *', /, '      2. -CALCULATED?')
      READ(1, 136)J
136 FORMAT(A2)
      WRITE(3, 137)
137 FORMAT(1X, 'WILL ION RATIOS AND SAR BE COMPUTED?', /,
      *'      1. -YES' /, '      2. -NO')
      READ(1, 138)N
138 FORMAT(I2)
      WRITE(3, 175)
175 FORMAT(' DO YOU WISH TO PRINT CHLORIDE AND SULFATE RATIOS?' /
      *'      1. =YES' /, '      2. =NO')
      READ(1, 136)RATIO
      WRITE(3, 176)
176 FORMAT(' DO YOU WISH TO CALCULATE EC AS A FUNCTION OF ION
      * CONCENTRATIONS?' /, '      1. =YES' /, '      2. =NO')
      READ(1, 136)SPEC
      WRITE(3, 177)

```

```

177 FORMAT(' DO YOU WISH HARD COPY OF INTERMEDIATE VALUES DURING
* ITERATIONS?'' 1.=YES'' 2.=NO')
  READ(1,136)WL
  WRITE(3,139)
139 FORMAT(1X,'WHAT ACTION IS TO BE TAKEN ON THE INPUT DATA?'
*,/, ' 1.-CONVERSION OF CA & MG HARDNESS (AS CACO3) TO
*MG/L OF CA OR MG?','/, ' 2.-CONVERSION OF MG/L TO MMOL/L?'
*,/, ' 3.-CONVERSION OF MMOL/L TO MEQ/L?','/,
*' 4.-CONVERSION OF MEQ/L TO EQ/L?')
  READ(1,138)M
  WRITE(2,132)M, J, N
132 FORMAT(1X, I2, 1X, I2, 1X, I2)
  CALL OPEN(6, FNAM, 2)
  1 READ(6, 128, END=60)DNO, DAY, DOX, EC, PH, TALK, TSI, TCL, TCHL, TCA,
  *TMG, TNA, TK, TFE, TC
  TSO4=30.
128 FORMAT(2F2.0, 13F4.0)
  WRITE(2, 181)
181 FORMAT(1X, 'RAW INPUT DATA (CA, MG, NA, K, CL, SO4, SI, TALK,
*PH, TEMP)')
  WRITE(2, 120) TCA, TMG, TNA, TK, TCL, TSO4, TSI, TALK, PH, TC
120 FORMAT(7(E9.3, 2X), /, 4(E9.3, 2X))
C M=INPUT FORMAT; J=CALCULATE VS. GIVEN CARBONATES (1=GIVEN);
C N=ION RATIOS AND SAR (1=COMPUTE)
C THESE DATA REPRESENT DISSOCIATION AND SOLUBILITY PRODUCT
C CONSTANTS CORRECTED FOR TEMPERATURE USING VANT HOFF'S
C LAW OR EMPIRICAL RELATIONSHIPS (SEE TABLE 3.1), AND THE
C 'EPSILON' AND 'A' TERMS FOR THE DEBYE-HUCKEL EQUATION.
TKL=TC+273.15
RL=(1.987E-03)*2.303
TTRM=(TKL-298.)/(TKL*298.)
WRITE(3, 140)TKL, RL, TTRM
140 FORMAT(1X, 3(E9.3, 3X))
KD1=10. **(-2.31+(1.65/RL)*TTRM)
KD2=10. **(-2.238+(4.92/RL)*TTRM)
KD3=10. **(-.0226+(2.229/RL)*TTRM)
KD4=10. ** (5.3505-.0183412*TKL-557.2461/TKL)
KD5=10. **(-3.106+673.6/TKL)
KD6=10. **(-3.15+(3.13/RL)*TTRM)
KD7=10. **(-1.129+(6.33/RL)*TTRM)
KD8=10. **(-1.303+(1.19/RL)*TTRM)
KD9=10. **(-2.548+(2.14/RL)*TTRM)
KD10=10. **(-3.24+(.058/RL)*TTRM)
KD11=10. **(-1.071+(10.37/RL)*TTRM)
KD12=10. **(-1.2684+(8.911/RL)*TTRM)
KD13=10. ** (14.8453-.032786*TKL-3404.71/TKL)
KD14=10. ** (6.498-.02379*TKL-2902.39/TKL)
KW=10. **(-13.998-(13.345/RL)*TTRM)
EPS=87.74-.4008*TC+9.3398E-04*TC**2-1.410E-06*TC**3.
