CHEMICAL AND BIOLOGICAL CHARACTER OF RIO GRANDE WATER IN THE BOSQUE DEL APACHE WILDLIFE REFUGE

Donald K. Brandvold, *Biochemist*
James A. Brierley, *Microbiologist*
Carl J. Popp, *Inorganic Chemist*

TECHNICAL COMPLETION REPORT
Project No. A-038-NMEX

New Mexico Water Resources Research Institute
in cooperation with
Department of Chemistry
and
Department of Biology
New Mexico Institute of Mining and Technology
Socorro, New Mexico

August, 1973

The work upon which this publication is based was supported in part by funds provided through the New Mexico Water Resources Research Institute by the United States Department of Interior, Office of Water Resources Research, as Authorized under the Water Resources Research Act of 1964, Public Law 88-379, under project number: A-038-NMEX.

Abstract

The project purpose was to study the effects of a waterfowl refuge on water quality using an interdisciplinary approach by monitoring the physical, chemical, and biological character of the water in the refuge. The study was undertaken on the Bosque del Apache Wildlife Refuge along the Rio Grande in Socorro County, New Mexico. A regular monthly monitoring program over the three-year study period was set up to collect and analyze water samples from eight points within the refuge. This was done to establish the base-line characteristics of the refuge waters and to enable detection of both seasonal and waterfowl-caused changes.

The types of water monitored were as follows; water entering the refuge, water leaving the refuge, Rio Grande water within the refuge which served as a control since it was not used in refuge management, swamp water, irrigation water, fishing pond water, and high-waterfowl-use temporary ponds.

The water used as a waterfowl habitat is not degraded in quality as a result of the presence of waterfowl. There was no increase in soluble nitrogen compounds or any other nutrient associated with eutrophication problems. There were no apparent bird-related changes in the microbiological parameters of water quality. However, impoundment of water for habitat ponds results in an increase of water salinity through concentration of dissolved ions by evaporation.

The water of the middle Rio Grande used by the refuge has a high concentration of suspended sediments. This appears to effect the concentration of inorganic compounds and microbial populations by adsorption.

The large amount of data from the analyses had been computer-stored to facilitate handling of the data. The computer was used to: one, print out the data sheets by sampling station and date; two, perform regression analyses on the data to determine correlations; three, determine data averages and standard deviations for selected time periods within the study; and four, plot the data for given stations vs. time and also in a parameter vs. parameter format.

ACKNOWLEDGEMENTS

This work was initiated in 1970 as an interdisciplinary approach to the determination and estimation of water quality problems associated with a water modifier-the Bosque del Apache Wildlife Refuge- in New Mexico. The following is a list of individuals and agencies without whose help this study would have been more difficult if not impossible.

We thank the Research Corporation of Burlingame, California for a "starter" grant which carried us through the first year of the study. We are grateful to the New Mexico Water Resources Research Institute for grant support during the final two years of the project. We also thank the Bureau of Sport Fisheries and Wildlife for contract support of water analysis during a portion of the study.

The work would surely have been impossible without the complete cooperation and support of Mr. Richard Rigby, "Bosque" refuge manager, and the refuge personnel.

We are grateful to the Bureau of Reclamation for leaving operative their water guaging stations on the refuge past their appointed time limit in order to allow us to gather needed water flow data.

We thank Dr. Alan Gutjahr of the New Mexico Institute of Mining and Technology Mathematics Department for his help with the statistical analysis of the data.

Finally, we are indebted to the New Mexico State Bureau of Mines and Mrs. Lynn Brandvold for use of Bureau of Mines facilities and performance of many cation analyses. We also thank the New Mexico Tech Computer Center for allowing us to stretch our computer budget considerably in order to complete the study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Introduction

In this report is included the data obtained from chemical, physical, and biological analyses carried out on water and sediment from the Bosque del Apache National Wildlife Refuge. This refuge is located in Socorro County, New Mexico. Also included are discussions of the data and conclusions about what effects the water passing through the refuge, especially that used by waterfowl, has on the quality of water in the Rio Grande.

A. Purpose

In recent years it has become obvious that the fixed amount of available water must be reused more and more often as demand grows. Such a situation can result in an accumulation of undesirable substances in the water. Pinning down the sources of unwanted or other extraneous material in water is becoming essential. This is particularly true in areas of low precipitation. In these areas, all potential, major factors should be studied and the effects analyzed.

The purpose of this project was to determine what effects, if any, a major wildlife refuge specializing in waterfowl management would have on water quality within the refuge and on water leaving the refuge. The large numbers of waterfowl were certain to cause some changes in the water. What these changes are had never been determined. The results would be useful in management of any refuge of this type and also potentially of value for determining the effects of duck and goose farms on water quality.

