I84.31
I85.09

FINAL REPORT

EFFECTS OF CALCIUM MAGNESIUM ACETATE ON SMALL LENTIC ENVIRONMENTS IN INTERIOR ALASKA

by

Caryn L. Rea
Graduate Research Assistant
and
Jacqueline D. LaPerriere
Associate Professor of Water Resources
Associate Professor of Fisheries

Water Research Center
Institute of Northern Engineering
University of Alaska-Fairbanks
Fairbanks, AK 99775

August 1986

ALASKA DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES
RESEARCH SECTION
2301 Peger Road
Fairbanks, AK 99701

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Alaska Department of Transportation and Public Facilities. This report does not constitute a standard, specification or regulation.

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vii
INTRODUCTION	1
LITERATURE REVIEW	3
Introduction	3
Environmental Evaluation	4
Current Studies	8
OBJECTIVES OF STUDY	11
MATERIALS AND METHODS	13
Study Site	13
CMA Application	15
Sampling Schedule	15
Analysis of CMA	16
Physical Measurements	16
Air and Water Temperatures	16
Light Availability	18
Chemical Measurements	18
Alkalinity and pH	18
Major Cations	18
Dissolved Oxygen	18
Nutrients	19
Biological Measurements	19
Planktonic Chlorophyll *a*	19
Planktonic Bacteria	20
Acetate Turnover Times	20
Dominant Phytoplankton	21
Relative Abundance of Zooplankton	21
Statistical Analysis	21
RESULTS	23
Analysis of CMA	23
Physical Measurements	26
Air and Water Temperatures	27
Light Availability	28

TABLE OF CONTENTS (Continued)

	Page
Chemical Measurements	28
Alkalinity and pH	28
Dissolved Oxygen	28
Major Cations	35
Nutrients	37
Biological Measurements	44
Planktonic Chlorophyll *a*	44
Planktonic Bacteria	45
Acetate Turnover Times	45
Dominant Phytoplankton	45
Relative Abundance of Zooplankton	45
DISCUSSION	53
CONCLUSIONS	57
RECOMMENDATIONS	59
IMPLEMENTATION	61
LITERATURE CITED	63

LIST OF TABLES

Table		Page
1	Results of 96-hour acute toxicity bioassays of rainbow trout and fathead minnow with CMA, as LC50s (Winter et al., 1985)	5
2	Summary of sample manipulations	17
3	Chemical analysis of calcium acetate solution, 1985.	23
4	Chemical analysis of calcium acetate solution, 1984.	24
5	Acetate concentrations with test ponds and CMA mixture (July 5, 1985)	25
6	Calculated approximate concentrations of heavy metals entering the ponds with CMA treatment	25
7	Morphometric parameters of the study ponds	26
8	Climatic conditions within study area, 1985	27
9	Light extinction coefficients and percent absorbances	29
10	Physical/chemical data for pond C-1	30
11	Physical/chemical data for pond TR-1	30
12	Physical/chemical data for pond C-2	31
13	Physical/chemical data for pond TR-2	31
14	Physical/chemical data for pond C-3	32
15	Physical/chemical data for pond TR-3	32
16	Depth profile of dissolved oxygen concentration and percent saturation (July 30, 1985)	37
17	Concentrations of major cations for pond C-1	38
18	Concentrations of major cations for pond TR-1	38
19	Concentrations of major cations for pond C-2	39
20	Concentrations of major cations for pond TR-2	39
21	Concentrations of major cations for pond C-3	40
22	Concentrations of major cations for pond TR-3	40

LIST OF TABLES (Continued)

Tables		Page
23	Mean concentrations and standard deviations of nutrients for pond C-1	41
24	Mean concentrations and standard deviations of nutrients for pond TR-1	41
25	Mean concentrations and standard deviations of nutrients for pond C-2	42
26	Mean concentrations and standard deviations of nutrients for pond TR-2	42
27	Mean concentrations and standard deviations of nutrients for pond C-3	43
28	Mean concentrations and standard deviations of nutrients for pond TR-3	43
29	Calculated turnover times for acetate (0.15 mg/l) uptake by planktonic organisms	51
30	Relative abundance of zooplankton in July, August and September, 1985	52

LIST OF FIGURES

Figure		Page
1	Inset map of Alaska showing Delta Junction and a detailed map of study ponds on Fort Greely Military Reservation	14
2	Mean concentrations of dissolved oxygen for pair one ponds	33
3	Mean concentrations of dissolved oxygen for pair two ponds	33
4	Mean concentrations of dissolved oxygen for pair three ponds	34
5	Mean calcium concentrations plus or minus one standard error for pair one ponds	34
6	Mean calcium concentrations plus or minus one standard error for pair two ponds	36
7	Mean calcium concentrations plus or minus one standard error for pair three ponds	36
8	Mean chlorophyll a concentrations plus or minus one standard error for pair one ponds	46
9	Mean chlorophyll a concentrations plus or minus one standard error for pair two ponds	46
10	Mean chlorophyll a concentrations plus or minus one standard error for pair three ponds	47
11	Mean number of bacteria per ml, plus or minus one standard error for pair one ponds	47
12	Mean number of bacteria per ml, plus or minus one standard error for pair two ponds	48
13	Mean number of bacteria per ml, plus or minus one standard error for pair three ponds	48
14	Concentration of dissolved oxygen and total bacteria for pond TR-1	49
15	Concentration of dissolved oxygen and total bacteria for pond TR-2	49
16	Concentration of dissolved oxygen and total bacteria for pond TR-3	50

INTRODUCTION

The use of deicing compounds on winter roads has become an accepted practice for snow and ice removal in northern areas. The most commonly employed compounds have been the chloride salts sodium chloride (NaCl) and calcium chloride ($CaCl_2$). The application of these deicing agents to roadways has increased dramatically in recent years due to the demand for safer winter driving conditions. In 1974, less than half a million tons were used in the United States to maintain ice-free conditions. By 1975, the amount had increased to 12 million tons (USEPA, 1971).

Road salts are known to cause significant damage, environmentally and economically. Contamination of groundwaters, public water supplies, roadside wells, farm supply ponds and soils, and harm to vegetation and trees have been documented. Salt loads enter sewage treatment plants and surface streams via combined and storm sewers, and direct runoff. Chloride levels as high as 2,730 mg/l have been measured in surface streams along highways (USEPA, 1971).

Chlorides of the chemical deicers accelerate the corrosion of highway structures and pavements, motor vehicles, and underground cables and equipment in the area exposed to deicing. Although the damage is not recognized immediately, the long-term costs of replacing damaged structures and materials will eventually be borne by the public.

The chloride salts are efficient melters of ice and snow. They are readily available and relatively inexpensive. Chemical deicers have replaced sand and cinders, which are used as abrasive methods for ice control. Abrasives are applied after the ice and snow are deposited, but remain on the road only a short time due to spreading of the grains by traffic. Chemicals are fast-acting and work to break the bond between the snow and ice, and the road. Deicers are applied to maintain a "bare pavement" policy (i.e., to achieve summer driving conditions in winter). To maintain this condition, however, numerous applications are necessary. In most cases, approximately 400 to 1,200 pounds of salt are applied per road mile per application. The quantity of salt and its frequency of application vary with ambient temperature, storm conditions, volume of traffic and degree of public demand for bare pavement (Roth and Wall, 1976). Over a winter season, many highways may

have received up to 24 tons of salt per lane mile (Hoffman et al., 1981).

The possibility for salt pollution is not limited to the winter season. Some states (including Alaska) use $CaCl_2$ on highways and road shoulders as a means of controlling dust. An average application rate for this procedure is approximately six to 12 tons per mile of a 20 foot stretch of highway (Roth and Wall, 1976). Information on the frequency of application over the course of a season is not available.

A summary of research on the environmental impacts due to road salts is presented in the Literature Review. The main focus of this study was an evaluation of the impacts on small ponds in interior Alaska by the experimental road salt called calcium magnesium acetate (CMA) through experimental additions to test ponds. Results from this study should help guide future consideration of using CMA in Alaska.

LITERATURE REVIEW

Introduction

CMA is first identified as a viable alternative to chloride salt by Dunn and Schenk (1980). Ongoing studies are being conducted to determine the ice melting characteristics of CMA solids, the best methodology for acetic acid production, the corrosion characteristics on highway structures, the effects on pavements and motor vehicles, and the effects on environmental systems such as roadside vegetation, soils, groundwater and surface water (Chollar, 1985).

The necessity for finding an alternative deicer to road salt (NaCl, $CaCl_2$) has arisen because significant detrimental impacts are associated with salt usage. Groundwater contamination is reported in Massachusetts (Huling and Hollocher, 1972), lake stratification in New York (Bubeck et al., 1971) and Michigan (Judd, 1970). Roadside ponds in Maine developed increased chloride concentrations (Hutchinson, 1967). Impacts on the terrestrial environment include an upset in the ionic balance of soils, trees and other roadside vegetation. Total soluble salts, and sodium and chloride ions reduce soil fertility and structure, depress water uptake by plants, and are toxic to certain plants and vegetation (Hutchinson and Olson, 1967; Prior and Berthouex, 1967).

Problems have arisen due to mishandling of deicers through excessive application, misdirected spreading and improper storage. Stockpiling in open areas without sufficient protection may lead to spillage and concentration of the chemical in nearby soils or water supplies. Additives to the chloride salts have also caused some problems. Sodium ferrocyanides have been used as additives to serve as anticaking agents, and chromate compounds have been added as corrosion inhibitors (Ecological Research Associates, 1975). Both substances are toxic to aquatic life. Phosphates added to reduce corrosion may cause nutrient-enrichment problems in nearby receiving waters.

Road salt inputs to the Great Lakes in the 1960s were reported as 2,002,000 tons: 750,000 tons in Lake Erie; 525,000 tons in Lake Ontario; 438,000 tons in Lake Michigan; 198,000 tons in Lake Huron; and 91,000 tons in Lake Superior (Roth and Wall, 1976).

The actual chemical deicing mechanism depends upon the general effect of dissolved substances or solutes on the melting point of the solvent (Dunn and Schenk, 1980). The effect is to lower the melting point, and the amount of lowering is roughly proportional to the concentration of solute ions in solution. The solubility of the solute, therefore, is critical in determining the amount of lowering it will exert on the melting point of the solvent in which it is dissolved. Chemical deicers attack snow and ice at the upper surface. Salts dissolve and melt the surface, creating a brine solution that penetrates the remaining ice and breaks the bond between the ice and the road. Deicers must be able to melt at least 10% of the ice cover on roads; movement of traffic will usually take care of the remainder (Roth and Wall, 1976).

Dunn and Schenk (1980) report a comprehensive study testing alternative deicing compounds. Compounds were eliminated on the basis of expense, toxicity, availability, solubility, corrosivity and the potential for ecological damage. The choices were narrowed down to methanol and a mixture of calcium and magnesium salts of organic acids, primarily acetic.

Methanol reacts immediately with snow and ice upon application, but is less persistent than either NaCl or CMA. CMA exhibits significant deicing capabilities at a relatively low cost. CMA is also low in extended costs (i.e., CMA is less corrosive) and has no known potential for harming drinking water supplies.

With CMA identified as a promising alternative to NaCl, the Federal Highway Administration (FHWA) sponsored several research projects to investigate its environmental acceptability, manufacturing technology and economic feasibility (Chollar, 1983).

Environmental Evaluation

Environmental studies were implemented to measure the environmental consequences associated with producing, storing, handling or using CMA (Chollar, 1983). The results of these and ongoing studies should provide a better understanding of the fate, transport and effects of CMA on surrounding waters, soils and vegetation.

A preliminary environmental study was undertaken by the California Department of Transportation (CALTRANS). They conducted a literature review of air quality, groundwater quality, surface water quality, aquatic ecology, terrestrial vegetation, soils, and public health related to CMA. They performed their own studies on the aquatic ecology, terrestrial vegetation and soils (Winters et al., 1984). The CALTRANS study did not find any information regarding effects of CMA on surface water or groundwater quality, air quality or public health.

Winters et al. (1984) conducted bioassays of fishes, macroinvertebrates, zooplankton and phytoplankton. In addition, they evaluated certain soils and terrestrial vegetation via irrigation and foliar testing. Bioassays determine the toxicity of a substance, exposing organisms to known concentrations of a potentially toxic substance for a standardized period of time. CALTRANS synthesized CMA by reacting dolomite with glacial acetic acid. They do not report the effects of possible impurities in their product.

Short-term static bioassays were performed on both the fathead minnow (Pimephales promelas) and rainbow trout (Salmo gairdneri) to determine acute toxicity of CMA, and calcium acetate and magnesium acetate (Table 1; Winters et al., 1985).

Short-term bioassays show that the equimolar mixture and calcium acetate (CaAc) are less toxic to both fishes than NaCl. Magnesium acetate (MgAc) is more toxic to both fishes than NaCl or the other CMA mixtures.

TABLE 1. Results of 96-hour acute toxicity bioassays of rainbow trout and fathead minnow with CMA, as LC50s* (Winters et al., 1985).

	Rainbow trout (mg/l)	Fathead minnow (mg/l)
Calcium Acetate	16,200	14,300
Magnesium Acetate	4,300	9,000
Equimolar Mixture	18,700	--
Sodium Chloride	12,200	11,400

* 96-hour LC50 is that concentration at which 50% of the test organisms are killed during a 96-hour period.

Results of chronic bioassays of longer duration than 96 hours were performed on rainbow trout to evaluate the effects of CMA on egg development, hatching and larval development. Results show a slight delay in hatching success of rainbow trout when exposed to an equimolar CMA solution at a continuous 5,000 mg/l concentration. The lower concentrations of 1, 50, 100, 500 and 1,000 mg/l exerted no significant effect (Winters et al., 1985).

Their zooplankton bioassays were conducted using Daphnia magna, a waterflea of the order Cladocera. Both short- and long-term bioassays were performed using reproductive success as the measure of chronic toxicity. Test results apparently show that the CMA mixtures had no toxic effects on the population numbers or reproductive successes of Daphnia magna. Some test jars, however, experienced bacterial blooms which resulted in complete mortality due to oxygen depletion.

They also conducted bioassays of unialgal and natural algal populations to test the effects of CMA mixtures and NaCl on the growth of the respective populations. Unialgal bioassays were performed using the green alga Selenastrum capricornutum and the blue-green alga Anabaena flos-aquae. The unialgal bioassays tested the growth response of one organism under laboratory conditions, using an artificial growth medium. The natural population bioassays tested the growth response of indigenous algae using natural waters to study the effects of an aquatic bacterial population on the algal interaction with the deicers. Both the specific growth rate and the maximum standing crop were measured. The maximum specific growth rate is the maximum change in biomass production over time. The maximum standing crop is the maximum biomass per volume or area that is present and measurable.

Except for the highest NaCl level (1,000 mg/l), there was little difference in the maximum specific growth rate among the treatments and controls for natural water bioassays. In the natural water bioassays, the 1,000 mg/l NaCl (the highest dose) treatment caused an initial depression in growth, followed by a recovered growth by the end of the experiment. Within the unialgal bioassays, A. flos-aquae showed a significant depression in growth when exposed to a 1,000 mg/l concentration of NaCl. S. capricornutum showed no significant responses to any tested concentrations.

CMA treatments, however, show a significant decrease in the maximum specific growth rate at high CMA concentrations (1,671 mg/l) in the bioassays. A significant decrease in growth is reported at the 83.55, 167.1 and 1,671 mg/l treatment levels for the unialgal bioassays, but only the highest level of treatment (1,671 mg/l) causes a significant decrease in the natural water bioassays. Calcium acetate and magnesium acetate cause growth responses similar to the CMA treatments. Tests of algal response to CMA concentrations show a 17% reduction in biomass when exposed to a concentration of 10 mg CMA/liter. A concentration of 50 mg CMA/liter results in a biomass loss of 43% more than the control (Chollar, 1985). Concentrations of 100, 500, 1,000 and 4,000 mg CMA/liter all result in an algal biomass loss of more than 95%.

The algae cultures were undoubtedly not axenic because bacterial blooms occurred within the test chambers. Therefore, the toxicity of CMA on algae cannot be determined from these experiments. Competition for an essential nutrient with the bacteria may have caused the observed effects. Winters et al. (1984) state a conservative estimate for an acceptable CMA concentration. The maximum concentration at which little effect from CMA, calcium acetate or magnesium acetate would occur is less than 50 mg/l.