ATRM=1.82483E+06*(EPS*TKL)**(-1.5)
SP1JL=10. ** (13.87-0.04035*TKL-3059./TKL)
SP2=10. **(-4.64+(.34/RL)*TTRM)
SP3=10. **(-18.52-(7.28/RL)*TTRM)
SP4=10. **(-8.19-(2.84/RL)*TTRM)
SP1SW=10. **(-8.42-(2.94/RL)*TTRM)
WRITE(2, 182)
182 FORMAT(1X, 'DISSOCIATION CONSTANTS, SOLUBILITY PRODUCT CONSTANTS,
* AND ANALYTICAL CONCENTRATION (MOL/L)')
  WRITE(2, 154)KD1, KD2, KD3, KD4, KD5, KD6, KD7, KD8, KD9, KD10,
  *KD11, KD12, KD13, KD14, SP1SW, SP1JL, SP2, SP3, SP4
154 FORMAT(1X, 'KD1=', E9.3, ' KD2=', E9.3, ' KD3=', E8.3, ' KD4=', E8.3,
*' KD5=', E8.3, ' KD6=', E8.3, /, ' KD7=', E8.3, ' KD8=', E8.3,
*' KD9=', E8.3, ' KD10=', E8.3, ' KD11=', E8.3, ' KD12=', E8.3, /, ' KD13=',
*E8.3, ' KD14=', E8.3, ' SP1SW=', E8.3, ' SP1JL=', E8.3, ' SP2=', E8.3,
*'/ SP3=', E8.3, ' SP4=', E8.3//)
C THIS ROUTINE ALLOWS FLEXIBILITY IN INPUT DATA. IF
C M=1 ;CONVERSION OF CA & MG HARDNESS (AS CACO3) TO MG/L OF CA OR MG
C M=2 ;CONVERSION OF MG/L TO MMOL/L
C M=3 ;CONVERSION OF MMOL/L TO MEQ/L
C M=4 ;CONVERSION OF MEQ/L TO EQ/L
GO TO (27, 28, 29, 30), M
27 TCA=TCA*0.4

```



```

      TMG=TMG*.24
28  TCA=TCA/40.
      TMG=TMG/24.4
      TSO4=TSO4/96.
      TSI=TSI/60.
      TNA=TNA/23.
      TK=TK/39.1
      TCL=TCL/35.5
29  IF (N.NE.1)GO TO 30
      TCA=TCA*2.
      TMG=TMG*2.
      TSO4=TSO4*2.
      TCO3=TCO3*2.
      TSI=TSI*4.
C   CALCULATION OF NONCONSERVATIVE/CONSERVATIVE ION RATIOS AND
C   SODIUM ABSORPTION RATIO (SAR) PRINT STMTS
      CLCAR=TCA/TCL
      CLMGR=TMG/TCL
      CLNAR=TNA/TCL
      CLKR=TK/TCL
      CLSIR=TSI/TCL
      SFCAR=TCA/TSO4
      SFMGR=TMG/TSO4
      SFNAR=TNA/TSO4
      SFKR=TK/TSO4
      SFSIR=TSI/TSO4
      SAR=TNA/SQRT((TCA+TMG)/2.)
      TCA=TCA/2.
      TMG=TMG/2.
      TSO4=TSO4/2.
      TCO3=TCO3/2.
      TSI=TSI/4.
30  CONTINUE
      TCA=TCA/1000.
      TMG=TMG/1000.
      TNA=TNA/1000.
      TK=TK/1000.
      TCL=TCL/1000.
      TSO4=TSO4/1000.
      TSI=TSI/1000.