B. Background

The Bosque del Apache Refuge is located on the Rio Grande

River system. The refuge is maintained by the Bureau of Sports Fisheries and Wildlife which is part of the Department of the Interior. Its location is on the most important source of water for much of New Mexico. The major part of this water originates from precipitation in Southern Colorado and Northern New Mexico. The Rio Grande receives scant recharge waters through most of its length in New Mexico.

Within New Mexico the water is reused several times for such activities as farming, municipal and industrial needs and recreation. The Rio Grande Valley contains a major part of New Mexico's population. It also is intensively farmed with a large quantity of foodstuffs produced. Any discharge into Rio Grande water which might produce deleterious effects on water quality could have serious consequences.

The northern limit of the "Bosque" refuge is about 12 miles south of the city of Socorro. The southern end of the refuge is another 12 miles further south. The refuge is an excellent study area for several reasons. First, water flows through a controlled system of guaged canals and ditches. Second, agricultural use of fertilizers on that part of the refuge farmed is carefully controlled. Third, rainfall is light (annual average of about 8.5 inches) particularly during the time of the year when the waterfowl are present, reducing any dilution effects. The largest bird populations are present from late October to early March and average 6,000 sandhill cranes, 3,000 Canada geese, 4,000 snow geese and 25,000 ducks. This bird population could be expected to alter the water quality significantly.