The terrestrial ecology portion of the CALTRANS study was a limited laboratory analysis of effects on roadside vegetation and various representative soil types. In the soils study, they applied a 1.0 N solution of CMA to determine if certain nutrients and metals were leached out. Soils tested were sent to CALTRANS from Minnesota, West Virginia, Maryland and California. The soils were packed in lysimeters and treated with the 1.0 N CMA solution or a distilled water control. The elutrate was immediately frozen and later analyzed for pH, specific conductance, hydrolyzable orthophosphate, nitrate, potassium, and chemical oxygen demand. The results show that CMA is capable of extracting substantial amounts of iron, aluminum, potassium and hydrolyzable orthophosphate in five out of seven soils tested. The vegetation study consisted of an evaluation of 18 woody species selected from plants found adjacent to highways in northern areas. Concentrations of CMA and NaCl expected to occur in spray from deicing

applications were applied by spray and irrigation to the plants. These tests show severe damage to nine plants by NaCl, and one plant by CMA.

An environmental evaluation of CMA is under way to expand upon previous laboratory analyses, and to conduct some actual field testing via controlled field studies. The research is being conducted at the University of Washington at Seattle under the direction of Dr. Richard Horner, and is of a much larger scale than the CALTRANS study involving both laboratory and control-plot field work. The UW study intends to determine: the transport and environmental fate of CMA; impacts on soils, surface water and groundwater; impacts on terrestrial ecosystems; and impacts on runoff water (Horner, 1984). Unlike the CALTRANS study, the University of Washington study will investigate the effects of any additives or impurities that might occur in an actual highway-grade CMA mixture.

Current Studies

Several ongoing projects will further define the capabilities of CMA for use as a deicing agent. Federally funded research is being undertaken to supplement the already existing information regarding the manufacturing technology, economic and technical feasibility, and environmental acceptability. Studies include evaluating the extent of corrosion of highway structures by CMA, monitoring the effects of CMA on pavements and motor vehicles, determining ice-melting characteristics of CMA solids, identification of an improved bacterial strain for acetic acid production, and environmental monitoring and evaluation of CMA via laboratory and field tests (Chollar, 1985).

State-funded projects are active in CMA-related research (Chollar, 1985). Pennsylvania and Washington are performing automobile skid tests, Maine is establishing a process to produce an impure CMA solution by reacting a dilute acetic acid mixture (50%) with dolomite, followed by solar drying. The resultant product is a mixture of CMA and unreacted limestone, so the mixture serves as both a deicer and an abrasive. Iowa is testing the effectiveness of an abrasive-CMA combination by using CMA-coated sand on their highways.

Alaska's Department of Transportation and Public Facilities (DOT&PF) conducted studies on the manufacturing technology, economic feasibility and environmental acceptability (Ostermann and Economides, 1986). Corrosion studies were conducted by Venkatesh and Kutterer (1985). Before conducting field-scale testing of CMA deicing, DOT&PF funded the Water Resources Center of the University of Alaska-Fairbanks to evaluate CMA effects on various water quality characteristics, and our evaluation is presented in this document.

OBJECTIVES OF STUDY

The effect of CMA on the natural environment has not been fully documented anywhere. The only full-scale field study is currently being conducted in Washington by Horner (1984). Separate environmental studies for Alaska are warranted due to extreme climatic conditions. Because of the absence of major thaws during the winter in most of Alaska, the deicer would move in higher concentrations at less frequent intervals, instead of impacting the environment in small concentrations at frequent intervals as in the contiguous United States. Mechanical snow removal pushes snow to the side of the road throughout the winter, forming a ridge of snow, ice and deicer. Before melt, therefore, high concentrations of salts and residue might accumulate immediately adjacent to the road. Since there is usually one big melt event in the spring, the dilution factor might be so great for spring runoff into streams that impacts could be minimal. Of concern, however, is the accumulation of the deicer into small roadside ponds at snowmelt.

A likely effect of CMA might be to increase the water hardness by increasing the calcium and magnesium ions. Associate changes on ionic strength may affect aquatic plants and animals. The organic material (the acetate) may exert an oxygen demand on the receiving water during biodegradation (primarily by bacteria), thus lowering the amount of oxygen available to aquatic life. Since CALTRANS reports a significant decrease in algal growth when exposed to various CMA concentrations, we decided to focus on algae in our field study.

We outlined specific procedures to obtain information on the response of small ponds to various concentrations of Alaska-made CMA by comparing teated and untreated (control) ponds for the following variables:

1. major cations within the water column (calcium, magnesium, sodium and potassium);
2. important nutrients in the water column (nitrate-nitrite nitrogen, ammonia nitrogen, orthophosphate phosphorus and total phosphorus);

3. colonization of benthic algae onto substrates (Rea and LaPerriere, 1985);
4. standing crop of planktonic algae;
5. standing crop of planktonic bacteria;
6. dissolved oxygen levels; and
7. dominant phytoplankton and zooplankton.

MATERIALS AND METHODS

Study Site

In 1985, six ponds near Delta Junction were selected for study because they were relatively close together, which provided for efficient sampling. They were accessible by road, fishes were absent, and the area did not receive a substantial influx of traffic. The use of expensive equipment left on site necessitated the latter criterion. The ponds were paired as a treatment (TR) and a control (C) by matching their initial (May 23, 1985) calcium concentrations. They are numbered as pairs (Figure 1). Ponds TR-1 and TR-3 had also been dosed with CMA in 1984 (Rea and LaPerriere, 1985) as had pond C-3, which was used as an untreated control in 1985. The ponds lie between the Delta River and Richardson Highway on the Fort Greely Military Reservation (Figure 1) approximately 160 km southeast of Fairbanks (63°58'N, 145°45'W).

The surface morphology of the area contains depositional and erosional topography; the study area lies on a terminal moraine formed during Donnelly glaciation (correlative with Wisconsinan glaciation), approximately 20,000 years ago (Pewe, 1975). The area is dotted with kettle lakes and thaw ponds. Some of the lakes contain 3 to 5 meters of silt overlain by peat. The surrounding soils contain sand and gravel with interbedded silt layers, and areas of discontinuous permafrost can be found from the moraine south of Fort Greely to the Tanana River 19.2 km north of Fort Greely (Pewe and Reger, 1983). The study area is drained by the Delta River and its tributary Jarvis Creek.

The surrounding terrestrial vegetation consists of mixed evergreen, deciduous scrub and shrub vegetation. Forest and forest scrub occupy the most extensive areas. Repeated fires over the past two centuries have made the forest stands largely a patchwork of fire scars populated by aspen (*Populus tremuloides*) and black spruce (*Picea mariana*). Alder (*Alnus tenuifolis*) with willow (*Salix* spp.) and other shrubs populate the understory (Holmes and Benninghoff, 1957). Bog vegetation and black spruce muskeg occupy undrained depressions. The shores of the many lakes and ponds are fringed by sedge marsh and bog vegetation. Aquatic vegetation includes sedges, reeds, dwarf buttercup, smartweeds, moss,

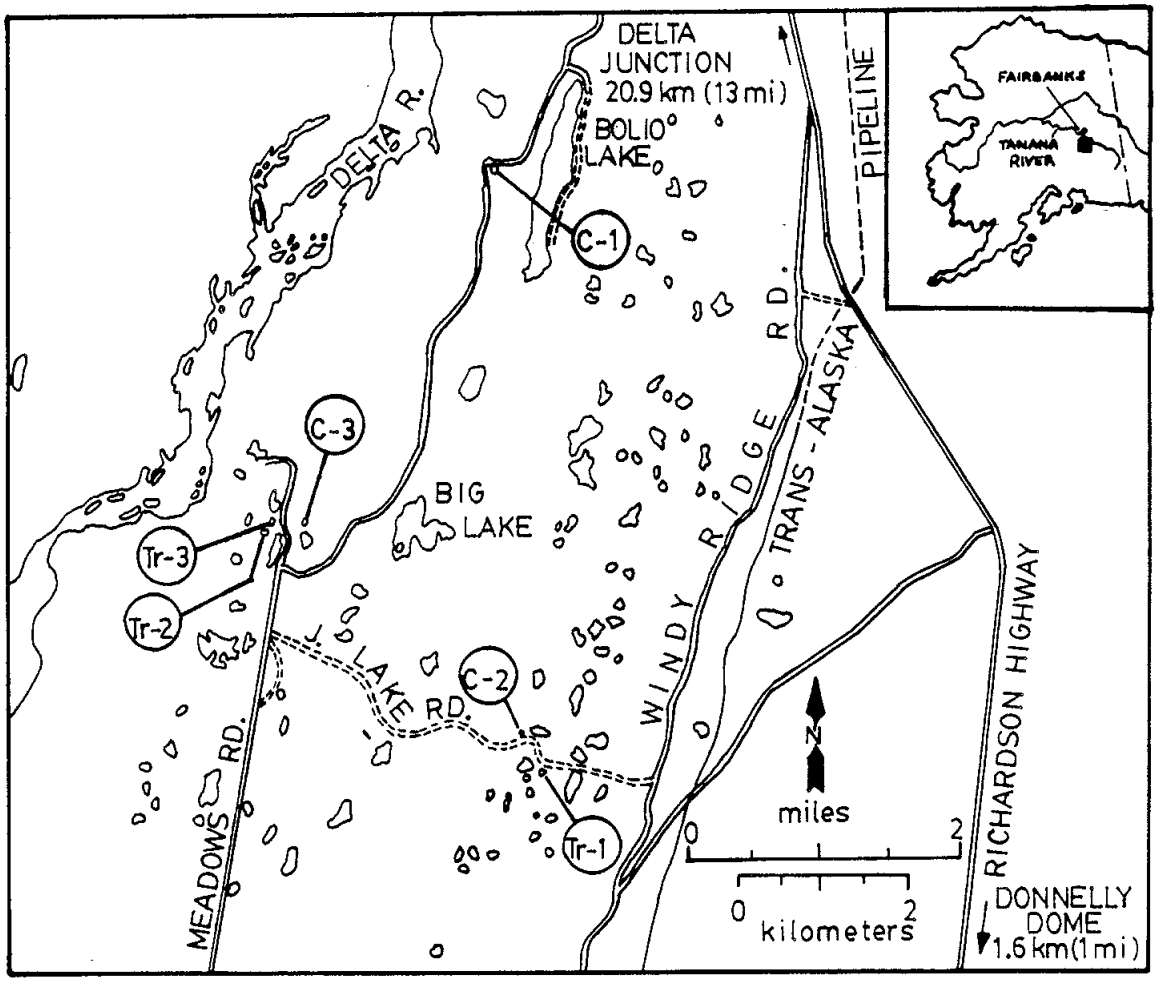

Figure 1. Inset map of Alaska showing the study area and a detailed map of study ponds on Fort Greely Military Reservation (TR-treated; C-control).

water lily and grasses. Aquatics identified were Equisetum sp., Utricularia sp., Rannunculus sp. and Polygenom sp.

The Delta Junction area has a high frequency of strong winds compared to other interior regions of Alaska, especially during the winter. From 20 years of data, the Federal Aviation Administration at the Big Delta Airfield reports a mean wind velocity of 4.2 meters per second compared to 2.2 meters per second in Fairbanks (Pewe and Reger, 1983). With such winds, the ponds treated with CMA should be thoroughly mixed within a couple of days after treatment, and thermal stratification should be temporary in ponds less than 8 meters deep throughout the ice-free season.

CMA Application

On June 16, 1985, the three test ponds were treated with specific amounts of CMA. Since the exact concentration of calcium acetate in the test solution was unknown at the time, the ponds were treated to attempt to bracket the 50 mg/l CMA concentration believed to be the highest concentration that would not cause harm. The ponds were dosed with an amount that was calculated to elevate the concentration of TR-1 by 30 mg/l CMA, TR-2 by 88 mg/l CMA and TR-3 by 61 mg/l CMA. A small gas-powered pump with 61 to 91 meters of hose was used to pump the CMA solution from 208-liter barrels to the ponds. The final dose to all three ponds (as calculated from calcium concentrations measured on June 20, 1985) was less than intended: about 47 mg/l CMA in TR-1 and TR-2, and about 23 mg/l CMA in TR-3. This was due both to hydrologic changes in the ponds after they were mapped and to varying concentrations of CMA among barrels.

Sampling Schedule

The ponds were paired by attempting to match them morphometrically and for other measured cations in addition to trying to match calcium concentrations. Initial mapping of the ponds was completed in late April to determine outer boundaries and establish transects. Surveying procedures utilized a Topcon GTS-2 Total Station Electronic Distance

Measurer (EDM). Depth soundings of the ponds were conducted in mid-May, from which volumes and mean depths were calculated.

Collection of water samples for the 1985 season was begun the third week of May and completed by the second week in September. Pond sites were visited semimonthly for a total of nine field trips. Each pair of treated and control ponds was sampled on the same day, and in different orders each sampling trip (e.g., TR-1 would be sampled first and C-1 second on one trip and vice versa the next trip). Water samples for the major cations, nutrients, alkalinity, bacteria, chlorophyll a, dissolved oxygen and pH were taken at the initial visit to a site. All samples were taken at a depth of 0.5 m from the surface, over the deepest part of the pond unless otherwise noted. Another dissolved oxygen and pH measurement was taken six to eight hours later, to obtain a midmorning and early evening measurement for each. Samples taken for determining the dominant forms of phytoplankton and zooplankton were usually taken in the early evening. Certain samples were preserved and analyzed at a later time, and some were analyzed immediately. Table 2 summarizes the sample manipulations.

Analysis of CMA

Acetate concentrations within the ponds and the CMA mixture were determined using a Dionex Model 2000i ion chromatograph. The results were recorded on a Hewlett Packard Model 3390A integrator. Calibration standards were made through dilutions of glacial acetic acid. Sample concentrations were read from a standard curve of peak areas versus known concentrations (Doug McIntosh, Research Associate, 1985, Institute of Marine Sciences, University of Alaska-Fairbanks, personal communication). The stock CMA samples had to be diluted before analysis.

Physical Measurements

Air and Water Temperatures. Air and water temperatures (at 0.5 m) were measured at each sampling site. Temperature readings were made with hand-held pocket thermometers. Supplementary information regarding

TABLE 2. Summary of sample manipulations.

Determination	Sample size (ml)	Preservation	Analysis
Acetate	200	NaOH to pH 10 and refrigerate	Ion chromatograph
Alkalinity	200	refrigerate	Titration
Bacteria numbers	60	2% formaldehyde and refrigerate	Epifluorescence
Turnover times	250	Scintillation cocktail	Scintillation counter
Chlorophyll a	1000	filter/freeze	Fluorometry
Metals	125	refrigerate	Atomic absorption
Nitrogen:			
Ammonia	125	filtered and frozen immediately	Autoanalyzer
Nitrate	125	filtered and frozen immediately	Autoanalyzer
Oxygen, dissolved	300	analyze immediately	Winkler titration
pH	N/A	analyze immediately	pH meter
Phosphorus:			
Orthophosphate	125	filtered and frozen immediately	Autoanalyzer
Total phosphorus	125	frozen immediately	Autoanalyzer
Phytoplankton:			
Dominance	125	Lugol's sol'n	Microscope
Zooplankton:			
Dominance	250	4% formalin	Microscope

daily air temperatures, precipitation and wind speeds for the study site was provided by the Fort Greely Meteorological Team.

Light Availability. Light at depth data were collected at least monthly to calculate total extinction coefficients using a LI-COR 188B integrating quantum radiometer photometer and two quantum sensors; a 192 SB sensor was used for underwater readings, and a 190 SB sensor was used for surface readings. A LI-COR SS-3 calconnector switchbox was used to switch between the surface and underwater sensors. An integration time of 100 seconds was used, and two to three readings were usually taken at each depth. Readings were taken from the center of each pond. The surface sensor was placed on the raft, and the underwater sensor was attached to a frame and lowered by cable to the designated depth. Total extinction coefficients were derived by linear regression of the log of the light intensity at depth versus depth (Wetzel and Likens, 1979).

Chemical Measurements

Alkalinity and pH. Alkalinity was measured as mg/l as $CaCO_3$ via potentiometric titrations (Stumm and Morgan, 1970). Samples were kept cold and titrated within six hours at the temporary field station at the Alaska Department of Fish and Game in Delta Junction. Measurements of pH were taken with a HACH digital pH meter calibrated with buffers.

Major cations. The major cations measured were calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}). All were determined using a Perkin Elmer Model 107 Atomic Absorption Spectrophotometer coupled with an HP-3478A multimeter following procedures set out in Standard Methods (APHA et al., 1980). Standard additions of known standards to samples were done periodically to check the accuracy of the procedure.

Dissolved Oxygen. Triplicate samples for dissolved oxygen (DO) were collected with a dissolved oxygen sampler in 300-ml BOD bottles, and DO was determined immediately via the Winkler method using HACH powder pillow reagents and titrating with HACH phenylarsine oxide

reagent (PAO). The PAO was periodically standardized with an iodate-iodide standard solution.

Replicate samples were taken at three depths in mid-July to get a profile of dissolved oxygen concentrations within each pond. These were taken within minutes for each pair of ponds.