C   CALCULATES INITIAL BICARBONATE SYSTEM PARAMETERS
      AH=1./(10.** (PH))
      AOH=KW/AH
      IF (J.NE.1)GO TO 20
C   THIS ALGORITHM CALCULATES THE CONCENTRATIONS, HCO3, AND CO3 AS
C   A FUNCTION OF ALKALINITY AND PH
      THCO3=((TALK/50000.)+AH-(KW/AH))/(1+(2.*KD14/AH))
      TCO3=(.5*((TALK/50000.)+AH-(KW/AH)))/(1+(AH/(2.*KD14)))
20  CONTINUE
C   PRINT NEW ION CONCENTRATIONS
      TCAN=TCA
      TMGN=TMG
      TNAN=TNA
      TKN=TK
      TCLN=TCL
      TSO4N=TSO4
      TSIN=TSI
      THCO3N=THCO3
      TCO3N=TCO3
      WRITE(2,150)TCAN, TMGN, TNAN, TKN, TCLN, TSO4N, TSIN, THCO3N, TCO3N
150  FORMAT(1X, 'TCAN=',E9.4, ' TMGN=',E9.4, ' TNAN=',E9.4, ' TKN=',E9.4,
* ' TCLN=',E9.4,/, ' TSO4N=',E9.4, ' TSIN=',E9.4, ' THCO3N=',E9.4,
* ' TCO3N=',E9.4/)
C   LOOP CALCULATES NEW IONIC STRENGTHS, COMPARES THEM WITH OLD IONIC
C   STRENGTHS, AND ITERATES UNTIL THE DIFFERENCE IS NEGLIGIBLE
      TOLD=TCAN+TMGN+TNAN+TKN+TCLN+TSO4N+THCO3N+TCO3N+TSIN
      DO 40 I=1,10
      U=(( (TCAN+TMGN+TSO4N+TCO3N)*4. )
** (TNAN+TKN+TCLN+THCO3N+TNASO4+THSO4+TCHCO3+
* TCAOH+TMGOH+TMHCO3+TNACO3)
** (TSI*16. ))/2.
      WRITE(3,152)TOLD, U

```

```

152 FORMAT(1X, 'TOLD & U =', 2(E9.4, 2X))
    UTRM=(SQRT(U))/(1+SQRT(U))-(.3*U)
    WRITE(3, 153)UTRM, ATRM
153 FORMAT(1X, 'UTRM= ', E9.4, ' ATRM=', E9.4)
    ACT1=10. **(-ATRM*UTRM)
    ACT2=10. **(-ATRM*4. *UTRM)
    ACT3=10. **(-ATRM*9. *UTRM)
    ACT4=10. **(-ATRM*16. *UTRM)
    ACT7=1.
    ACA=ACCA*TCAN
    AMG=ACMG*TMGN
    ANA=ACNA*TNAN
    AK=ACK*TKN
    WRITE(2, 183)
183 FORMAT(1X, 'ITERATIONS')
    WRITE(2, 101)TOLD, U, ACT1, ACT2, ACT4
101 FORMAT(1X, 'TOLD=', E8.2, ' U=', E8.2, ' ACT1=', E8.2, ' ACT2=',
+ E8.2, ' ACT4=', E8.2)
    IF(WL.NE.1)GO TO 160
    WRITE(2, 102)ACA, AMG, ANA, AK
102 FORMAT(1X, ' ACA=', E8.2, ' AMG=', E8.2, ' ANA=',
+ E8.2, ' AK=', E8.2, )
160 ACL=ACCL*TCLN
    ASO4=ACS04*TSO4N
    ASI=ACSI*TSIN
    IF (WL.NE.1)GO TO 161
    WRITE(2, 119)ACL, ASO4, ASI
119 FORMAT(1X, 'ACL=', E8.2, ' ASO4=', E8.2, ' ASI=', E8.2)
161 IF (J.EQ. 1) GO TO 7
    IF(I.GT.1)GO TO 7