II. Experimental:

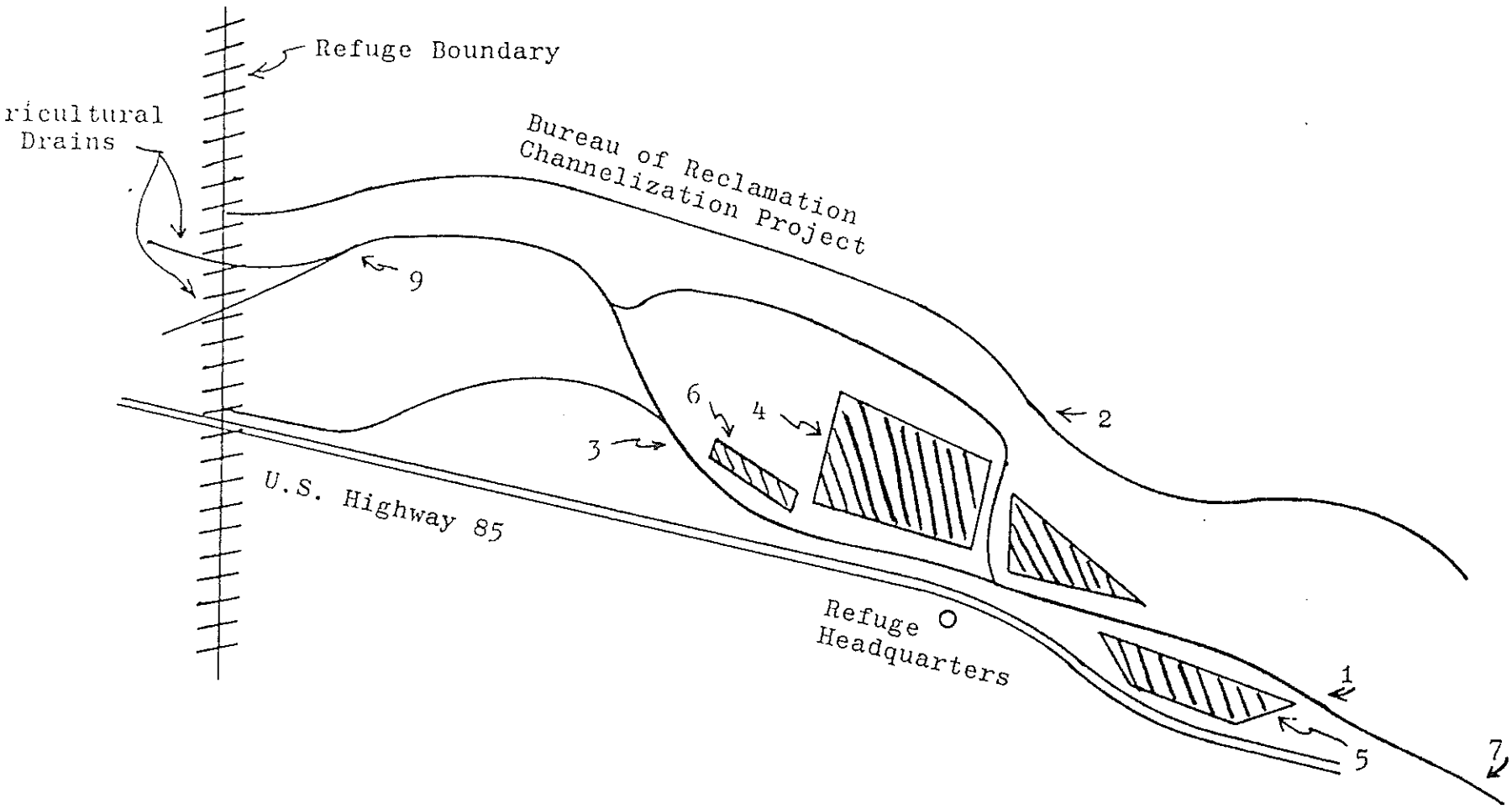
A. Sampling sites

The locations of the sampling stations are shown on the enclosed map (Figure 1). There were eight sites numbered 1-9 (Station 8 was disregarded following its designation). The sites were chosen for the following reasons. Stations 3, 1, 7, and 9 were all on the main drainage ditch through the refuge. Station 3 was above the area of main waterfowl use, station 1 was roughly adjacent to areas of high waterfowl use and station 7 was well below these areas. Substances in the water at station 3 were either in the water when it entered the refuge or most probably originated from agricultural activities in the northern part of the refuge. Station 9 was located at the extreme northern end of the refuge. Station number 4 was located on a seasonally controlled pond which had heavy use by waterfowl. The concentrations of the measured chemical and biological substances at this station were dependent on the waterfowl present and the water used to fill the pond. The other three stations were selected as "controls". Station number 5 was located on a permanent but shallow swamp which supports fairly heavy vegetation, but receives little waterfowl use. Station 6 was located on a fishing pond where the water source was primarily ground water. Station 2 was located on the main irrigation diversion canal (the Bureau of Reclamation Channel) and was representative of Rio Grande water not used by the refuge.

Besides those regular stations, other areas were sampled at times when conditions existed which made sampling desirable.

Figure 1

Schematic Map of Sampling Areas[a,b] - Bosque Del Apache Refuge



[a]Numbers refer to sampling stations. See text for description.

[b]Shaded areas contain ponded water.

B. Sampling Methods

The majority of samples were gathered by a "grab" method where the sample was taken slightly below the surface. Generally, samples were collected in acid-washed plastic bottles though glass containers were used a few times. Water for mercury analyses was collected in bottles containing a small quantity of nitric acid. Water for analyses of nitrogen species was collected in bottles containing a small amount of H_2SO_4+$CHCl_3$.

Water samples for microbiological analysis were collected at the time of sampling for chemical analysis. Sterile 250-ml polypropylene screw-cap bottles were used for sample collection. One sample of surface water was collected at each sampling station. These samples were returned to the laboratory and the analyses performed within 24 hours of the time of collection

Samples for BOD were also collected at each station. Standard APHA BOD bottles, "Hach" BOD-manometer bottles, or 500 ml opaque polypropylene bottles were used for sample collection.

Towards the end of the study, samples were collected from the bottom water by use of stainless steel tubes fitted with a rubber stopper which could be removed when the proper depth was attained. This device could also be used to collect sediment samples.

C. Analysis Methods

Since a large number of parameters was determined for each of the water samples, this section is broken down into the methods for physical, chemical, and biological parameters tested.

1. Physical Parameters

The physical parameters determined were pH, temperature, specific conductance, dissolved oxygen, total dissolved solids, and sediment. Dissolved oxygen and temperature were measured in the field using a Model 54 Oxygen Meter and combination probe manufactured by the Yellow Springs Instrument Company, Yellow Springs, Ohio. The pH values were determined in the field using an Orion Model 407 portable pH meter. Specific conductance values were calculated from resistance values measured in the laboratory using a Model RC-1B conductivity bridge manufactured by Industrial Instruments, Inc.. The 1.0 cm platinum electrode was calibrated with standard potassium chloride solution. Total dissolved solids[1] and sediment[2] were measured following the procedures outlined in Standard Methods for the Examination of Water and Wastewater.

2. Chemical Parameters

Silica[3], dissolved phosphate[4], sulfate[5], nitrite[6], chloride[7], and chemical oxygen demand[8] were determined according to procedures outlined in Standard Methods for the Examination of Water and Wastewater. Mercury was measured using the flameless atomic absorption method of Hatch & Ott[9] except that tin (II) chloride was used to reduce mercury rather than tin (II) sulfate. The analysis data labelled "inorganic mercury" is that mercury which is immediately reduced by tin (II) chloride without digestion. The data labelled "organic mercury" was obtained by digesting the sample for 24 hours with sulfuric acid and excess potassium permanganate to determine total mercury, then subtracting "inorganic mercury". Total dissolved phosphate was determined by digestion of unfiltered samples with sulfuric

acid and hydrogen peroxide as described by Golterman[10] and subsequent colorimetric estimation as with dissolved orthophosphate. Bicarbonate and carbonate were determined in the field using a field test kit, Model AL-AP manufactured by the Hach Chemical Co., Ames, Iowa. The results of the field tests were checked in the laboratory by titration using a pH meter and found to agree within 5%. It was felt that the field results were more valid since temperature changes in taking the sample from field to laboratory which can affect the CO_2 : HCO_3^- : $CO_3^=$ ratio did not occur. Sodium and potassium were determined by atomic absorption using a model 303 spectrophotometer manufactured by Perkin-Elmer Corp.. Calcium and magnesium were analyzed either by atomic absorption spectroscopy or by titration with EDTA.