Nutrients. Analyses for nitrite-nitrate nitrogen, ammonia and orthophosphate were conducted using a Technicon AutoAnalyzer II and Standard Methods (APHA et al., 1980). Peak heights were measured using an HP Model 9845 digitizer. Concentrations were calculated from the peak heights compared to regression data from sets of standards and their peak heights. Total phosphorus was analyzed using the persulfate digestion method (Eisenreich et al., 1975). This was followed by analysis on the Technicon II AutoAnalyzer for orthophosphate.

Biological Measurements

Planktonic Chlorophyll *a*. Chlorophyll constitutes approximately 1 to 2% of the dry weight of organic matter in all planktonic algae, and it is the preferred indicator for estimating algal biomass.

Nine samples for chlorophyll *a* determinations were collected from each pond biweekly at random sites along established transects. A random numbers table was used to choose the transect to be sampled, and then the table was used again to select the distance along the transect at which the sample would be taken. Samples were collected using a Van Dorn sampler and filtered through a Gelman A-E glass fiber (0.3 μm) filter. One dropperful (1.0 ml) of saturated magnesium carbonate suspension was added during filtering to prevent acidification during transport and storage of the samples. Filtered samples were placed into a glassine envelope, placed in a dessicator and kept frozen until analysis. Analysis for chlorophyll *a* was done within five days of collection.

Chlorophyllous pigments were extracted using a 90% (v/v) acetone solution, followed by masceration of the sample on the filter and centrifugation. The supernatant was decanted after being held overnight in darkness at 4°C and measured on the Turner Model 10 Fluorometer.

Because the output from the fluorometer is in arbitrary units, it must be standardized using a chlorophyll a solution of known concentration. We used the method by Wetzel and Likens (1979) of calibrating the fluorometer against the spectrophotometer.

Samples were not acidified and corrected for phaeophytin a to determine physiological state of the algae. The methodology has not been standardized for fluorometry, so all chlorophyll a concentrations reported are for total chlorophyll a.

Planktonic Bacteria. Triplicate 60 ml samples were collected using a Van Dorn water sampler and the total number of bacteria cells determined. The samples were preserved with 2% formaldehyde solution and refrigerated until analysis. Total cells were determined using the acridine orange epifluorescent direct count method (AODC) (Francisco et al., 1973; Hobbie et al., 1977). A subsample (0.2 ml) was diluted to 2 ml and mixed with a 1 ml aliquot of prefiltered 0.1% fluorescent stain (acridine orange), allowed to incubate approximately two minutes and filtered through a Nuclepore filter (0.2 µm pore size, 25-mm diameter) that had been stained with irgalan black dye to give a dark background. We used a Zeiss Standard research microscope equipped with an IV FI epifluorescence condenser. For each of the three samples treated as above, 10 random fields per filter were counted within a known field area. Thus, by knowing the sample volume, area of the counting field, diameter of filter, and total number of fields, the number of bacteria per unit volume could be estimated. Results are expressed as numbers per milliliter in this paper. Replicate samples were collected in mid-July at three different depths to get a profile of cell numbers for each pond.

Acetate Turnover Times. Samples of 250 ml of the natural waters were collected for determining acetate turnover time. Each sample was spiked with a known amount of radiolabeled acetate solution (specific activity 54.7 µCi/mmole; contained in 100 ml autoclaved deionized-distilled water). Subsamples of 5 ml were taken at selected time interals and filtered through a Millipore filter (0.45 µm) into acid-washed test tubes. One ml was removed from the filtrate and put into

10 ml of a scintillation cocktail mixture (toluene, Triton-x and omnifluor), and counts per minute (cpm) were recorded on a Beckman Liquid Scintillation Counter, 5801 series. Plotting the natural logarithm of the cpm remaining in solution versus time, an estimated turnover time, T_t, was calculated as the negative inverse of the slope (Brown et al., 1978).

Dominant Phytoplankton. Three 125 ml samples were collected monthly using a Van Dorn water sampler at 0.50 m depth to identify the most dominant phytoplankton taxa. Samples were preserved in Lugol's iodine solution until analysis. Samples of 10 ml were filtered onto 25 mm Millipore filters (0.45 μm) through a swinex filter holder and cleared with immersion oil. Visually dominant taxa were identified under a compound microscope at up to 1,000X magnification.

Relative Abundance of Zooplankton. Three 250 ml samples were collected monthly for four months to estimate relative abundance of certain zooplankton populations. The samples for June were accidently frozen, so they cannot be used for analysis. Samples were collected in the early evening using a zooplankton net (250 μm pore size). The hauls were made vertically at the deepest part of the pond and samples were preserved with a 4% final concentration of formalin and held for analysis. By knowing the sample volume, the amount of water filtered (calculated from depth of haul and net diameter), and the number of organisms in the sample, the abundance of a particular organism in each pond was estimated. All organisms were identified using a stereo microscope at 100X magnification.

Statistical Analysis

A randomized complete block analysis (pond pairs = block, and treatment versus control = factor) was performed with repeated measurements over time (the seven dates after CMA treatment). Several variables such as chlorophyll *a*, calcium, magnesium, sodium and potassium were measured repeatedly at random points along preset

transects (selected randomly) within a pond on each date. When this was done for a measured characteristic, sampling error was calculated.

A sample ANOVA is shown for number of bacteria/ml*10^6. Units are not shown for simplicity.

ANOVA

		DF	SS	MS	F
	Pair	2	3.91	1.96	
	Treatment	1	25.00	25.00	3.04
Error I	Pair x treatment	2	16.46	8.23	
	Date	6	159.11	26.52	19.36**
	Treat x date	6	43.12	7.19	5.24**
Error II	Pair x date	12	12.42	1.04	
	Pair x treatment x date	12	20.51	1.71	
	Sampling error	--	---		

Sampling error (if samples were taken repeatedly on a date) was tested against Error II to determine significance (F test). If no significance was found, the errors were pooled to account for within-group variability, providing a more powerful test (Zar, 1984). Calculated Fs are considered significant when the probability, p, is <0.05, and highly significant when p <0.01. The statistical package SAS was used to perform the calculations.

RESULTS

This section will present data collected over the 1985 sampling season in tabular and figure form. The raw data are presented in appendices of another publication (Rea, 1986).

Analysis of CMA

Chemical analysis was performed in the summer of 1985 on the calcium acetate solution produced in the summer of 1984 by the Department of Petroleum Engineering at the University of Alaska-Fairbanks. Two subsamples were collected from the mixture: from a gray slurry at the bottom of a barrel of CMA which probably contained undissolved lime, and from the clear supernatant. The samples were analyzed for calcium, chloride, magnesium, phosphorus, sodium and sulfate (Table 3).

TABLE 3. Chemical analysis of calcium acetate solution 1985.

Parameter	Concentration (mg/l)	Standard deviation
Supernatant:		
Calcium	56,200	3,100
Chloride	150	--
Magnesium	243	4
Phosphorus	2,500	200
Sodium	4,100	300
Sulfate	580	--
Slurry*:		
Calcium	102,000	400
Chloride	300	--
Magnesium	253	9
Phosphorus	3,600	100
Sodium	4,100	1,100
Sulfate	1,050	--

* Slurry sample was analyzed for dissolved sulfate and chloride. Analysis was done by Northern Testing Laboratories, Inc., Fairbanks, Alaska.

Calcium, chloride, phosphorus and sulfate concentrations were higher within the slurry, while magnesium and sodium were in equal concentrations in the slurry and the supernatant. Compared to a 1984 analysis of the freshly made chemical (Table 4), calcium and chloride concentrations were lower in the supernatant in 1985. Magnesium, phosphorus, sodium and sulfate were higher in the 1985 analyses.

Acetate concentrations were determined directly for the CMA mixture used in 1985 and for each pond after treatment (July 5, 1985) (Table 5). The amount of acetate measured in the 1985 CMA mixtures was half of that calculated by Northern Testing Lab for the 1984 CMA mixture based on complete combination with the calcium present. The detection limit for acetate using the ion chromatograph is 10 μM (0.59 mg/l); many pond samples were below this concentration. Both samples for C-3 and TR-2 were below the detection limit for acetate. The other ponds all had at least one sample above the detection limit.

The 1984 analysis of the CMA solution showed measurable concentrations of arsenic, cadmium, chromium, lead, mercury, nickel and selenium (Table 4). Of these trace metals, nickel and selenium were

TABLE 4. Chemical analysis of calcium acetate solution 1984.

Parameter	Concentration (mg/l)	Standard deviation
Acetate ion	399,000*	--
Arsenic	0.607	0.069
Cadmium	0.159	0.001
Calcium	67,800	640
Chloride	2,100	--
Chromium	0.440	0.002
Lead	0.287	0.038
Magnesium	21.3	0.1
Mercury	<0.002	--
Nickel	3.99	0.09
Phosphorus	200	100
Selenium	1.60	0.31
Sodium	14.0	0.3
Sulfate-S	304	--

* By calculation, if all calcium is combined with acetate. Analysis done by Northern Testing Laboratories, Inc., Fairbanks, Alaska.

TABLE 5. Acetate concentrations within test ponds and CMA mixture (July 5, 1985).

Pond	Acetate concentration (mg/l)	Pond	Acetate concentration (mg/l)
C-1	ND*	TR-1	ND
	0.84		1.20
C-2	1.44	TR-2	ND
	ND		ND
C-3	ND	TR-3	ND
	ND		0.72

CMA Mixture (concentration g/l):

Clear supernatant	174.0	Yellow/brown supernatant	180.0
Clear supernatant	180.0	Grey slurry	144.0

* ND = none detected.

TABLE 6. Calculated approximate concentrations of heavy metals entering the ponds with CMA treatment.

Heavy metal	USEPA[a] criterion concentration (µg/l)	TR-1 (µg/l)	TR-2 (µg/l)	TR-3 (µg/l)
Arsenic	440*	0.09	0.12	0.05
Cadmium	1.5*	0.02	0.03	0.02
Chromium	2,200*	0.06	0.09	0.04
Lead	74*	0.04	0.06	0.02
Mercury	0.14*	--**	--	--
Nickel	13.4*	0.6	0.8	0.4
Selenium	10	0.2	0.3	0.1

[a] Source: USEPA, 1980.

* All as total recoverable, not to be exceeded at any time (associated hardness of 50 mg/l as $CaCO_3$ when appropriate) for the protection of aquatic life. A specific valence state is designated for As (+3) and Se (+2)

** Negligible concentration.

present in the highest quantities (3.99 mg/l and 1.60 mg/l, respectively). The remaining trace metals were less than 1.00 mg/l; mercury was the lowest at <0.002 mg/l. Concentrations of trace metals which might have occurred in the ponds in 1985 upon addition of CMA were calculated based on the amount of added calcium measured after the ponds were treated (Table 6). Neither the 1985 CMA solutions nor the treated ponds were acutally tested for these metals.

Physical Measurements

The study ponds are located in an area of kettle lakes and thaw ponds 16 km north of Donnelly Dome. The surface areas range from 1,292 m^2 with a mean depth of 0.33 m, to an area of 4,494 m^2 with a mean depth of 0.62 m (Table 7).

TABLE 7. Morphometric parameters of the study ponds.

Pond	Volume ($L*10^6$)	Surface area (m^2)	Mean depth (m)
C-1	2.79	4,494	0.62
TR-1	4.38	4,467	0.98
C-2	1.45	1,395	1.04
TR-2	0.43	1,292	0.33
TR-2+	4.93	2,620	1.88
C-3	2.58	4,035	0.64
TR-3	2.56	3,372	0.76

+ As surveyed second time; July 5, 1985.

These ponds begin to freeze by late September and remain frozen until mid-to-late May, varying by one or two weeks for a given year. They freeze completely to the bottom during the winter season. Three to four weeks after snowmelt in 1985, the ponds experienced an increase in surface area and volume. Pond TR-2 had more than doubled its surface area from 1,292 m^2 in early June to 2,620 m^2 by early July, with an

accompanying increase in mean depth from 0.33 to 1.88 m. This was the most dramatic change in any of the study sites.

The greatest monthly precipitation as rain occurred during June, with a total of 13.56 centimeters (Table 8). The least amount of monthly precipitation as rain was recorded in May, with 0.56 cm. The greatest period of snowfall occurred during October, with a monthly total of 30.99 cm. The least amount recorded was in May, at 1.27 cm.

Air and Water Temperatures. Temperatures in the air and water were recorded biweekly. Mean daily air temperatures rose rapidly from mid-June to July, reaching a maximum by the end of July and steadily decreasing to the end of the season (Table 8). Water temperatures were as high or higher than air temperatures from June 5 to August 28. The greatest difference between air and water temperatures occurred June 5 at temperatures of 8°C and 15°C, respectively. The highest water temperature was 22°C on July 20 in Pond C-1. Other ponds experienced their maximum temperatures of 21°C on that same day.

TABLE 8. Climatic conditions within study area for 1985.

	Pond	May	Jun	Jul	Aug	Sep	Oct
Air temp (avg. °C)		7	12	18	13	10	-9
Water temp (avg. °C)	C-1	13	14	19	13	8	4
	TR-1	12	15	18	12	7	4
	C-2	19	14	18	12	7	4
	TR-2	17	13	19	14	7	4
	C-3	17	13	19	12	8	4
	TR-3	16	13	17	12	8	4
Precip.* (monthly, cm)	water:	0.56	13.56	4.50	6.27	5.69	3.38
	snow:	1.27				2.54	30.99
Wind speed (knots)	mean:	4	3	2	3	4	2
	peak:	40	35	24	40	44	40

* Precipitation and wind speed data from Fort Greely Meteorological Team.

The winds speeds were variable throughout the summer; the highest winds occurred in September, with a peak wind speed of 44 knots. The highest average wind speed was 4 knots in May and September. The lowest recorded wind speeds were in July and October.

Light Availability. The extinction coefficients (k) ranged from 4.11 to 1.00 in all ponds, which is equivalent to 2% to 37% of surface light reaching depths of 1.5 m (Table 9). C-1 showed the maximum transmittance (37%/m) and TR-3 the minimum transmittance (2%/m). Seasonally, k was maximum in mid-August, transmission averaging 3%/m of the surface light. Within pairs, the control ponds generally transmitted a greater percentage of surface light per meter.

Chemical Measurements

Alkalinity and pH. Data for alkalinity (mg/l as $CaCO_3$), pH, dissolved oxygen (mg/l) and percent saturation of dissolved oxygen are presented in Tables 10 to 15 for all ponds. Pond TR-3 showed the greatest increase in alkalinity over the season. TR-1 showed the most significant increase immediately after CMA addition (17.50 to 40.06 mg/l as $CaCO_3$).

Initially, pH was 6.9 to 7.2 in all ponds. In treated ponds 1 and 2, the pH looked generally higher than the controls. TR-2 and C2 showed the largest difference in pH. The most radical change in pH occurred in TR-1; it had a pH of 6.4 before treatment and 7.8 two weeks later.

Dissolved Oxygen. Concentrations of dissolved oxygen (D.O.) were initially near saturation (except for pond C-1), decreasing in July and increasing slightly by mid-September (Figures 2-4). The largest change in D.O. occurred within TR-3, where it decreased from 8.25 mg/l (85.9% saturated) in mid-June to 1.55 mg/l (17.2% saturated) in late July. In comparison, C-3 remained at relatively constant levels throughout the season. Pair two also showed significant differences in D.O., which decreased from 9.00 mg/l (95.8% saturated) in mid-June within TR-2 to 2.60 mg/l (31.8% saturated) in mid-July. C-2 had an initial concentration of 9.14 mg/l (95.2% saturated), which did not change

TABLE 9. Light extinction coefficients and percent absorbances.

Pond	Date	Extinction coefficient (k)	Percent absorbance per meter
C-1	5 Jul 85	1.39	75
	20 Jul 85	2.28	90
	15 Aug 85	2.60	93
	12 Sep 85	1.00	63
TR-1	20 Jul 85	2.65	93
	30 Aug 85	2.63	93
	12 Sep 85	2.97	95
C-2	5 Jul 85	1.93	86
	20 Jul 85	1.20	70
	30 Aug 85	1.62	80
	12 Sep 85	1.70	82
TR-2	5 Jul 85	2.06	70
	20 Jul 85	3.46	97
	30 Aug 85	3.46	97
	12 Sep 85	2.11	88
C-3	5 Jul 85	2.20	89
	30 Jul 85	2.71	93
	12 Sep 85	2.42	91
TR-3	5 Jul 85	1.42	76
	30 Jul 85	4.11	98
	12 Sep 85	2.37	91

Calculations:

Lambert-Beer Law: $I = I_o e^{-kz}$

where

I = light intensity at depth, z
I_o = light intensity at surface
e = base natural logarithms
z = depth, meters

$$k = (\ln I_1 - \ln I_2)/(z_2 - z_1)$$

percent transmission:

$$\% T = 100\ e^{-k}$$

percent absorbance:

$$\% Abs = 100\% - \% T$$

TABLE 10. Physical/chemical data for pond C-1.