C THIS ALGORITHM CALCULATES THE ACTIVITES OF H2CO3, HCO3, AND CO3
C AS A FUNCTION OF KELVIN TEMP(SEE TABLE 3.1)
    AH2CO3=10. **(ALOG(PCO2)-14.0184+0.01526*TKL+2385.73/TKL-
1U*(0.84344-0.004471*TKL+0.00000666*TKL*TKL))
    WRITE(2, 133)KD13, KD14
133 FORMAT(1X, 'KD13=', E9.4, ' KD14=', E9.4)
    THCO3N=KD13*AH2CO3/AH
    TCO3N=KD14*THCO3N/AH
    THCO3=THCO3N
    TCO3=TCO3N
    WRITE(2, 103)THCO3N, TCO3N, AH2CO3
103 FORMAT(1X, 'THCO3N=', E8.2, ' TCO3N=', E8.2, ' AH2CO3=', E8.3)
7 CONTINUE
    AHC03=ACHCO3*THCO3N
    ACC03=ACCO3*TCO3N
    IF (WL.NE.1)GO TO 8
    WRITE(2, 130)AHC03, ACC03
130 FORMAT(1X, 'AHC03=', E8.2, ' ACC03=', E8.2)
8 CONTINUE
    ACAS40=(ACA*ASO4)/KD1
    AMGS40=(AMG*ASO4)/KD2
    ANASO4=(ANA*ASO4)/KD3
    IF (WL.NE.1)GO TO 162
    WRITE(2, 104)AHC03, ACC03, ACASO4, AMGSO4, ANASO4
104 FORMAT(1X, 'AHC03=', E8.2, ' ACC03=', E8.2, ' ACASO4=', E8.2, ' AMGSO4=',
+ E8.2, ' ANASO4=', E8.2)
162 AHSO4=(AH*ASO4)/KD4
    AKSO4=(AK*ASO4)/KD5
    ACCO30=(ACA*ACC03)/KD6
    ACHC3=(ACA*AHC03)/KD7
    ACAOH=(ACA*AOH)/KDB
    IF (WL.NE.1)GO TO 163
    WRITE(2, 105)AHSO4, AKSO4, ACCO30, ACHC3, ACAOH
105 FORMAT(1X, 'AHSO4=', E8.2, ' AKSO4=', E8.2, ' ACCO30=', E8.2,
+ ' ACHC3=', E8.2, ' ACAOH=', E8.2)
163 AMGOH=(AMG*AOH)/KD9
    AMCO30=(AMG*ACC03)/KD10
    AMHCO3=(AMG*AHC03)/KD11
    ANACO3=(ANA*ACC03)/KD12
C MASS BALANCE ON INITIAL ION CONCENTRATIONS
    TSO4N=TSO4/(1.0+((ACA*ACS04)/(KD1*ACCS40))+((AMG*ACS04)/
+ (KD2*ACMS40))+((ANA*ACS04)/(ACNSO4*KD3))+((AH*ACS04)/(KD4*ACHSO4))

```

```

++(AK*ACS04)/(KD5*ACKS04))
IF (WL.NE.1)GO TO 164
WRITE(2,106)AMGOH,AMC030,AMHC03,ANAC03,TS04N
106 FORMAT(1X,'AMGOH=',E8.2,' AMC030=',E8.2,' AMHC03=',E8.2,' ANAC03=
+,E8.2,' TS04N=',E8.2)
164 TCAN=TCA/(1.0+(AS04*ACCA)/(ACCS40*KD1)+(AC03*ACCA)/(ACCC30*KD6)+
+(AHC03*ACCA)/(ACCHC3*KD7)+(AOH*ACCA)/(ACCAOH*KD8))
TMGN=TMG/(1.0+(AS04*ACMG)/(ACMS40*KD2)+(AOH*ACMG)/(ACMGOH*KD9)
++(AC03*ACMG)/(ACMC30*KD10)+(AHC03*ACMG)/(ACMH03*KD11))
THC03N=THC03/(1.0+(ACA*ACHC03)/(ACCHC3*KD7)+(AMG*ACHC03)/
*(ACMH03*KD11))
TC03N=TC03/(1.0+(ACA*ACC03)/(ACCC30*KD6)+(AMG*ACC03)/