Kjeldahl nitrogen was analyzed by the method of Golterman[10] except that the Nessler's Reagent was made up by the method of Hawk[11]. Also, the digestion mixture was 10% Nacl and 10% $KHSO_4$ saturated with $CuSO_4$. This was necessary because of the high suspended or dissolved solids content of many of the samples. Nitrate, ammonia, and easily hydrolyzed nitrogen were run according to Golterman[10]. Urea analyses were based on the method of Emmett[12]. Uric acid measurements were loosely based on Sigma Technical Bulletin 680[13]. Many modifications were necessary. The method is based on using uric acid to reduce phosphotungstic acid to a highly colored blue complex.

The procedure was as follows; a 4 ml sample was pipetted into a test tube and 1.5 ml sodium carbonate buffer (pH = 10) and 1 ml phosphotungstate reagent were added and the contents mixed well by inversion. The samples were centrifuged for 15 minutes,

transferred to cuvettes and the absorbance read at 680 nm. The samples must be read within 25 minutes since the color slowly fades. Uric acid in sediment was analyzed as follows. Four grams of sediment (wet weight) were dried at low temperatures and the dried solid was then powdered and extracted first with 1.5 ml of sodium carbonate and then twice with 2 ml of distilled water. The extracts were mixed together and then with 1 ml phosphotungstate reagent and treated as above.

3. Biological Parameters

Two different procedures were examined for determining the 5-day Biochemical Oxygen Demand (BOD) at 20°C. Initially the procedure described in Standard Methods for the Examination of Water and Wastewater[14] was used. Also dissolved oxygen uptake was determined during 5-day incubation using the oxygen meter previously described with an electrode adapted for 300 ml standard BOD bottles. Subsequently, the BOD was determined by the "Hach" manometric method (Hach Chemical Co., Ames, Iowa) for reasons of simplicity. The BOD determinations were initiated for samples within six hours of the time of their collection. The procedures and methods recommended in Standard Methods for the Examination of Water and Wastewater served as guidelines for analyses and plate count procedures. Standard Methods Agar (BBL) was used for obtaining a total count of bacteria able to grow aerobically at 35°C after 48 hours incubation[15]. Endo Agar (BBL) was used for counting total and fecal coliform bacteria. The inoculated plates were incubated at 35 and 44°C for the respective determinations[16]. Colony counts were made after 48 hours incubation. Fecal streptococci numbers were determined using

M-Enterococcus Agar (BBL) following 48 hours incubation at 35°C[17]. The number of microorganisms able to grow anerobically was determined for a limited number of samples. Brewer's thioglycollate medium with 1.5% agar was used for pour-plates. The plates were incubated for 48 hours at 35°C in BBL "GasPak" jars and the colonies counted. Anaerobiosis in the jars was determined by methylene blue reduction. Quantitative enumeration of respective bacterial populations could only be performed by the pour-plate method. It was not possible to employ the membrane filter techniques because of the high concentration of suspended particulate matter in samples from the flowing water systems.

D. Data Handling and Analysis

Due to the large amount of data collected, an IBM 360-System 44 computer located at the Computer Center at New Mexico Tech was utilized. After completion of analysis of a particular parameter on a given sample data, the result was transferred to a data sheet containing a listing of all parameters. When the data sheet was completed, the total milliequivalents of cations vs. the total milliequivalents of anions was checked since the positive charges should equal the negative charges. If the percentage difference between the two values was <10%, the ion analyses were deemed acceptable. If the difference was >10%, individual analysis were repeated to find the error. The percentage differences were generally <5%.

When complete data for all the sample stations for a particular date were collected, the data were then keypunched on computer cards and stored on tape. The computer was then used to perform the following operations: one, print-out of the data and

calculation of percentage differences between milliequivalents of cations and anions; two, calculation of mean values and standard deviations for all the parameters for each sample station (see Table III); three, plotting of the data as parameter vs. time (Fig's 4 & 5) or parameter vs. parameter (Fig. 6); and four, calculation of correlation coefficients and regression analysis for parameter vs. parameter. These operations would be very tedious and time-consuming if done by hand.

It may be noted when examining the means and standard deviations in Table III that the standard deviation may exceed the mean - i.e. COD for station 1 = 45± 114. This simply means that the variability is extremely large for that particular parameter.

III. RESULTS AND DISCUSSION

A. Effects of Waterfowl Pond Water Release

One of the major questions to be answered by this study was "what effect does release of impounded high-waterfowl-use water have on the quality of water leaving the refuge"? The high-waterfowl-use areas on the refuge are temporary impoundments which are flooded from approximately September through April or May. In the spring, most of the water is released into drains and leaves the refuge via station 7 (see map-Figure 1). The remainder of the water is allowed to evaporate and the areas grow to grass and other forage during the summer.