Sampling Date	Air temp (°C)	Water temp (°C)	D.O. (mg/l)	Percent saturation D.O.	pH	Alkalinity mg/l as $CaCO_3$)
23 May	20	13	---	---	7.2	20.12
5 June	8	13	6.96	70.9	6.4	17.79
20 June	18	15	5.70	60.6	7.0	22.48
5 July	14	18	3.98	44.8	6.2	22.70
20 July	22	22	1.75	21.1	6.1	31.25
31 July	20	18	4.34	49.6	6.0	26.20
15 August	12	14	8.96	93.4	6.6	27.81
28 August	15	12	7.15	71.3	6.5	26.67
12 September	9	8	6.17	56.1	6.4	33.79

TABLE 11. Physical/chemical data for pond TR-1.

Sampling Date	Air temp (°C)	Water temp (°C)	D.O. (mg/l)	Percent saturation D.O.	pH	Alkalinity (mg/l as $CaCO_3$)
23 May	20	12	9.90	98.7	6.7	25.45
5 June	7	10	9.50	90.6	6.4	17.50
20 June	18	20	7.90	89.4	7.8	40.06
5 July	14	16	5.92	62.4	6.7	40.25
20 July	22	21	5.03	60.4	6.4	38.68
31 July	18	18	4.95	55.4	6.2	39.07
15 August	12	10	9.76	94.1	6.8	30.76
28 August	15	12	7.15	71.3	6.5	36.37
12 September	9	7	7.18	63.7	6.4	44.86

TABLE 12. Physical/chemical data for pond C-2.

Sampling Date	Air temp (°C)	Water temp (°C)	D.O. (mg/l)	Percent saturation D.O.	pH	Alkalinity (mg/l as $CaCO_3$)
23 May	20	19	---	---	6.9	14.56
5 June	10	15	---	---	6.1	11.22
20 June	18	14	9.14	95.2	7.2	14.24
5 July	16	16	8.37	91.8	5.9	40.00
20 July	20	20	7.53	88.7	5.5	43.34
31 July	19	18	7.50	84.0	5.7	11.42
15 August	10	11	10.33	100.7	6.6	9.87
28 August	20	12	9.30	93.5	7.0	8.41
12 September	10	7	9.57	84.9	----	16.37

TABLE 13. Physical/chemical data for pond TR-2.

Sampling Date	Air temp (°C)	Water temp (°C)	D.O. (mg/l)	Percent saturation D.O	pH	Alkalinity (mg/l as $CaCO_3$)
23 May	20	17	---	---	6.6	11.63
5 June	10	13	000	000	6.6	18.45
20 June	18	15	9.0	95.8	7.3	27.16
5 July	14	16	4.58	50.2	6.4	11.83
20 July	24	21	3.64	43.4	6.3	10.92
31 July	16	18	4.41	49.5	6.6	53.46
15 August	15	13	5.36	36.7	6.8	51.82
28 August	14	14	6.73	69.4	6.6	74.25
12 September	12	7	3.88	34.4	7.0	---

TABLE 14. Physical/chemical data for pond C-3.

Sampling Date	Air temp (°C)	Water temp (°C)	D.O. (mg/l)	Percent saturation D.O.	pH	Alkalinity (mg/l as $CaCO_3$)
23 May	20	17	---	---	7.5	28.73
5 June	8	12	9.65	92.2	6.8	29.44
20 June	14	14	---	---	7.1	33.56
5 July	14	17	8.25	87.8	7.2	36.37
20 July	14	20	7.01	82.6	6.6	37.81
31 July	21	19	8.06	93.0	6.8	39.95
15 August	11	12	10.49	104.6	6.9	37.38
28 August	13	12	10.24	102.1	7.2	93.94
12 September	10	8	11.36	103.4	---	---

TABLE 15. Physical/chemical data for pond TR-3.

Sampling Date	Air temp (°C)	Water temp (°C)	D.O. (mg/l)	Percent saturation D.O.	pH	Alkalinity (mg/l as $CaCO_3$)
23 May	20	16	---	---	7.0	43.39
5 June	7	12	4.16	48.5	6.8	34.49
20 June	14	14	8.25	85.9	6.5	43.48
5 July	14	16	---	---	6.6	39.47
20 July	13	18	2.05	23.2	6.0	59.01
31 July	18	18	1.85	21.0	6.4	85.48
15 August	9	12	4.51	45.0	6.7	135.03
28 August	14	12	3.85	39.0	7.1	119.25
12 September	12	8	4.98	45.3	7.2	---

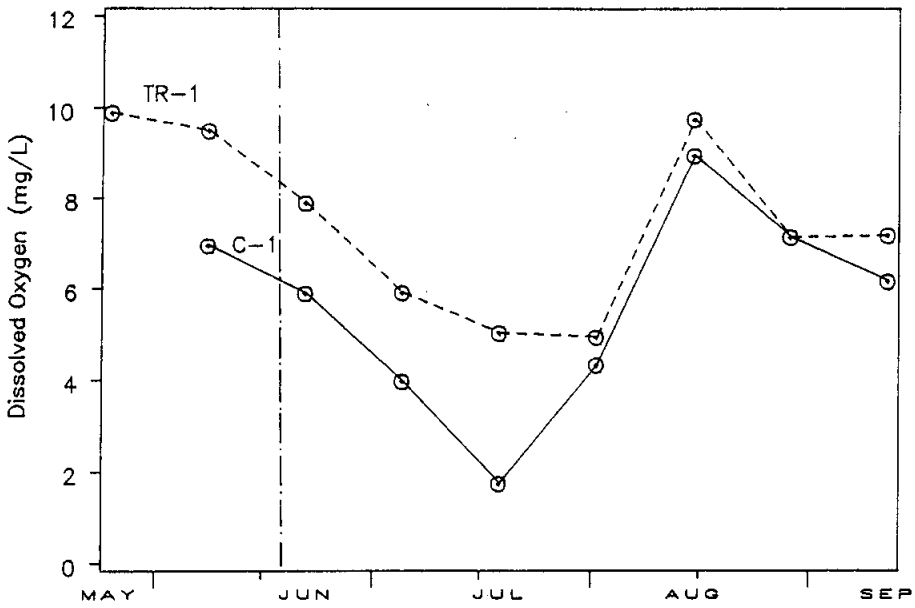

Figure 2. Mean concentrations of dissolved oxygen for pair one ponds. Vertical line indicates time of CMA addition.

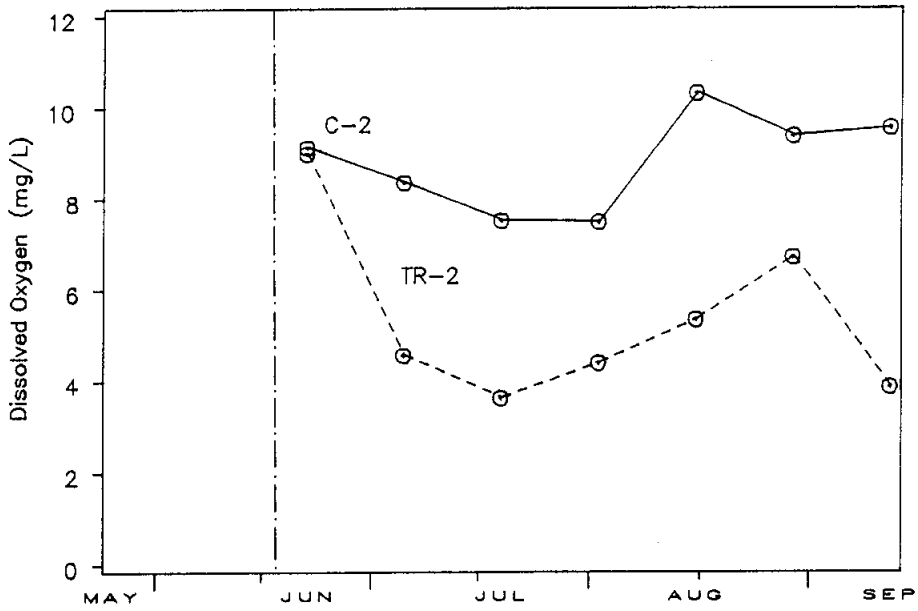

Figure 3. Mean concentrations of dissolved oxygen for pair two ponds. Vertical dashed line indicates time of CMA addition.

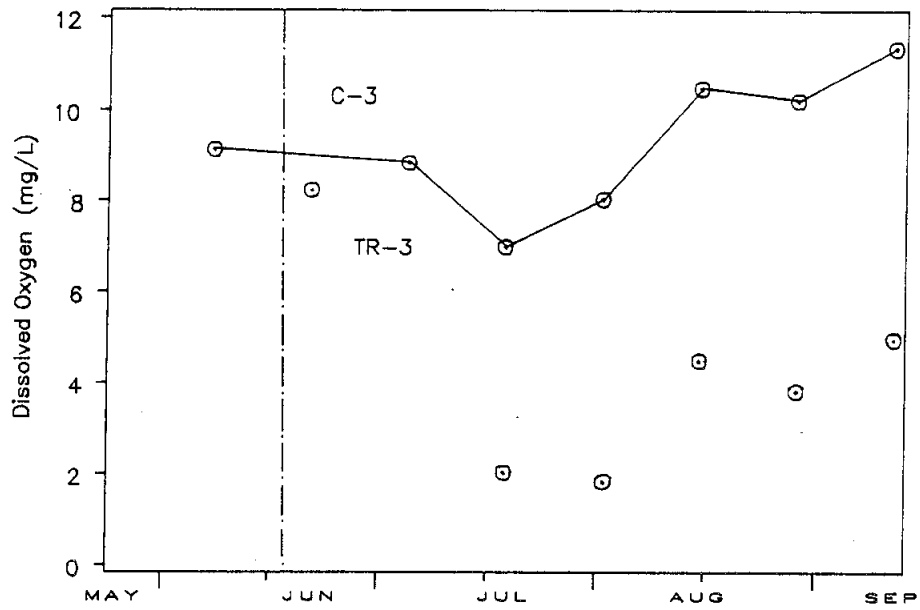

Figure 4. Mean concentrations of dissolved oxygen for pair three ponds. Vertical dashed line indicates time of CMA addition.

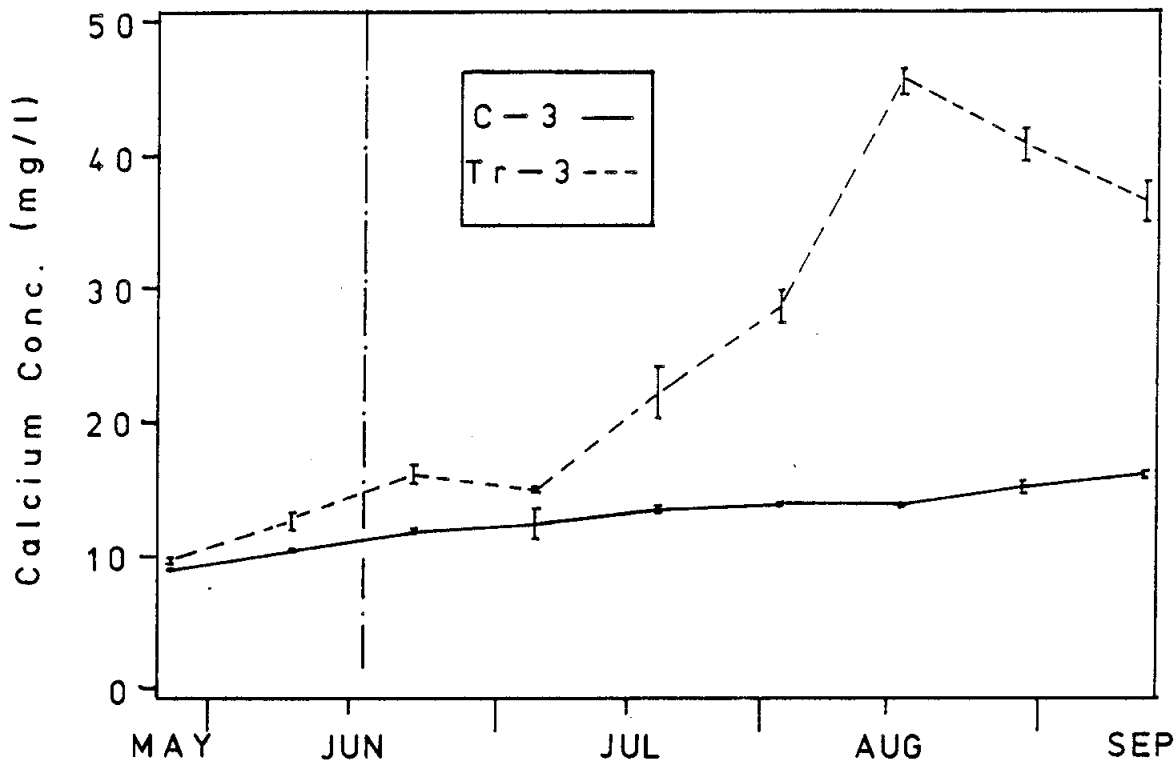

Figure 5. Mean calcium concentrations plus or minus one standard error for pair one ponds. Vertical dashed line indicates time of CMA addition.

drastically through the season. Pair one differed from the other two in that the control pond attained the lower D.O. values. Its lowest concentration, 1.10 mg/l (13.4% saturated), occurred in mid-July.

Dissolved oxygen concentrations were profiled with depth for each pond in late July of 1985. All ponds showed a decrease in D.O. levels with increased depth (Table 16). Within the first meter, concentrations had decreased by a maximum of 2.00 mg/l within the controls, while the treated ponds showed a decrease of 4.0 mg/l (TR-2). TR-3 had decreased to a zero concentration by 1.0 m depth, having a surface concentration of only 2.15 mg/l. By 1.50 m, the D.O. concentrations in all treated ponds had decreased to less than 1.00 mg/l. Analysis of variance on the effects of depth and treatment on dissolved oxygen levels showed a highly significant effect due to depth and treatment ($p<0.01$).

Major Cations. The concentration of measured cations (calcium, magnesium, sodium and potassium) are listed in Tables 17-22. Calcium levels within each pair are illustrated in Figures 5-7. After adding CMA, calcium concentrations increased dramatically in the treated ponds. Calcium in TR-1 declined slightly one month after application but maintained a relatively constant elevated concentration throughout the season. TR-2 doubled in calcium concentration after treatment, rising steadily through the summer to reach its maximum value by mid-September. The magnesium concentration in this pond showed a steady increase to its maximum value by September as well. The calcium level after treatment in TR-3 increased 30% from its concentration before treatment and continued a steady increase throughout the season. There was a significant increase in calcium over time in all ponds ($p<0.05$) and a highly significant increase in magnesium, sodium and potassium ($p<0.01$). After the CMA additions, increases and decreases in the concentration of the metals must have been mainly due to evaporation and precipitation. In fact, when calcium concentrations are normalized by dividing by the concentrations of an ion not added to the test ponds with the CMA (such as sodium), this ratio also is elevated in the test ponds when compared to their control ponds.

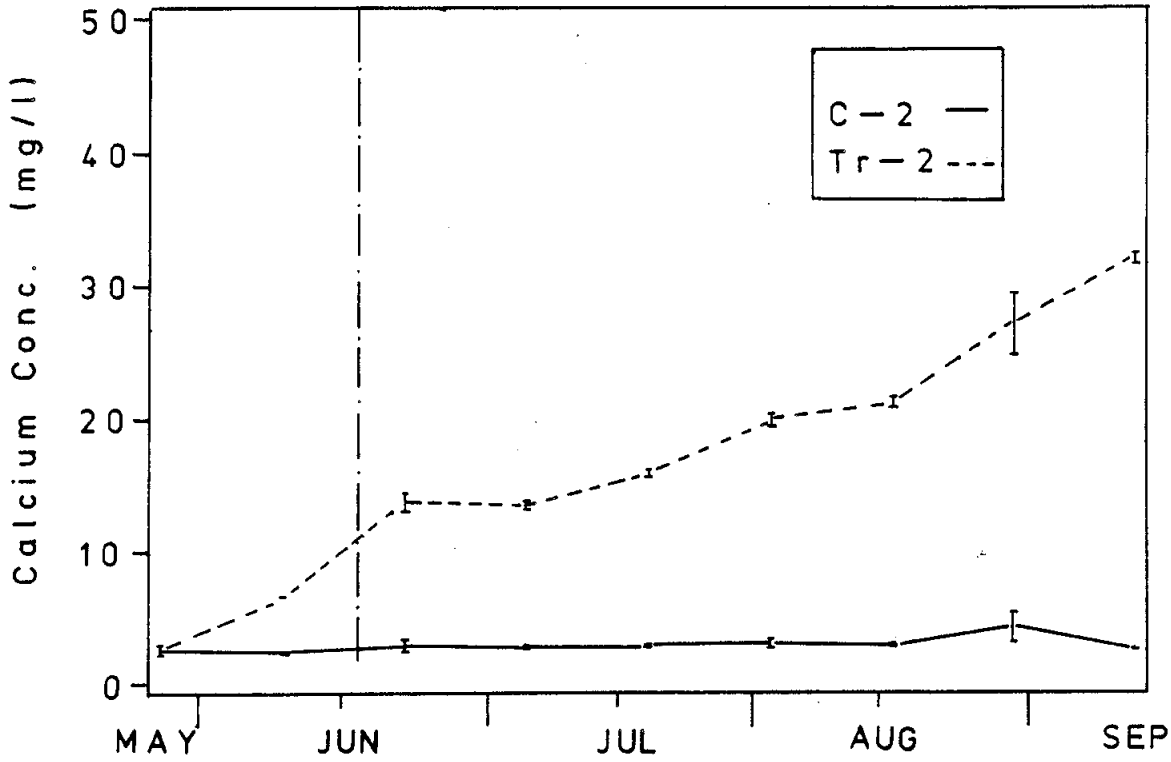

Figure 6. Mean calcium concentrations plus or minus one standard error for pair two ponds. Vertical dashed line indicates time of CMA addition.