*(ACMC30*KD10)+(ANA*ACC03)/(ACNC03*KD12))
TCLN=ACL/ACCL
TNAN=TNA/(1.0+(AS04*ACNA)/(ACNS04*KD3)+(ACNA*AC03)/(ACNC03*KD12))
TKN=TK/(1.0+(AS04*ACK)/(ACKS04*KD5))
IF (WL.NE.1)GO TO 165
WRITE(2,107)TCAN, TMGN, TCLN, TNAN, THC03N, TC03N
107 FORMAT(1X,'TCAN=',E8.2,' TMGN=',E8.2,' TCLN=',E8.2,' TNAN=',
+E8.2,' TCH03N=',E8.2,' TC03N=',E8.2)
165 THS04=HNS04/ACHS04
TCHC03=ACHC3/ACCHC3
TCAOH=ACAOH/ACCAOH
TMGOH=AMGOH/ACMGOH
TMHC03=AMHC03/ACMH03
TKS04=AKS04/ACKS04
TNAS04=ANAS04/ACNS04
TNAC03=ANAC03/ACNC03
TNEW=TCAN+TMGN+TNAN+TKN+TCLN+TS04N+THC03N+TC03N+TSIN
FLMT=0.002*TOLD
IF (WL.NE.1)GO TO 166
WRITE(2,108)TKN, TCHC03, TCAOH, TC03N, TNEW
108 FORMAT(1X,'TKN=',E8.2,' TCHC03=',E8.2,' TCAOH=',E8.2,' TC03N=',
+E8.2,' TNEW=',E8.2/)
166 IF (ABS(TNEW-TOLD).LT. FLMT) GO TO 50
TOLD=TNEW
ERRP=TNAN+TKN+AH+TCHC03+TCAOH+TMGOH+TMHC03+(2.*(TCAN+TMGN))
ERR=(ERRP-(TCLN+THS04+TKS04+TNAS04+TNAC03+AOH+(2.*TS04N)+
*THC03N+(4.*TSIN)))/ERRP
WRITE(2,167)ERR
167 FORMAT(1X,'ERROR=',E8.2/)
40 CONTINUE
C PRINT OUT TOTAL CONCENTRATIONS,ACTIVITY PRODUCTS, AND SATURATION INDICES
50 CONTINUE
TMGS40=AMGS40/ACMS40
TMC030=AMC030/ACMC30
TCC030=ACC030/ACCC30
TCAS40=ACAS40/ACCS40
IAP=ACA*AC03
SATIN1=(ACA*AC03)/SP1SW
SATIN2=(ACA*AS04)/SP2
SATIN3=(ACA*AMG*AC03*AC03)/SP3
SATIN4=(ACA*AC03)/SP4
SATIN5=(ACA*AC03)/SP1JL
IF (RATIO.NE.1.)GO TO 109
WRITE(2,170)CLCAR, CLMGR, CLNAR, CLKR, CLSIR
170 FORMAT(1X,'CA/CL=',E8.2,' MG/CL=',E8.2,' NA/CL=',E8.2,
*' K/CL=',E8.2,' SI/CL=',E8.2/)
WRITE(2,171)SFCAR, SFGMR, SFNAR, SFKR, SFSIR
171 FORMAT(1X,'CA/S04=',E8.2,' MG/S04=',E8.2,' NA/S04=',E8.2,
*' K/S04=',E8.2,' SI/S04=',E8.2/)
109 WRITE(2,180)
180 FORMAT(1X,'FINAL ION CONCENTRATION, IONIC STRENGTH, AND ACTIVITY
* COEFFICIENTS')
WRITE(2,110)TCAN, TMGN, TNAN, TKN, TCLN, AH, AOH
110 FORMAT(1X,'CA=',E8.2,' MG=',E8.2,' NA=',E8.2,3H K=',E8.2,' CL=',
+E8.2,' H=',E8.2,' OH=',E8.2)
WRITE(2,111)TS04N, THC03N, TC03N, TSIN, TNAS04
111 FORMAT(1X,'S04=',E8.2,' HC03=',E8.2,' C03=',E8.2,' SI=',E8.2,
+' NAS04=',E8.2)
WRITE(2,112)THS04, TKS04, TCHC03, TCAOH, TMGOH