Since the ponds are subject to evaporation, it was possible to chemically monitor the effects of water release by analyzing for sodium and chloride which build up in the ponds and which were diluted when pond and irrigation drain water mix. Also, during the water release period of February, 1971, the Bureau of Reclamation maintained a water guaging station near station 7. It was therefore possible to measure the increase in water flow when the pond water was released in addition to the chemical monitoring.

The total volume of water impounded each year was estimated to be 800 acre feet by refuge personnel. Of that total, about 625 acre feet of water were released in the spring of 1973 during which a high degree of control of the release was exercised. The analysis and release data for 1971-1973 are summarized in

Tables I & II. The increases in sodium, chloride, or both as a result of pond drainage range from 38% to 122% whereas the dilution of pond values ranges from 17-32%. The dilution values indicate that about the same volume of water is released each year with a dilution value of about 25%. The data in Table II corroborate this dilution result since the average flow during water release for 2/11, 2/12, and 2/13 was 106 cubic ft/sec. while "normal" flow for these dates should have been 28 x 3 or 84 cubic ft/sec. The average percentage increase was then (22/84) x 100 or 25%.

Two conclusions can be drawn from the release data: one, the release is about the same each year so that if a contaminant were present, its dilution could be calculated; and two, the New Mexico standard for chloride concentration of 250 ppm was exceeded in 1971 in the release water-irrigation drain mixture even after dilution while the standard was not exceeded in 1973 and probably not in 1972. This data indicates the need for monitoring of the pond water, especially before the water is released. The release can then be set at such a rate as not to exceed standards or pose a potential problem.

B. Data: Means and Standard Deviations

The mean values and standard deviations of the means for the parameters monitored during the study period of 7/70 - 5/73 are presented in Table III. The sample stations can be identified by reference to Figure 1. For comparison, stations 4, 5, and 6 are standing water while the remainder are running water. Since station 4 is a temporary pond area where the waterfowl concentrate and only contains water for a portion of the year,

Table I

Chemical Analyses Obtained During Water Release of Waterfowl Ponds 1971 - 1973

	1971	1972	1973	
	Chloride-ppm	Sodium-ppm	Sodium-ppm	Chloride-ppm
Waterfowl Pond	847 (20)[a]	394 (17)[a]	303 (32)[a]	317 (29)[a]
Upstream from Release	139 (122)[b]	160 (38)[b]	153 (63)[b]	154 (60)[b]
Downstream from Release[c]	309	320	250	246

[a] % decrease after release - i.e. for 1971, (607-139) ÷ 847 = 20%

[b] % increase after release - i.e. for 1971, (309-139) ÷ 139 = 122%

[c] Samples collected 3-12 hours after release began

Table II

Bureau of Reclamation Flow Data
Approximately 4 Miles Below Release*

Date	2/10/71	2/11/71	2/12/71	2/13/71
Flow-Cubic ft./sec.	28	44	34	28

*water released between chart readings of 2/10 and 2/11.

Table III

Analysis Means and Standard Deviations

Parameter*	Station Number 1	Station Number 2
pH	8.04 ± .37	7.99 ± .44
Temp °C	18.3 ± 9.1	16.3 ± 10.0
Spec. Cond. - ohm^{-1}	1183 ± 341	790.6 ± 511
Diss. Oxygen	7.38 ± 1.41	7.81 ± 1.72
BOD-Bio. Oxy. Dem.	3.6 ± 2.4	12 ± 39
COD-Chem. Oxy. Dem.	45 ± 114	90 ± 191
TDS-Tot. Diss. Sol'ls.	833 ± 207	971 ± 2503
Sediment	2109 ± 8078	3462 ± 8640
SiO_2	29.4 ± 7.0	25.1 ± 7.1
Calcium	92.5 ± 22.0	84.3 ± 71.9
Magnesium	19.3 ± 5.4	13.8 ± 7.6
Sodium	169 ± 49	92.0 ± 76.5
Potassium	8.6 ± 2.5	7.5 ± 4.8
Ammonia	.79 ± 1.53	.66 ± .72
Bicarbonate	215 ± 37	161 ± 38
Carbonate	4.4 ± 9.5	5.1 ± 10.9
Sulfate	284 ± 99	208 ± 220
Diss. PO_4	.39 ± .50	1.02 ± .68
PO_4-Total	2.9 ± 3.9	7.2 ± 6.6
Nitrite	.079 ± .292	.079 ± .108
Kjeldahl-N-as NH_3	7.48 ± 16.01	7.81 ± 23.40
Nitrate-as NH_3	1.11 ± 1.23	1.97 ± 3.08
Chloride	132 ± .20	74.7 ± 76.5
Fluoride	.54 ± .20	.48 ± .17
SPC‡-St. Plate Ct.	$(7.0 \pm 11.2) \times 10^4$	$(2.0 \pm 3.4) \times 10^5$
TCC‡-Tot. Coli. Ct.	$(2.8 \pm 7.1) \times 10^4$	$(7.4 \pm 12) \times 10^3$
FCC‡-Fec. Coli. Ct.	180 ± 331	640 ± 1760
FSC‡-Fec. Strep. Ct.	20 ± 33	21 ± 33
TAC‡-Tot. Anaer. Ct.	980 ± 953	2550 ± 4160