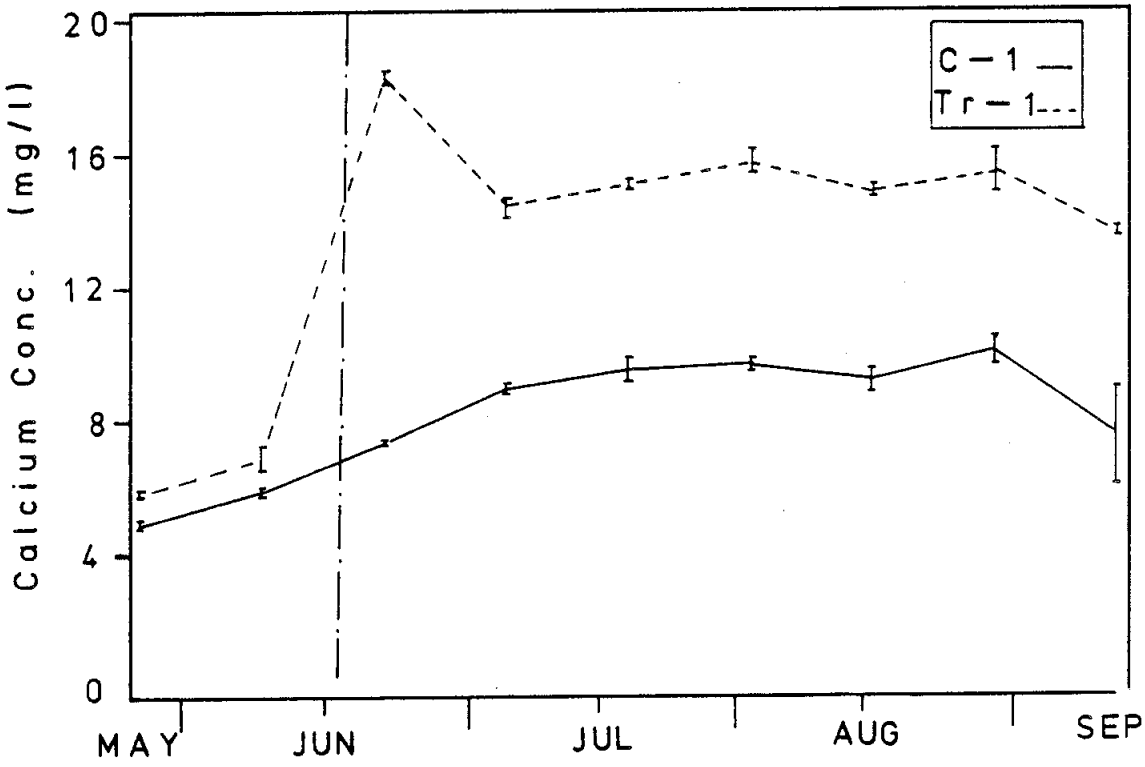

Figure 7. Mean calcium concentrations plus or minus one standard error for pair three ponds. Vertical dashed line indicates time of CMA addition.

TABLE 16. Depth profile of dissolved oxygen concentration and percent saturation on July 30, 1985.

	C-1		C-2		C-3	
Depth (m)	D.O. (mg/l)	%Sat	D.O. (mg/l)	%Sat	D.O. (mg/l)	%Sat
0.50	4.59	48.1	8.64	90.6	8.59	91.9
	3.73	39.1	8.37	87.7	8.96	95.2
0.75	--	--	--	--	8.37	89.5
	--	--	--	--	8.42	90.0
1.00	2.38	24.9	6.48	67.9	8.21	87.1
	1.13	11.9	4.05	60.6		
1.50			1.89	19.8		
			1.78	18.7		

	TR-1		TR-2		TR-3	
Depth (m)	D.O. (mg/l)	%Sat	D.O. (mg/l)	%Sat	D.O. (mg/l)	%Sat
0.50	5.56	58.3	5.02	52.6	2.75	2.89
	4.86	50.9	5.40	56.6	1.89	2.00
0.75	--	--	--	--	0.00	0.00
	--	--	--	--	0.00	0.00
1.00	4.05	42.4	0.92	9.64	0.00	0.00
	4.54	47.6	0.76	7.97	0.00	0.00
1.50	0.59	6.23	0.59	6.23		
	0.81	8.49	0.92	9.64		

Nutrients. Mean values for ammonia, nitrite/nitrate, orthophosphate, and total phosphorus are presented in Tables 23 to 28 (next several pages). Raw data are included in the appendices of another publication (Rea, 1986).

Initial concentrations of ammonia nitrogen (NH_3-N) were generally high in all ponds, decreasing in late June, and reaching a second peak in mid-July. Concentrations either remained relatively stable after this point or showed a third peak in September (C-1). The decrease in

TABLE 17. Concentrations of major cations for pond C-1.*

Date	N	CALCIUM Mean	CALCIUM SD	MAGNESIUM Mean	MAGNESIUM SD	SODIUM Mean	SODIUM SD	POTASSIUM Mean	POTASSIUM SD
23 May	12	4.92	0.25	2.04	0.06	0.35	0.01	1.89	0.06
5 June	6	5.91	0.17	2.38	0.04	0.37	0.01	2.04	0.09
20 June	6	7.36	0.09	3.09	0.04	0.46	0.00	1.50	0.04
5 July	6	8.94	0.20	3.61	0.08	0.51	0.02	0.88	0.04
20 July	6	9.51	0.44	3.83	0.14	0.63	0.08	1.16	0.05
30 July	6	9.66	0.24	3.87	0.21	0.77	0.17	1.33	0.07
15 August	6	9.19	0.42	4.06	0.08	0.60	0.03	1.37	0.08
28 August	6	10.04	0.50	4.22	0.10	0.88	0.10	1.93	0.24
12 September	3	7.49	1.25	3.33	0.61	0.51	0.04	1.61	0.33

* All concentrations expressed as mg/l.

TABLE 18. Concentrations of major cations for pond TR-1.*

Date	N	CALCIUM Mean	CALCIUM SD	MAGNESIUM Mean	MAGNESIUM SD	SODIUM Mean	SODIUM SD	POTASSIUM Mean	POTASSIUM SD
23 May	12	5.87	0.14	1.04	0.02	0.26	0.01	3.40	0.10
5 June	6	6.90	0.44	1.21	0.09	0.37	0.04	2.63	0.07
20 June	6	18.30	0.25	1.55	0.02	0.30	0.02	2.43	0.05
5 July	6	14.37	0.38	1.82	0.08	0.59	0.41	2.05	0.21
20 July	6	15.06	0.20	1.90	0.03	0.49	0.02	2.25	0.04
30 July	6	15.75	0.42	1.94	0.05	0.53	0.07	2.28	0.07
15 August	6	14.85	0.20	1.90	0.04	0.47	0.01	2.22	0.07
28 August	5	15.44	0.72	2.35	0.26	0.77	0.22	2.26	0.08
12 September	3	13.63	0.13	1.25	0.53	0.47	0.01	2.33	0.11

* All concentrations expressed as mg/l.

TABLE 19. Concentrations of major cations for pond C-2.*

Date	N	CALCIUM Mean	CALCIUM SD	MAGNESIUM Mean	MAGNESIUM SD	SODIUM Mean	SODIUM SD	POTASSIUM Mean	POTASSIUM SD
23 May	10	2.45	0.08	1.12	0.04	0.36	0.05	3.71	0.59
5 June	6	2.35	0.04	1.00	0.00	0.27	0.01	3.87	0.12
20 June	6	2.84	0.55	1.20	0.13	0.24	0.09	3.59	0.06
5 July	6	2.64	0.16	1.19	0.06	0.24	0.01	3.33	0.06
20 July	6	2.75	0.18	1.22	0.04	0.32	0.01	3.28	0.26
30 July	6	2.92	0.40	1.25	0.07	0.32	0.06	3.43	0.09
15 August	6	2.79	0.11	1.24	0.02	0.39	0.04	3.69	0.06
28 August	6	4.12	1.39	1.60	0.23	0.53	0.28	3.61	0.11
12 September	3	2.46	0.02	1.17	0.02	0.43	0.12	3.69	0.12

* All concentrations expressed as mg/l.

TABLE 20. Concentrations of major cations for pond TR-2.*

Date	N	CALCIUM Mean	CALCIUM SD	MAGNESIUM Mean	MAGNESIUM SD	SODIUM Mean	SODIUM SD	POTASSIUM Mean	POTASSIUM SD
23 May	8	2.54	0.55	0.72	0.16	0.19	0.03	0.70	0.14
5 June	6	6.47	0.04	1.74	0.02	0.52	0.01	1.28	0.08
20 June	6	13.65	0.86	3.70	0.09	0.98	0.05	1.94	0.04
5 July	6	13.42	0.40	4.05	0.06	0.92	0.02	1.88	0.07
20 July	6	15.79	0.34	4.69	0.06	1.08	0.02	2.08	0.03
30 July	6	19.69	0.55	5.53	0.09	1.19	0.02	2.22	0.05
15 August	6	21.02	0.46	5.74	0.05	1.28	0.02	2.30	0.04
28 August	6	26.91	2.81	6.81	0.90	1.88	0.58	3.14	1.03
12 September	3	31.89	0.37	7.78	0.04	1.75	0.02	2.47	0.09

* All concentrations expressed as mg/l.

TABLE 21. Concentrations of major cations for pond C-3.*

Date	N	CALCIUM Mean	CALCIUM SD	MAGNESIUM Mean	MAGNESIUM SD	SODIUM Mean	SODIUM SD	POTASSIUM Mean	POTASSIUM SD
23 May	13	8.94	0.18	2.64	0.12	0.70	0.05	2.31	0.53
5 June	6	10.38	0.15	2.97	0.03	0.74	0.01	2.18	0.10
20 June	6	11.85	0.22	3.69	0.14	1.00	0.07	1.61	0.04
5 July	6	12.37	1.37	3.94	0.14	1.09	0.22	1.39	0.05
20 July	6	13.44	0.34	4.28	0.10	1.02	0.01	1.28	0.04
30 July	6	13.80	0.26	4.52	0.05	1.08	0.03	1.27	0.08
15 August	6	13.69	0.25	4.60	0.05	1.12	0.01	1.25	0.05
28 August	6	15.09	0.60	5.21	0.13	1.40	0.12	1.24	0.14
12 September	3	16.07	0.24	5.23	0.06	1.38	0.03	1.28	0.03

* All concentrations expressed as mg/l.

TABLE 22. Concentrations of major cations for pond TR-3.*

Date	N	CALCIUM Mean	CALCIUM SD	MAGNESIUM Mean	MAGNESIUM SD	SODIUM Mean	SODIUM SD	POTASSIUM Mean	POTASSIUM SD
23 May	12	9.62	0.32	3.06	0.10	0.57	0.02	3.29	0.34
5 June	6	12.58	0.84	3.71	0.26	1.01	0.47	2.76	0.08
20 June	6	16.08	0.82	4.47	0.15	1.24	0.38	1.76	0.12
5 July	6	14.95	0.21	3.55	1.90	1.10	0.06	1.72	0.07
20 July	6	22.18	2.34	6.32	0.66	1.33	0.04	2.19	0.06
30 July	6	28.55	1.42	7.33	0.26	1.61	0.08	2.36	0.06
15 August	6	45.57	1.14	8.84	0.14	2.27	0.16	2.52	0.05
28 August	6	40.79	1.48	0.16	0.29	2.09	0.03	2.76	0.87
12 September	3	36.56	1.34	9.82	0.63	2.12	0.08	2.41	0.05

* All concentrations expressed as mg/l.

TABLE 23. Mean concentrations and standard deviations of nutrients for pond C-1.

Date	N	NH_3-N	NO_2/NO_3-N	PO_4-P	Total P
6/5/85	6	51.64 ± 31.16	17.87 ± 4.86	6.82 ± 6.48	15.86 ± 6.66
6/20/85	6	19.16 ± 9.32	<6.20 ---	9.40 ± 3.78	15.24 ± 7.85
7/15/85	6	70.00 ± 65.84	(1)19.04 ---	1.70 ± 0.17	17.36 ± 5.14
8/15/85	6	34.16 ± 25.97	(4)63.35 ± 31.15	12.50 ± 1.56	11.52 ± 3.85
8/30/85	2	16.03 ± 0.30	<6.20 ---	11.94 ± 3.73	13.33 ± 0.00
9/12/85	3	44.19 ± 37.86	<6.20 ---	14.05 ± 5.05	7.13 ± 0.93

* All concentrations are expressed in µg/l.
\+ Number in parenthesis is number of samples if different than N.

TABLE 24. Mean concentrations and standard deviations of nutrients for pond TR-1.

Date	N	NH_3-N	NO_2/NO_3-N	PO_4-P	Total P
6/5/85	6	30.22 ± 13.58	30.80 ± 8.59	4.91 ± 1.50	36.52 ± 2.66
6/20/85	6	7.93 ± 2.92	(1) 0.56 ---	12.04 ± 24.96	24.96 ± 3.66
7/20/85	6	20.39 ± 2.87	(1) 0.56 ---	2.84 ± 0.30	30.64 ± 5.27
8/15/85	6	15.84 ± 5.79	(5)16.35 ± 20.16	15.29 ± 1.68	30.22 ± 3.67
8/30/85	2	24.71 ± 0.30	<6.20 ---	14.42 ± 0.22	35.65 ± 4.38
9/12/85	3	25.53 ± 8.19	<6.20 ---	13.43 ± 0.36	34.82 ± ±.76

* All concentrations are expressed in µg/l.
\+ Number in parenthesis is number of samples if different than N.

TABLE 25. Mean concentrations and standard deviations of nutrients for pond C-2.

Date	N	NH_3-N	NO_2/NO_3-N	PO_4-P	Total P
6/5/85	6	99.12 ± 65.12	(5)13.41 ± 5.98	4.60 ± 1.84	26.50 ± 15.94
6/20/85	6	15.00 ± 9.37	(1)16.94 ---	8,89 ± 0.38	12.97 ± 4.49
7/20/85	5	44.35 ± 9.33	<6.20 ---	1.92 ± 0.14	14.82 ± 6.42
8/15/85	5	11.23 ± 3.39	(2) 9.17 ± 2.28	11.10 ± 0.94	31.74 ± 34.93
8/28/85	2	8.12 ± 1.19	(1)13.58 ---	9.76 ± 0.66	15.81 ± 2.19
9/12/85	3	8,96 ± 3.40	(2) 3.78 ± 1.19	11.16 ± 3.49	9.09 ± 3.67

* All concentrations are expressed in µg/l.
\+ Number in parenthesis is number of samples if different than N.

TABLE 26. Mean concentrations and standard deviations of nutrients for pond TR-2.

Date	N	NH_3-N	NO_2/NO_3-N	PO_4-P	Total P
6/5/85	6	48.16 ± 36.38	8.87 ± 1.60	3.82 ± 0.85	38.90 ± 15.63
6/20/85	6	2.75 ± 3.68	<6.20 ---	9.92 ± 0.48	27.18 ± 5.52
7/20/85	5	19.18 ± 13.19	<6.20 ---	4.34 ± 1.58	31.31 ± 18.08
8/15/85	6	11.06 ± 1.96	(4)13.58 ± 13.58	14.05 ± 1.24	32.70 ± 7.54
8/30/85	2	6.37 ± 0.69	<6.20 ---	14.72 ± 6.36	44.33 ± 5.26
9/12/85	3	10.45 ± 7.31	<6.20 ---	11.88 ± 0.90	37.51 ± 7.91

* All concentrations are expressed in µg/l.
\+ Number in parenthesis is number of samples if different than N.