112 FORMAT(1X,'HS04=',E8.2,' KS04=',E8.2,' CAHC03=',E8.2,' CAOH=',

```

```

+E8. 2, ' MGOH=', E8. 2)
WRITE (2, 113) TMC030, TCC030, TMHC03
113 FORMAT(1X, 'MGC03=', E8. 2, ' CAC03=', E8. 2,
+ ' MGHCO3=', E8. 2)
WRITE (2, 114) TNAC03, TCAS40, TMGS40, U, ACT1, ACT2
114 FORMAT(1X, 'NAC03=', E8. 2, ' CAS040=', E8. 2, ' MGS040=', E8. 2, /,
* ' IONIC STRENGTH=', E8. 2, ' ACT1=', E8. 2, ' ACT2=', E8. 2)
WRITE (2, 115) ACT3, ACT4, I
115 FORMAT(1X, 'ACT3=', E8. 2, ' ACT4=', E8. 2, ' ITERATIONS=', I5/)
WRITE (2, 116) IAP, SATIN1, SATIN5, SATIN4, SATIN2, SATIN3, TC, SAR
116 FORMAT(1X, 'IAP CALCITE=', E9. 3, ' SAT INDEX CALCITE (SW)=', E9. 3, /
+ ' SAT INDEX CALCITE (JL)=', E9. 3,
+ ' SAT INDEX ARAGONITE=', E9. 3, /, ' SAT INDEX GYPSUM=',
*E9. 3, ' SAT INDEX DOLOMITE=', E9. 3, /, ' TEMP-C=', E8. 3, ' SAR=', E9. 3//)
IF (SPEC. NE. 1.) GO TO 65
C CALCULATE EC AS AN EMPIRICAL FUNCTION OF ION CONCENTRATIONS
TNA=TNA*1000.
THC03=THC03*1000.
TK=TK*1000.
TC03=TC03*2000.
TS04=TS04*2000.
TCA=TCA*2000.
TMG=TMG*2000.
TSI=TSIN*4000.
TCL=TCL*1000.
WRITE (2, 155) TNA, THC03, TK, TC03, TS04, TCA, TMG, TSI, TCL
155 FORMAT(1X, 5(E9. 4, 2X), /, 4(E9. 4, 2X))
CALL ECIII(TCA, TMG, TNA, TK, TC03, THC03, TCL, TS04, EC)
WRITE (2, 117) TCA, TMG, TNA, TK, TC03
117 FORMAT(1X, 'CA=', E8. 2, ' MG=', E8. 2, ' NA=', E8. 2, 3H K=', E8. 3, ' CO3=',
*E8. 3)
WRITE (2, 118) THC03, TCL, TS04, EC
118 FORMAT(1X, 'HCO3=', E8. 2, ' CL=', E8. 2, ' SO4=', E8. 2, ' EC=', E9. 3//)
65 GO TO 1
60 CONTINUE
END
SUBROUTINE ECIII(TCA, TMG, TNA, TK, TC03, THC03, TCL, TS04, EC)
REAL MG
CA=TCA
MG=TMG
S04=TS04
IF (S04 .GT. CA) GO TO 10
CAS04=S04
CA=CA-S04
S04=0. 0
GO TO 30
10 CAS04=CA
S04=S04-CA
IF (S04. GT. MG) GO TO 20
CAS04=CAS04+S04
MG=MG-S04
S04=0. 0
GO TO 30
20 CAS04=CAS04+MG
S04=S04-MG
MG=0. 0
30 WRITE (3, 156)
156 FORMAT(1X, 'ECIII-21')
EC=. 05641*CA**. 9202+. 05099*MG**. 9102+. 04748*NA**. 9495+
2. 07263*TK**. 9706+. 069*S04**. 8973+. 0733*TC03**. 8719+
3. 04143*THC03**. 9501+. 07206*TCL**. 9671+. 1133*CAS04**. 8463
WRITE (3, 157) EC
157 FORMAT(1X, 'EC=', E9. 4)
RETURN
END

```