*Values in ppm unless otherwise indicated

‡organisms per ml

Table III (cont'd)

Parameter*	Station Number 3	4
pH	8.05 ± .31	7.95 ± .39
Temp °C	17.7 ± 7.8	12.2 ± 6.3
Spec. Cond.-ohm^{-1}	1060 ± 324	2125 ± 1571
Diss. Oxygen	6.3 ± 1.2	7.43 ± 1.96
BOD-Bio. Oxy. Dem.	4.5 ± 4.3	19.0 ± 60.0
COD-Chem. Oxy. Dem.	47 ± 124	17.2 ± 23.9
TDS-Tot. Diss. Sol's.	953 ± 1237	1523 ± 1006
Sediment	2310 ± 9491	136.1 ± 202.8
SiO_2	28.0 ± 10.3	21.8 ± 10.9
Calcium	91.7 ± 22.9	96.2 ± 23.9
Magnesium	17.8 ± 5.5	28.3 ± 13.3
Sodium	139 ± 35	361 ± 281
Potassium	7.7 ± 1.7	15.1 ± 10.9
Ammonia	.42 ± .27	.44 ± .34
Bicarbonate	231 ± 207	283 ± 89
Carbonate	6.2 ± 11.9	0.0 ± ****
Sulfate	266 ± 101	391 ± 208
Diss. PO_4	.33 ± .34	.301 ± .357
PO_4-Total	2.9 ± 3.7	2.30 ± 3.20
Nitrite	.032 ± .139	.045 ± .079
Kjeldahl-N-as NH_3	6.41 ± 17.81	3.35 ± 2.07
Nitrate-as NH_3	1.39 ± 1.41	1.78 ± 1.94
Chloride	105 ± 31	379 ± 350
Fluoride	.51 ± .31	1.41 ± 2.05
SPC‡-St. Plate Ct.	(9.5 ± 19.7) x 10^4	(2.9 ± 3.7) x 10^4
TCC‡-Tot. Coli. Ct.	(4.4 ± 9.8) x 10^3	(2.0 ± 3.3) x 10^3
FCC‡-Fec. Coli. Ct.	212 ± 357	126 ± 226
FSC‡-Fec. Strep. Ct.	23 ± 35	6.5 ± 5.0
TAC‡-Tot. Anaer. Ct.	1474 ± 1128	1258 ± 681

*Values in ppm unless otherwise indicated

‡organisms per ml

Table III (cont'd)

Parameter*	Station Number 5	6
pH	8.07 ± .29	8.33 ± .48
Temp°C	19.3 ± 10.3	18.9 ± 9.2
Spec. Cond.-ohm^{-1}	1627 ± 697	2134 ± 895
Diss. Oxygen	7.96 ± 1.69	9.09 ± 2.12
BOD-Bio. Oxy. Dem.	5.8 ± 8.1	3.1 ± 1.8
COD-Chem. Oxy. Dem.	19 ± 18	14 ± 12
TDS-Tot. Diss. Sol'ts.	1174 ± 381	1424 ± 458
Sediment	81.7 ± 119	162 ± 406
SiO_2	13.0 ± 8.9	28.0 ± 10.8
Calcium	80.8 ± 15.5	82.9 ± 32.2
Magnesium	27.2 ± 7.8	40.0 ± 12.7
Sodium	261 ± 112	337 ± 117
Potassium	12.4 ± 4.2	18.9 ± 6.7
Ammonia	.85 ± 2.09	.46 ± .40
Bicarbonate	237 ± 48	154 ± 75
Carbonate	8.9 ± 13.3	9.8 ± 10.7
Sulfate	414 ± 165	378 ± 115
Diss. PO_4	.070 ± .13	.040 ± .056
PO_4-Total	.93 ± 1.26	.80 ± .99
Nitrite	.015 ± .031	.015 ± .021
Kjeldahl-N-as NH_3	5.64 ± 11.74	2.71 ± 1.79
Nitrate-as NH_3	.885 ± .824	.800 ± 1.37
Chloride	201 ± 94	423 ± 148
Fluoride	.82 ± .27	.49 ± .13
SPC‡-St. Plate Ct.	(1.1 ± 1.5) x 10^4	(4.9 ± 5.0) x 10^3
TCC‡-Tot. Coli. Ct.	(1.6 ± 7.2) x 10^3	191 ± 383
FCC‡-Fec. Coli. Ct.	32 ± 110	65 ± 191
FSC‡-Fec. Strep. Ct.	3.2 ± 11.7	.97 ± 1.97
TAC‡-Tot. Anaer. Ct.	308 ± 355	257 ± 315