TABLE 27. Mean concentrations and standard deviations of nutrients for pond C-3.

Date	N	NH_3-N	NO_2/NO_3-N	PO_4-P	Total P
6/5/85	6	27.37 ± 6.84	203.21 ± 104.49	6.97 ± 0.78	25.63 ± 5.49
6/20/85	6	9.35 ± 1.96	<6.20 ---	28.66 ± 1.26	--- ---
7/20/85	6	38.33 ± 29.84	<6.20 ---	8.87 ± 2.30	28.11 ± 20.43
8/15/85	6	14.51 ± 1.31	(2)56.73 ± 56.55	34.20 ± 3.45	11.94 ± 3.82
8/30/85	2	14.70 ± 11.07	(1)10.36 ---	9.92 ± 2.63	15.04 ± 0.66
9/12/85	3	9.71 ± 4.48	<6.20 ---	8.78 ± 1.00	10.44 ± 5.80

* All concentrations are expressed in µg/l.
\+ Number in parenthesis is number of samples if different than N.

TABLE 28. Mean concentrations and standard deviations of nutrients for pond TR-3.

Date	N	NH_3-N	NO_2/NO_3-N	PO_4-P	Total P
6/5/85	6	23.80 ± 8.41	45.43 ± 32.42	3.41 ± 1.88	22.78 ± 5.08
6/20/85	6	1.68 ± 0.99	<6.20 ---	9.14 ± 0.32	--- ---
7/20/85	6	65.99 ± 57.31	(1) 6.58 ---	2.69 ± 0.38	22.94 ± 5.05
8/15/85	6	9.92 ± 0.52	(2)18.55 ± 3.46	12.40 ± 0.78	18.81 ± 4.36
8/30/85	1	11.48 ---	64.26 ---	10.23 ---	19.53 ---
9/12/85	3	16.15 ± 5.72	<6.20 ---	8.58 ± 0.18	13.95 ± 1.24

* All concentrations are expressed in µg/l.
\+ Number in parenthesis is number of samples if different than N.

ammonia nitrogen with time (after treatment) was highly significant in all ponds ($p<0.01$).

Since the concentration of nitrite is probably negligible, the oxidized inorganic form of nitrogen should be primarily nitrate. Nitrite and nitrate were analyzed together and are referred to as nitrate in the remainder of the text. Nitrate levels were generally low in all ponds. Many concentrations were reported as less than 6.20 µg/l NO_2/NO_3-N which was the detection limit of the autoanalyzer for that nutrient. C-3 had the highest initial concentration at 203.2 µg/l NO_2/NO_3-N. Levels remained low through the summer, and the concentrations again decreased to below the detection limit by late August and mid-September. No significant trend in nitrate concentration was found for time or treatment.

Initial orthophosphate concentrations (PO_4-P) were the lowest values for C-3, TR-2 and TR-3. The remaining three ponds reached their minimum PO_4-P concentrations in mid-July. Treated ponds 1 and 3 showed a maximum concentration by mid-August; all treated ponds decreased in PO_4-P by September. The controls showed a minimum concentration in mid-July, increased to a maximum in mid-August and remained relatively stable through September (i.e., changes are within 3 µg/l between mid-August and September). The increase in orthophosphate phosphorus with time (after treatment) was highly significant in all ponds ($p<0.01$).

All ponds have relatively high concentrations of total phosphorus (P) at the beginning of the season (average 20 to 40 µg/l). The control ponds trend from highest to lowest concentration from June to September, although C-1 and C-3 showed a surge in concentrations in mid-July and C-2 in mid-August. After their maximum concentrations, all show a steady decline to their minimum concentrations for the season. No significant trend in total phosphorus concentration was found for time or treatment.

Biological Measurements

Planktonic Chlorophyll *a*. Mean chlorophyll *a* concentrations with one standard error are presented in Figures 8 through 10. Raw data are

presented in an appendix to another publication (Rea, 1986). Maximum concentrations of chlorophyll a (chl a) occurred at the beginning of the season. Within the controls, chl a decreased by more than 10 times by early June. Then concentrations fluctuated slightly through the season, with final concentrations ranging from 1 to 50 µg/l chl a. The chl a concentrations in treated ponds were still two to eight times higher than controls at the end of the season.

Planktonic Bacteria. Figures 11 through 13 illustrate mean number of bacteria cells. The raw data are included within an appendix to another publication (Rea, 1986). Initial cell numbers approached $3*10^6$/milliliter for controls and from $3-5*10^6$/milliliter among treated. All ponds decreased in numbers until early July. After this point, populations showed a steady slight increase within the controls. The treated ponds showed a greater increase in numbers to a maximum concentration by late August. Total numbers of bacteria showed a highly significant increase with date (after treatment) in all ponds ($p<0.01$), but treatment pond numbers were significantly higher than control pond numbers over time ($p<0.01$).

Figures 14 through 16 show the relationship between dissolved oxygen concentration and number of bacteria. Bacterial populations appear to fluctuate inversely with the concentration of dissolved oxygen.

Acetate Turnover Times. Samples were collected in late September and early October to determine the turnover time of the acetate by the bacteria, using radiolabeled acetate (Table 29). Results of the tests varied between pairs. Within pair one, the control pond had a faster turnover time, and within pair three, the treated pond had only a slightly faster turnover time.

Dominant Phytoplankton. Cryptophytes and green algae (colonial and filamentous) were dominant in all ponds.

Relative Abundance of Zooplankton. The control ponds generally had a higher abundance of copepods than cladocerans, ranging from 420 to

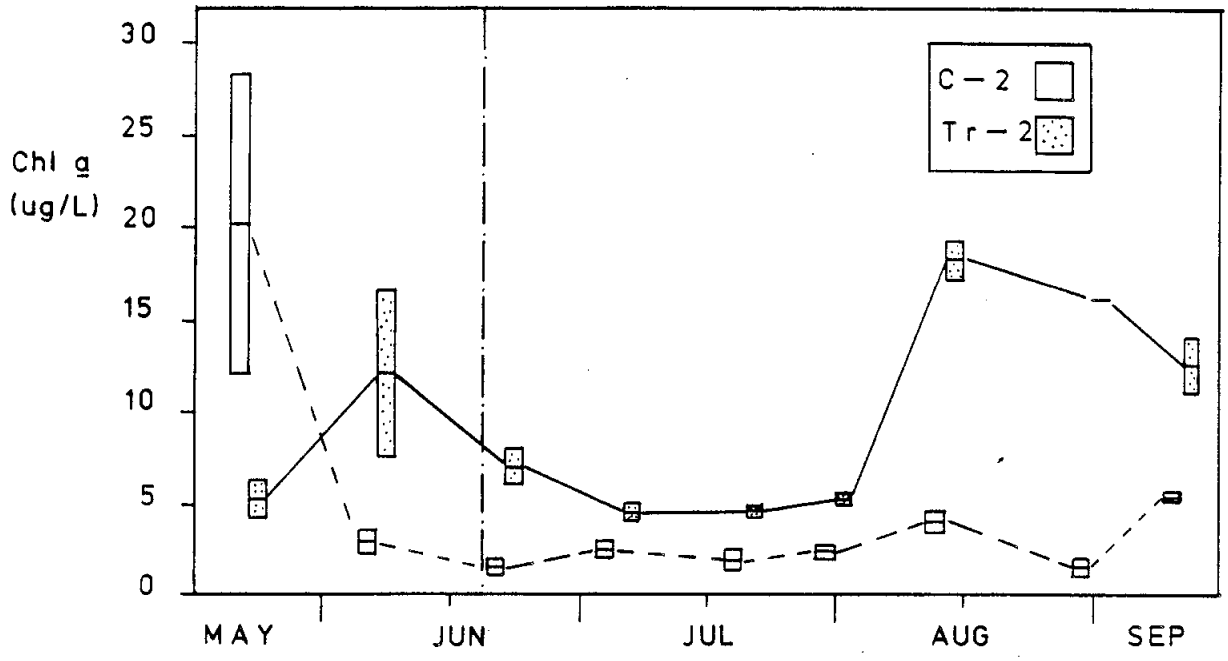

Figure 8. Mean chlorophyll a concentrations plus or minus one standard error for pair one ponds. Dashed line indicates time of CMA addition.

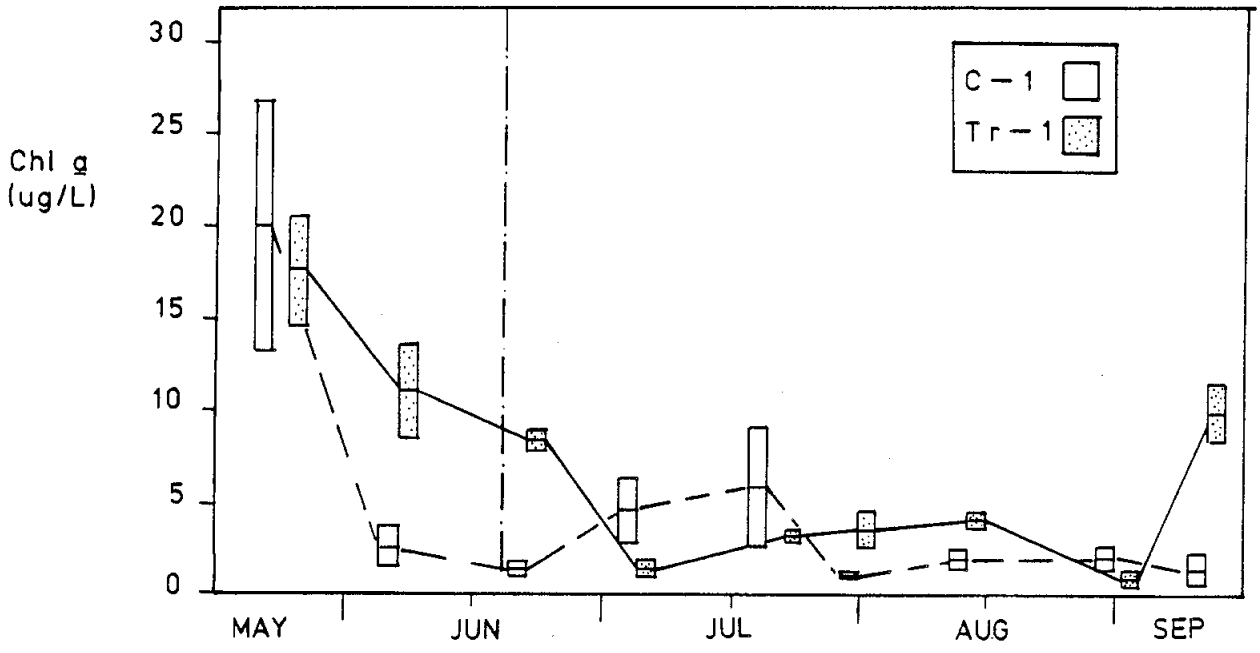

Figure 9. Mean chlorophyll a concentrations plus or minus one standard error for pair two ponds. Dashed line indicates time of CMA addition.

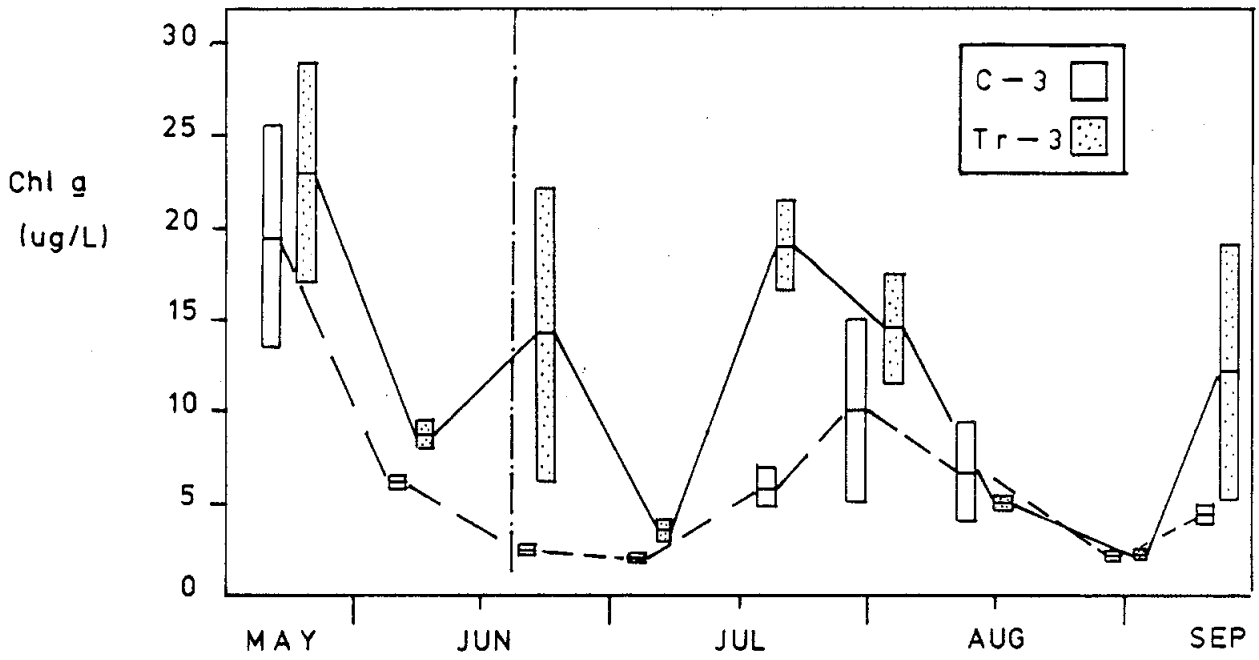

Figure 10. Mean chlorophyll a concentrations plus or minus one standard error for pair three ponds. Dashed line indicates time of CMA addition.

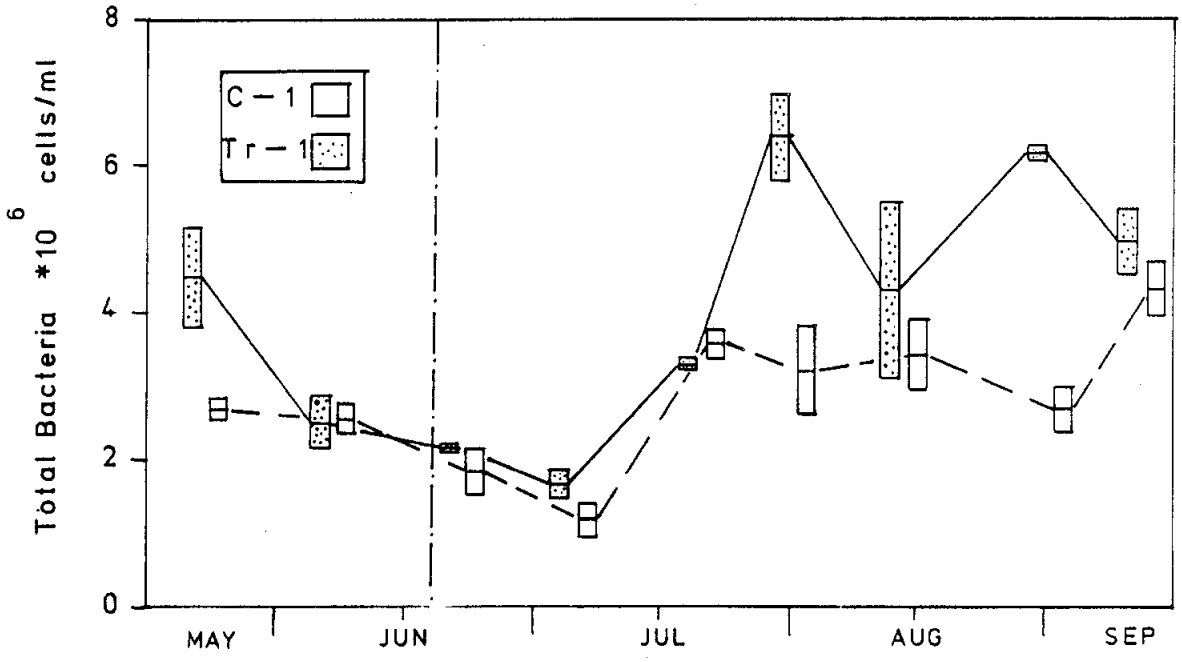

Figure 11. Mean number of bacteria per milliliter, plus or minus one standard error for pair one ponds. Dashed line indicates time of CMA addition.

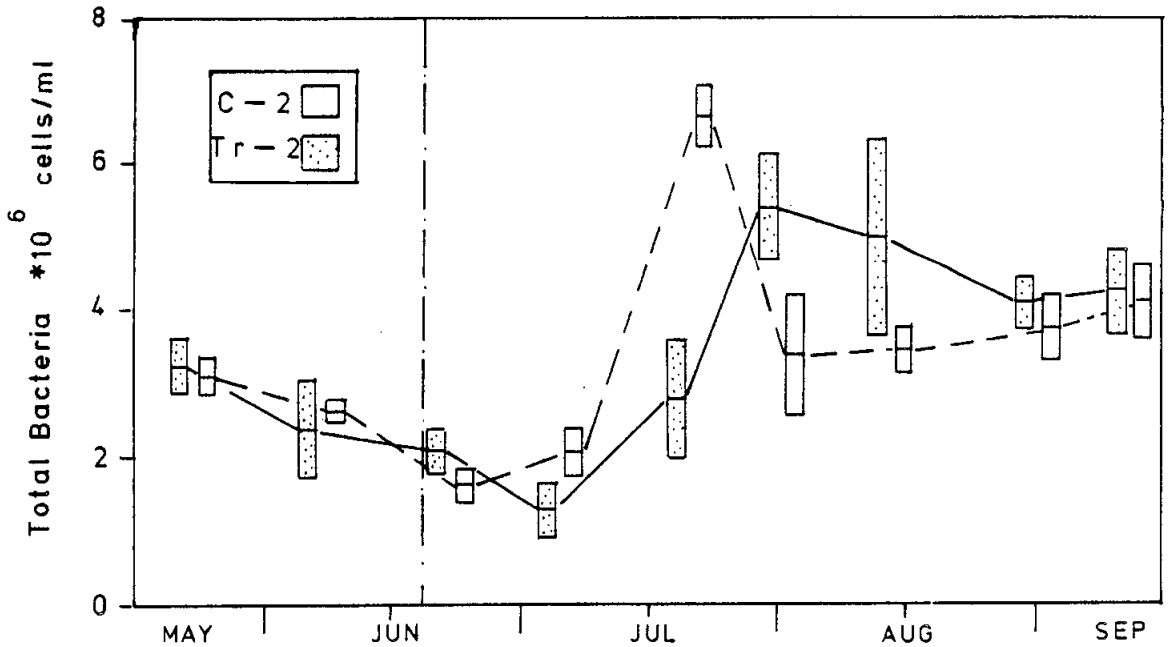

Figure 12. Mean number of bacteria per milliliter, plus or minus one standard error for pair two ponds. Dashed line indicates time of CMA addition.

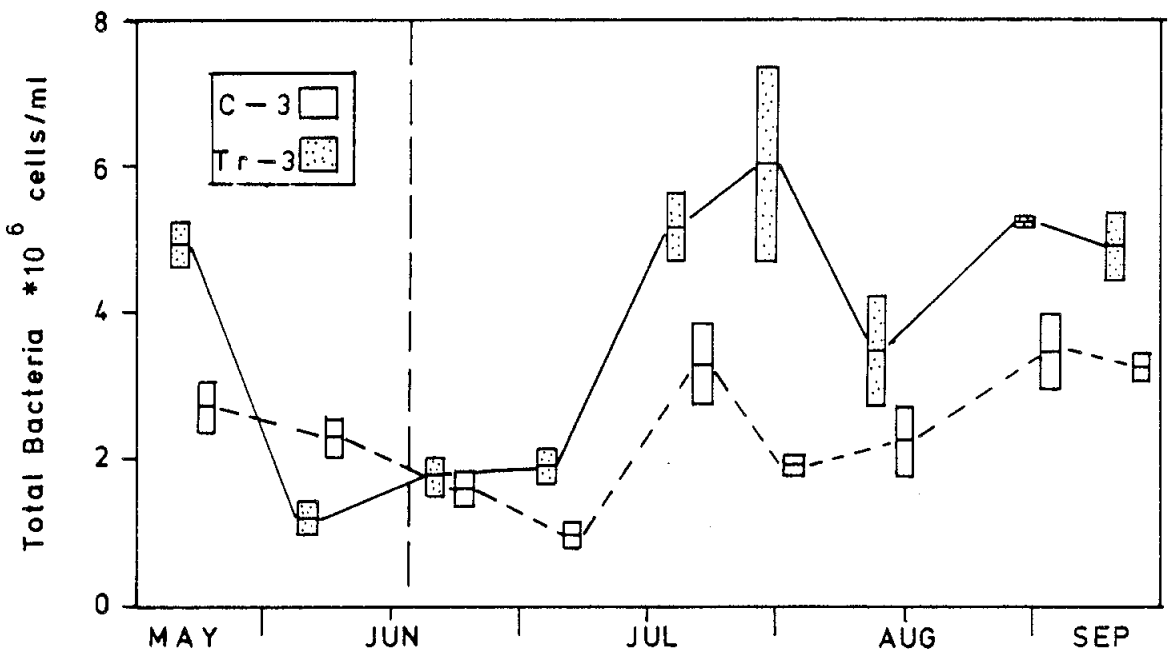

Figure 13. Mean number of bacteria per milliliter, plus or minus one standard error for pair three ponds. Dashed line indicates time of CMA addition.

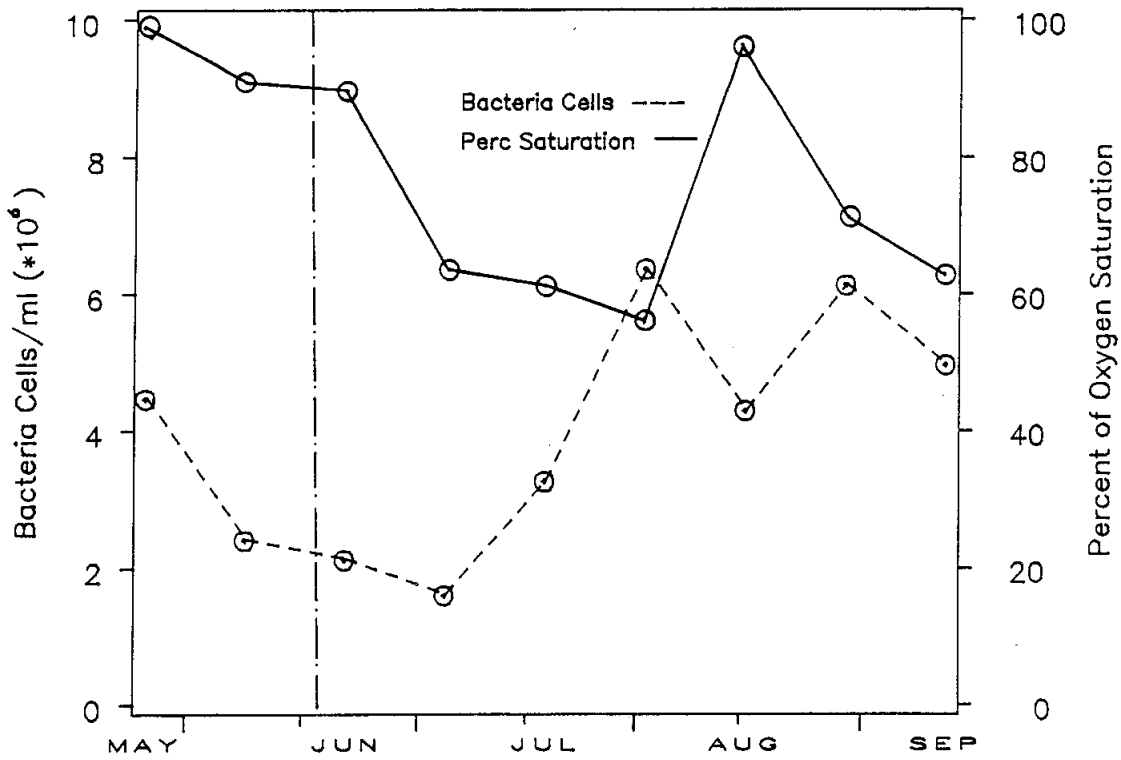

Figure 14. Concentration of dissolved oxygen and total bacteria for pond TR-1.

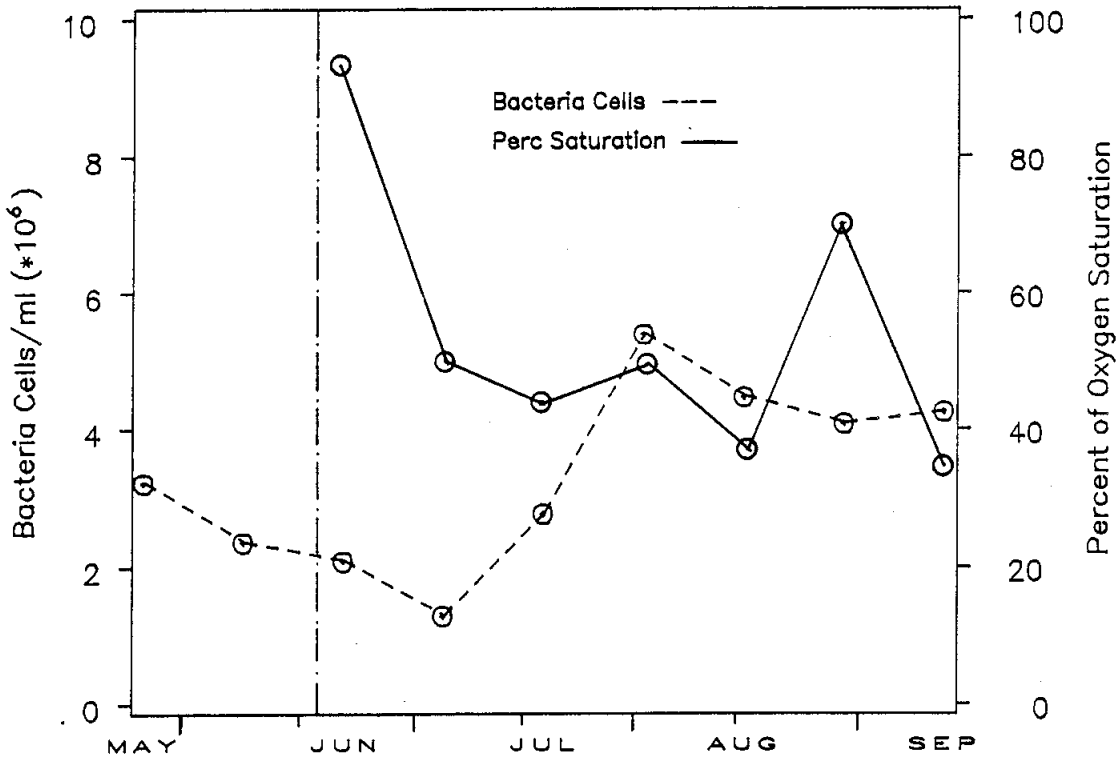

Figure 15. Concentration of dissolved oxygen and total bacteria for pond TR-2.

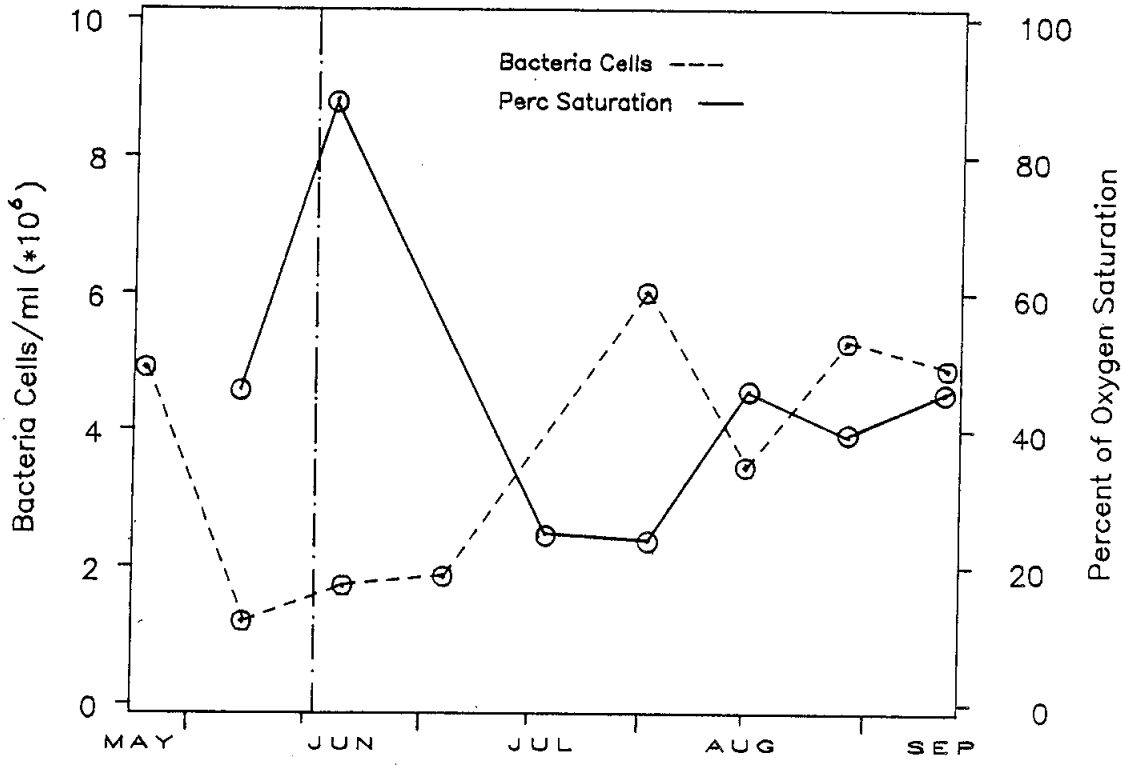

Figure 16. Concentration of dissolved oxygen and total bacteria for pond TR-3.

TABLE 29. Calculated turnover times for acetate (0.15 mg/l) uptake by planktonic organisms.

Date	Pond	Turnover time (min)
24 September	C-3	64
	TR-3	57
25 September	C-2	70
	TR-2	17
8 October	C-1	84
	TR-1	173
	C-2	285
	TR-2	71
	C-3	167
	TR-3	138

1,860 organisms per m^3 (Table 30). Their copepod concentrations were high in July and August and decreased significantly by September. Treated ponds showed a somewhat higher number of cladocerans than copepods; the minimum concentrations of cladocera occurred in August. TR-1 differs from the other two treated ponds in that it has a somewhat higher abundance of copepods than cladocera; its maximum concentrations of copepods occurred in August. TR-1 at least once also had the overall highest number of copepod larvae (1,140 per m^3, in July).

TABLE 30. Relative abundance of zooplankton in July, August and September, 1985.

Pond	Month	Cladocera (per m^3)	Copepods (per m^3)	Giant copepods (per m^3)	Copepod larvae (per m^3)
C-1	July	50	1,860	20	10
	August	40	1,580	30	30
	September	0	510	10	0
TR-1	July	150	290	50	1,140
	August	250	3,120	10	350
	September	70	970	20	0
C-2	July	10	420	20	330
	August	130	380	40	80
	September	0	460	120	0
TR-2	July	960	20	10	0
	August	180	290	40	130
	September	800	30	20	0
C-3	July	120	1,740	50	580
	August	0	1,750	190	640
	September	0	440	30	0
TR-3	July	150	80	240	0
	August	40	20	190	0
	September	380	10	40	0

DISCUSSION

The CMA was provided to us in barrels. It is obvious from the limited analyses that were conducted that there may have been wide variation in concentration of chemical species from barrel to barrel. This probably depended on what proportions of supernatant and slurry were present in each barrel. To dose the ponds, we calculated the number of barrels of a saturated solution of CMA needed to raise the calcium acetate concentration to predetermined final concentrations. In 1984, the goal was to at least double the calcium concentration. In 1985, the goal was to bracket the 50 mg/l CMA concentration that had been identified as the highest concentration at which no toxic effects would be expected (Winters et al., 1984).

The CMA had all been prepared in 1984, so the CMA used in 1985 had been stored for about a year. Analyses of the CMA product in 1984 and 1985 (Tables 3 and 4) show that there were some changes that could be due to aging of the product, and some that could be due to precipitations from the solution into the slurry (which also may have contained unreacted raw materials, mainly lime). Some apparent changes are unexplainable (e.g., those for sodium) and may be due to laboratory error.

It is possible that microorganisms degraded some of the acetate during storage. As produced, it was supposed to be a completely saturated solution of calcium acetate which, according to handbook values, would have a concentration of 374 g/l (as the nonhydrated salt) of which the acetate would represent 223 g/l. Analysis of the product solution in 1985 found somewhat less acetate, about 180 g/l (Table 5).

In an experiment, Schenk (1986) reports mold growth in closed containers of CMA, with loss of approximately 11% of the acetate over nine months. This agrees with our apparent loss during storage of the CMA.