*Values in ppm unless otherwise indicated

‡organisms per ml

Table III (cont'd)

Parameter*	Station Number 7	9
pH	7.98 ± .37	7.91 ± .61
Temp °C	19.1 ± 8.8	16.8 ± 8.4
Spec. Cond.-ohm^{-1}	1191 ± 393	1015 ± 227
Diss. Oxygen	7.72 ± 1.55	7.90 ± 1.58
BOD-Bio. Oxy. Dem.	13.3 ± 46.7	20.3 ± 65.3
COD-Chem. Oxy. Dem.	31.0 ± 56.5	22.2 ± 50.1
TDS-Tot. Diss. Sol's	989.4 ± 402.5	808 ± 130
Sediment	2369 ± 8965	1081 ± 946
SiO_2	28.8 ± 8.5	24.6 ± 9.3
Calcium	93.8 ± 18.1	86.7 ± 12.2
Magnesium	21.5 ± 5.3	17.0 ± 1.9
Sodium	172 ± 52	151 ± 34
Potassium	8.6 ± 2.1	7.1 ± 1.2
Ammonia	.45 ± .32	.43 ± .33
Bicarbonate	216 ± 51	214 ± 28
Carbonate	5.6 ± 10.2	7.3 ± 11.0
Sulfate	311 ± 106	275 ± 36
Diss. PO_4	0.234 ± 26.5	.41 ± 1.20
PO_4-Total	2.08 ± 2.59	1.12 ± 1.35
Nitrite	.036 ± .053	.66 ± .73
Kjeldahl-N-as NH_3	7.37 ± 17.74	2.59 ± 2.62
Nitrate-as NH_3	1.02 ± 1.05	.67 ± .74
Chloride	149 ± 73	97.4 ± 23.5
Fluoride	.54 ± .11	.38 ± ***
SPC‡-St. Plate Ct.	(1.5 ± 2.8) x 10^5	(3.8 ± 5.7) x 10^4
TCC‡-Tot. Coli. Ct.	(4.1 ± 6.6) x 10^3	(3.6 ± 13.9) x 10^4
FCC‡-Fec. Coli. Ct.	212 ± 395	187 ± 430
FSC‡-Fec. Strep. Ct.	15.6 ± 27.7	11.0 ± 18.0
TAC‡-Tot. Anaer. Ct.	646 ± 449	590 ± 581

*Values in ppm unless otherwise indicated

‡organisms per ml

another set of means and deviations are presented in Table IV. The stations are compared for the same periods during which 4 contained waters in order to minimize seasonal variation effects on the data. For instance, the sodium concentration in station 5 (Table IV) for the cooler months was 178 ppm while the 3-year average for station 5 (Table III) was 261 ppm reflecting the effect of warmer temperatures on solubility.

In the following section, the data will be compared in these separate divisions; one, nitrogen data reflecting the presence of waterfowl; two microbiological data; and three, physical and chemical data excluding nitrogen analyses.

C. Nitrogen Related Parameters

Nitrogen data was expressed as ppm NH_3 except for NO_2^-, urea, and uric acid. Nitrogen in its various forms was of special interest since it is a critical factor in pollution and eutrophication. The large numbers of waterfowl were expected to contribute significant amounts of nitrogen to the study area. Using domestic ducks as a guide[12], a reasonable estimate of the amount of nitrogen excreted by 30,000 waterfowl over four months would be about eleven tons. Because of the metabolism of waterfowl, the major portion of the nitrogen would be excreted as uric acid with lesser amounts of protein, amino acids and creatine. Uric acid, when broken down biologically, is converted to allantoin and then urea. The urea nitrogen in turn is converted to ammonia, which can be oxidized to NO_2^- and NO_3^-. It thus seemed reasonable to expect that nitrogen levels in water utilized by waterfowl would be elevated. Somewhat surprisingly the dissolved nitrogen values for the water in the ponds were usually in the same range as the

Table IV

Selected Data Averages Comparing Station 4 to Stations 3, 5, 6 & 7 for Periods of 9-15-71 to 5-16-72 and 9-18-72 to 3-15-73 When High-Waterfowl-Use Station 4 is Operative

St. #*	BOD ppm	COD ppm	Ca^{++} ppm	Na^{+} ppm	Kjeldahl N as ppm NH_3	NO_3^- as ppm NH_3	Cl^- ppm	SPC-organisms/ml
3	5.1	8.8	83.4	131	3.10	1.10	124	4.2×10^4
4	19.0	17.2	96.2	361	3.35	1.78	379	2.9×10^4
5	6.9	15.9	78.4	178	2.77	0.86	133	9.2×10^3
6	3.0	12.4	92.2	346	2.78	0.49	429	4.5×10^3
7	4.2	10.2	83.0	177	3.36	0.80	145	7.2×10^4