Ion balance calculations for the supernatant and the slurry of CMA used in 1985 showed a noticeable difference between the sum of the cations and the sum of the anions in the slurry. The cations were present in excess of anions by about 1,049 meq/l. This may indicate the presence of unreacted lime in the slurry. Unfortunately, carbonate

analyses were not conducted on the product, so we cannot say there definitely was unreacted lime present.

We know from calcium measurements in the ponds right after the CMA additions that we probably did not dose them at as high a level as we intended. In 1984, two ponds (ponds 3 and 6) were dosed at about 27 mg/l CMA and one (pond 2) at about 67 mg/l (Rea and LaPerriere, 1985). In 1985, two ponds (ponds TR-1 and TR-2) were dosed at about 47 mg/l CMA, and the third (pond TR-3) at about 24 mg/l.

As mentioned before, two ponds were treated both years. One (pond 2) received about 67 mg/l in 1984 and as pond TR-2 received about 47 mg/l CMA in 1985. The other (pond 6) received about 27 mg/l CMA in 1984, and about 47 mg/l (as TR-1) in 1985. The third treated pond in 1984 (pond 3) was used as a control pond (C-3) in 1985. Calcium levels at the beginning of 1985 in the previously treated ponds were the same or lower than before additions of CMA in early 1984. Therefore, we believe there was no appreciable carry-over of the 1984 treatment chemicals into 1985.

If one assumes that typically 300 pounds of CMA could be applied in a single application and were to run off from a quarter mile stretch of road and enter a pond like TR-3 with the snowmelt (completely flushing the pond in the process), then the final concentration would be 54 mg/l CMA. Thus, the concentrations we achieved in the ponds are representative of only one application or less totally entering a nearby pond, providing there is approximately one-quarter lane-mile of highway within the pond's watershed. The University of Washington team has calculated that a single precipitation event might produce runoff containing between 100 and 5,000 mg/l CMA depending on conditions (Horner, R., 1986, personal communication), so our estimates are probably conservative.

Calculations based on amount of calcium added show TR-1 and TR-2 would have had a 35 mg/l acetate concentration, and TR-3 would have 18 mg/l acetate immediately after treatment in 1985. This is roughly 25 times higher than analytically determined values (Table 5). It is not surprising to find that the calculated values were not measured in the ponds since the actual sampling to determine the acetate concentrations was conducted two weeks following treatment. A probable reason for such

low values is that the acetate was utilized almost immediately by the heterotrophic organisms within the ponds. The heterotrophic bacteria are the most important users of the acetate, although evidence has been found that certain algae may also be utilizing it (Wright and Hobbie, 1966; LaPerriere et al., 1977). In untreated ponds, concentrations of acetate are naturally low because it is a labile compound. We found that the turnover time for 0.15 mg/l acetate was rapid (about 127 minutes), even months after dosing the ponds.

We estimate that the CMA doses to these ponds did not elevate heavy metal concentrations to levels exceeding water quality criteria (Table 6). This should be evaluated in future ecological studies of this chemical since carbonate rock sources that do have associated heavy metals might be used in making CMA.

Dissolved oxygen was drastically lowered by the CMA treatment in two out of three pairs of ponds in 1985. The control pond in pair one had the lower dissolved oxygen concentrations. This was probably due to its shallower mean depth (Table 7). We observed thick organic sediments and a very swampy nature of the edges, both of which would create oxygen demand.

In 1984, only one treated pond (pond 2, which had received about 67 mg/l CMA) was seen from our limited data to suffer significant oxygen depletion. From the time of the second treatment (August 16, 1984) it was about 30% less saturated with oxygen than its control (Rea and LaPerriere, 1985). From our limited evidence, it might be concluded that 27 mg/l CMA in a pond (as in the other two 1984 treated ponds) might be below the amount causing significant oxygen depletion, but undoubtedly this is affected by other factors such as pond morphometry since TR-3, dosed only 24 mg/l in 1985, suffered severe oxygen depletion.

A question then arises. Was the depleted dissolved oxygen a function of increased bacterial growth or of decreased algal growth?

Total bacteria counts did show a treatment effect (in the interaction of treatment and date) indicating that the addition of the acetate, an organic substrate, did cause an increase in bacterial growth reflected in increased numbers. Bacterial numbers were not higher in the treated ponds, however, during the short period in late June when we

assume the acetate was rapidly degraded (Figures 11-13). The higher numbers appeared in July and August in TR-1 and TR-3. Pond TR-2 did not show as many instances of clearly higher numbers of bacteria than its paired control C-2.

Algal response to the increased carbon in the system (from the bacteria initially degrading the acetate and then degrading products of their metabolism of the acetate) was measured as increased chlorophyll a in the treated ponds over the controls for varying periods of time (Figures 8 to 10). As mentioned before, since these ponds have small flagellated green algae which are known to use acetates heterotrophically, the algae may also have utilized some of the acetate directly.

The increase in cladoceran zooplankton measured in the treated ponds compared to the controls probably occurred because of increased food (algae and bacteria). They are known to eat organic detritus of any kind, as long as it is of filterable size, since they filter-feed. Copepods that filter-feed may be somewhat more selective choosing only particular kinds of algae (Pennak, 1953).

The ponds that we used for these experiments had no fish present. Had there been fish, it is likely that they might have been severely stressed or even killed by the low oxygen conditions that occurred throughout the ponds even in the wind-mixed upper layers (Table 16, Figures 15 and 16). Cold-water fish, particularly salmonids that dominate the Alaskan fish fauna, are quite sensitive to low dissolved oxygen, suffering population effects at and below 6 mg/l at 15°C and, possibly, lethal effects below 4 mg/l (Davis, 1975). Therefore, while the chemical CMA itself is less toxic than NaCl when tested in bioassay tests, its oxygen demand (which is negated by aeration in bioassay testing) may prove to be toxic to fish.

CONCLUSIONS

1. The CMA that we used was essentially calcium acetate with relatively little magnesium acetate present. We have assumed that the calcium acetate provided (in solution) was as the unhydrated salt, but it may have been the monohydrated or dihydrated salt.

2. The CMA that we used contained low amounts of heavy metals that were calculated to be considerably below harmful levels when diluted in the test ponds.

3. We assumed that our experiments modeled the normal occurrence in interior Alaska where deicing chemicals would accumulate on or immediately beside the roadbed and would enter ponds during one snowmelt event at the end of winter.

4. We calculated that the concentrations of CMA we added to the test ponds represent about one application of the chemical applied to a quarter mile (one lane) of a nearby road section as a deicer, entirely entering a pond of the size we used.

5. Apparently calcium acetate entering ponds of the type we used does not carry over through the next winter; it is probably flushed out by snowmelt.

6. Acetate associated with CMA appeared to be rapidly taken up by heterotrophic aquatic organisms and cycled through them for several months, depleting dissolved oxygen in the water in the process.

7. Extremely low dissolved oxygen conditions developed in a small pond of about 2,600 m^3 treated with 24 mg/l CMA (calculated from calcium elevation).

8. Bacteria and algae were both stimulated by CMA additions as shown by events of higher standing-crop in treated ponds. The algae were probably stimulated by products of bacterial metabolism of the

acetate. The algal nutrients other than carbon were not affected by the CMA treatment.

9. Cladoceran zooplankton were more concentrated in treated ponds than in control ponds probably because of increased availability of their foods (bacteria and algae).

12. Salmonid fishes, not present in our test ponds, might be stressed by the low dissolved oxygen conditions that CMA might produce in ponds.

RECOMMENDATIONS

1. Batches of CMA to be used in experiments should be analyzed completely for chemical and physical characteristics. Enough samples should be analyzed to adequately measure the variability as well as the average values of these characteristics within the batch.

2. Research should be conducted on transport of CMA from road deicer applications to local water bodies, to measure the actual amounts that would enter these bodies. This may be high in areas like interior Alaska where snowmelt often flows across frozen ground.

3. Research should be conducted on the specific interactions of aquatic ecosystems with CMA to determine its fate. These should probably be conducted with radioactively labeled CMA.

4. More experiments should be conducted with CMA additions to ponds to fully evaluate the oxygen depletion effects. More than three pairs of ponds should be used in order to be able to find a significant F statistic between the treatments and control.

5. Caged-fish bioassays should be conducted in ponds treated with CMA, to see how oxygen depletion caused by the breakdown of acetate might affect fish.

IMPLEMENTATION

Research by the Federal Highway Administration (FHWA), private research organizations, and universities have identified calcium magnesium acetate (CMA) as the most promising alternative to the present use of corrosive salts for highway deicing. It is well understood that there is an enormous cost to the public as a result of the present use of sodium chloride and calcium chloride for highway deicing. The total costs due to corrosion of vehicles and damage to vegetation are some 10 to 15 times the initial costs of purchasing and applying the salts.

Research on the economics of using CMA in Alaska was initiated by the Department of Transportation and Public Facilities for several reasons. The largest part of the cost of manufacturing CMA is for producing the required acetic acid. Since this can be made as a by-product of the petroleum industry, it was logical to investigate production in Alaska, thereby avoiding high shipping costs. In addition, Alaska has an abundance of limestone, the other principal ingredient of CMA. Finally, it was deemed necessary to determine the potential environmental effects resulting from the use of CMA in Alaska, most of which would be washed into watersheds in a relatively short time during spring breakup.

Several studies have been completed on the manufacture and application of CMA, with favorable results. A study was completed on the corrosiveness of the CMA produced by the University of Alaska, also with encouraging results.

Prior to a full-scale, winter-long demonstration of CMA, two environmental studies were performed. The results of those studies are included in this report. The investigators determined that the CMA added to the lakes resulted in oxygen depletion in some of the lakes. If a full-scale demonstration of CMA is conducted, the environmental impact statement which accompanies that demonstration should address this situation, and any possible effects should be carefully watched during the demonstration.

The status of the FHWA research on CMA is contained in the report entitled "Ice-Melting Characteristics of Calcium Magnesium Acetate," Report FHWA/RD-86/180, January 1986.

LITERATURE CITED

American Public Health Association, American Water Works Association and Water Pollution Control Federation. 1980. Standards methods for the examination of water and wastewater: 15th ed. American Public Health Association, Washington, DC. 1193 pp.

Brown, E.J., R.F. Harrison, and J.F. Koonce. 1978. Kinetics of phosphate uptake by aquatic microorganisms: deviations from a simple Michaelis-Menton equation. Limnology and Oceanography. 23(1):26-34.

Bubeck, R.D., W.H. Diment, B.L. Peck, A.L. Baldwin, and S.D. Lipton. 1971. Runoff of deicing salt: effect on Irondequoit Bay, Rochester, NY. Science. 172:1128-1132.

Chollar, B.H. 1983. Calcium magnesium acetate (CMA) as an alternate deicer. Federal Highway Administration, Washington, DC. 10 pp.

Chollar, B.H. 1985. Calcium magnesium acetate (CMA) as an alternate deicer. Federal Highway Administration, McLean, VA. 24 pp.

Davis, J.C. 1975. Minimal dissolved oxygen requirements of aquatic life with emphasis on Canadian species. J. Fish. Res. Board. Can. 32:2295-2332.

Dunn, S.A., and R.O. Schenk. 1980. Alternate highway deicing chemicals. Federal Highway Administration, Offices of Research and Development. Report No. FHWA-RD-79-108. Washington, DC. 9 pp.

Ecological Research Associates. 1975. A study of the influence of highway deicing agents on aquatic environments in the Lake Tahoe basin and drainages along Interstate 80. Report to California Department of Transportation. CA-DOT-TL-7153-1-75-27.

Eisenreich, S.J., R.T. Bannerman, and D.E. Armstrong. 1975. A simplified phosphorus analysis technique. Environmental Letters. 9:43-53.

Francisco, D.E., R.A. Mah, and A.C. Rabin. 1973. Acridine orange epifluorescence technique for counting bacteria in natural waters. Transactions of the American Microscopical Society. 92:416-421.

Hobbie, J.E., R.J. Daley, and S. Jasper. 1977. Use of Nuclepore filters for counting bacteria by fluorescence microscopy. Applied and Environmental Microbiology. 5:1225-1228.

Hoffman, R.W., C.R. Goldman, S.P. Paulson, and G.R. Winters. 1981. Aquatic impacts of deicing salts in the central Sierra Nevada Mountains, California. Water Resources Bulletin. 17(2):280-285.

Holmes, G.W., and W.S. Benninghoff. 1957. Terrain study of the Army Test Area, Fort Greely, Alaska. Military Evaluation of Geographical Areas: A Contribution to Project 8-97-10-004. Prepared by U.S. Geological Survey for Waterways Experiment Station, Corps of Engineers, U.S. Army. Vicksburg, MS. 287 pp.

Horner, R. 1984. Environmental monitoring and evaluation of calcium magnesium acetate (CMA). National Cooperative Highway Research Program Project Summary. 29 pp.

Huling, E.E., and T.C. Hollocher. 1972. Groundwater contamination by road salt -- steady state concentrations in east central Massachusetts. Science. 176:288.

Hutchinson, F.E. 1967. The influence of salts applied to highways on the levels of sodium and chloride ions present in water and soil samples. Project No. R1084-8. 26 pp.

Hutchinson, F.E., and B.E. Olson. 1967. The relationship of road salt applications to sodium and chloride ion levels in soils bordering major highways. Highway Research Record 193:1-7.

Judd, J.H. 1970. Lake stratification caused by runoff from street deicing. Water Research. 4:521-532.

LaPerriere, J.D., T. Tilsworth, and L.A. Casper. 1977. Nutrient chemistry of a large, deep lake in subarctic Alaska. Institute of Water Resources, University of Alaska-Fairbanks. Report IWR-80. Report for Corvallis Environmental Research Lab, Office of Research and Development, U.S. Environmental Protection Agency. 128 pp.

Ostermann, R.D., and M.J. Economides. 1986. Pilot plant studies and process design for the production of calcium magnesium acetate. Report to the Alaska Department of Transportation and Public Facilities, Research Section. Report No. AK-RD-86-24. 66 pp.

Pennak, R.W. 1953. Fresh-water invertebrates of the United States. The Ronald Press Company, New York. 769 pp.

Pewe, T.L. 1975. Quarternary geology of Alaska. U.S. Geological Survey. Professional Paper No. 835.

Pewe, T.L., and R.D. Reger. 1983. Delta River area, Alaska Range. Pages 47-135 in T.L. Pewe and R.D. Reger. Guidebook to Permafrost and Quarternary Geology Along the Richardson and Glenn Highways Between Fairbanks and Anchorage, Alaska. Conference on Permafrost, University of Alaska-Fairbanks.

Prior, G.A., and P.M. Berthouex. 1967. A study of salt pollution of soil by highway salting. Highway Research Record. 193:8-21.

Rea, C.L. 1986. Effects of calcium magnesium acetate on small ponds in interior Alaska. Unpublished M.S. thesis, University of Alaska-Fairbanks. 191 pp.

Rea, C.L., and J.D. LaPerriere. 1985. Effects of calcium magnesium acetate, a road deicer, on the lentic environment in interior Alaska. Interim Report to Alaska Department of Transportation and Public Facilities, Fairbanks, AK. 48 pp.

Roth, D., and G. Wall. 1976. Environmental effects of deicing salts. Groundwater. 14:286-289.

Schenk, R.W. 1986. Ice-melting characteristics of calcium magnesium acetate. Final Report to Federal Highway Administration, Madison, WI. FHWA/RD-86/005. 56 pp.

Stumm, W., and J.J. Morgan. 1970. Aquatic Chemistry. J. Wiley-Interscience, New York. 583 pp.

U.S. Environmental Protection Agency. 1971. Environmental impact of highway deicing. Water Pollution Control Series, Edison, OH. 121 pp.

U.S. Environmental Protection Agency. 1980. Water quality criteria documents; availability. Federal Register. 45(231):79318-79379.

Venkatesh, E.S., and S. Kutterer. 1985. Corrosion of steel in calcium-magnesium-acetate (CMA) deicer. Final Report to Alaska Department of Transportation and Public Facilities, Fairbanks, AK. 29 pp.

Wetzel, R.G., and G.E. Likens. 1979. Limnological analyses. W.B. Saunders, Philadelphia. 357 pp.

Winters, G.R., J. Gidley, and H. Hunt. 1984. Environmental evaluation of calcium magnesium acetate (CMA). Executive Summary to California Department of Transportation, Sacramento, CA. 19 pp.

Winters, G.R., J. Gidley, and H. Hunt. 1985. Environmental evaluation of calcium magnesium acetate (CMA). Final Report to California Department of Transportation, Sacramento, CA. 75 pp.

Wright, R.T., and J.E. Hobbie. 1966. Use of glucose and acetate by bacteria and algae in aquatic ecosystems. Ecology. 47:447-464.

Zar, J.H. 1984. Biostatistical analysis. Prentice-Hall, Inc., Englewood Cliffs. 718 pp.