*See Figure 1 for location

water entering the refuge. There was a slight increase, but the elevation would not cause immediate problems. The potentially toxic species NO_3^- and NO_2^- were well below danger levels, which are set at 12 ppm NO_3^- as NH_3-N and about 1 ppm NO_2^- by the U.S. Public Health Service. Kjeldahl nitrogen values for the water were also lower than expected during periods of very low water. The Kjeldahl values were in the range 2-20 ppm. By using rough estimates for water volume, bird population, and nitrogen loss, the Kjeldahl nitrogen values would be as high as 100 ppm. The Kjeldahl nitrogen includes all nitrogen in a reduced state such as pyridines, proteins, urea, amino acids, and purines such as uric acid. Ammonia levels were always low, and of little significance. The levels found for urea are given in Table V.

Urea levels were low, never exceeding 1.1 ppm for any of the sampling stations as shown in Table V.

A new pond recently constructed by refuge personnel was first sampled in April, 1973 and showed no urea or uric acid present.

The uric acid analyses on the water either indicated no dissolved uric acid or else only trace amounts. It was found that under the conditions which exist in the refuge, uric acid is insoluble and settles to the bottom. Unfortunately, this was found late in the study and it took some time to develop an analytical method. By this time, most of the birds were gone. The data available for uric acid in sediment is given below (Table VI). Once settled out, the uric acid probably remains unchanged until broken down by microorganisms to urea and ammonia. In the refuge water the breakdown is very slow. This was studied by adding uric acid to refuge samples and analyzing for a decrease in uric acid

Table V

Urea in Water-ppm

Sampling Dates

Station #	1/29/73	2/1/73	2/5/73	2/14/73	3/15/73
1	0.60	0.50	0.50	0.20	0.60
2	0.50	0.70	----	0.70	0.80
3	0.40	0.30	----	0.10	0.20
4	0.30	0.20	----	0.50	0.20
5	0.20	0.40	----	<0.01	0.20
6	0.10	0.10	----	<0.01	0.10
7	0.70	0.30	0.70	0.20	0.50
9	0.40	----	----	0.20	0.20
Pond center (#4)	0.50	----	1.10	0.20	----
Pond edge (#4)	0.20	----	----	0.20	----

#	4/12/73	4/16/73	5/16/73
1	0.14	0.25	0.05
2	0.14	0.30	0.05
3	----	0.25	0.05
4	0.04	----	----
5	0.05	<0.01	<0.01
6	----	<0.01	<0.01
7	0.08	0.25	<0.01
9	----	0.30	<0.01

Table VI

Uric Acid in Water-ppm

Station #	5/10/73	5/13/73
1	---	---
2	---	---
3	---	---
4	367	128
5	---	---
6	72	---
7	---	81
9	---	151
newly constructed pond	---	36

concentration and an increase in urea concentration. When refuge water only was used, this conversion was not apparent. However, if mud from the pond bottoms was shaken with the water, the conversion of uric acid to urea was rapid. Under the conditions in the refuge it would seem that the uric acid is relatively unavailable for utilization by microorganisms until the water is mostly gone. The rate of breakdown in the laboratory experiments depends on the microbial population of course, but a typical half-life for uric acid was about 15 hours. This was with an original uric acid concentration of 1 ppm and a bacterial population of $\sim 10^6$ aerobic and 3×10^4 anaerobic bacteria per ml. The breakdown half-life was also determined for urea and found to be about 60 hours. It is probable that the uric acid is broken down in the sediment when the ponds are drying. The nitrogen compounds produced could then be used by plants or end up in ground water. Since the ponds are either allowed to go to ground cover or

utilized as cropland for part of the year, it is likely that most of the nitrogen produced is ultimately used by plants and removed from the environment although soil samples analyzed during the dry period would be necessary to prove this.

For the flowing water (Stations 1, 3, 7, and 9) there was a correlation between Kjeldahl nitrogen and sediment. This could be due to adsorbed uric acid or other nitrogen or to bacteria being adsorbed on the particle surface.

D. Biological Parameters

The concentration of suspended bacterial populations in flowing water appears to follow a cycle. The standard plate count analysis indicated a relatively stable, low bacterial count from January through June during 1971 and 1972 (Figure 2). The count increases beginning in July reaching peaks in September, 1971 and November, 1972 followed by a decline in numbers through December. This trend was noted for all samples from stations located on flowing water.

The standard plate count values for samples from standing water (stations 5 & 6) also were lower during the January through June period. However, the counts from July through December were rather variable. A similar trend also occurs for dissolved inorganic species (note Figure 4) and organic matter (as demonstrated by BOD and COD, Figure 5). Thus, bacterial populations appear to be larger during periods of increased nutrient availability in water. The increased number of bacteria to elevated nutrient concentrations in flowing water has previously been suggested (18).

The amount of sediment suspended in the water from the

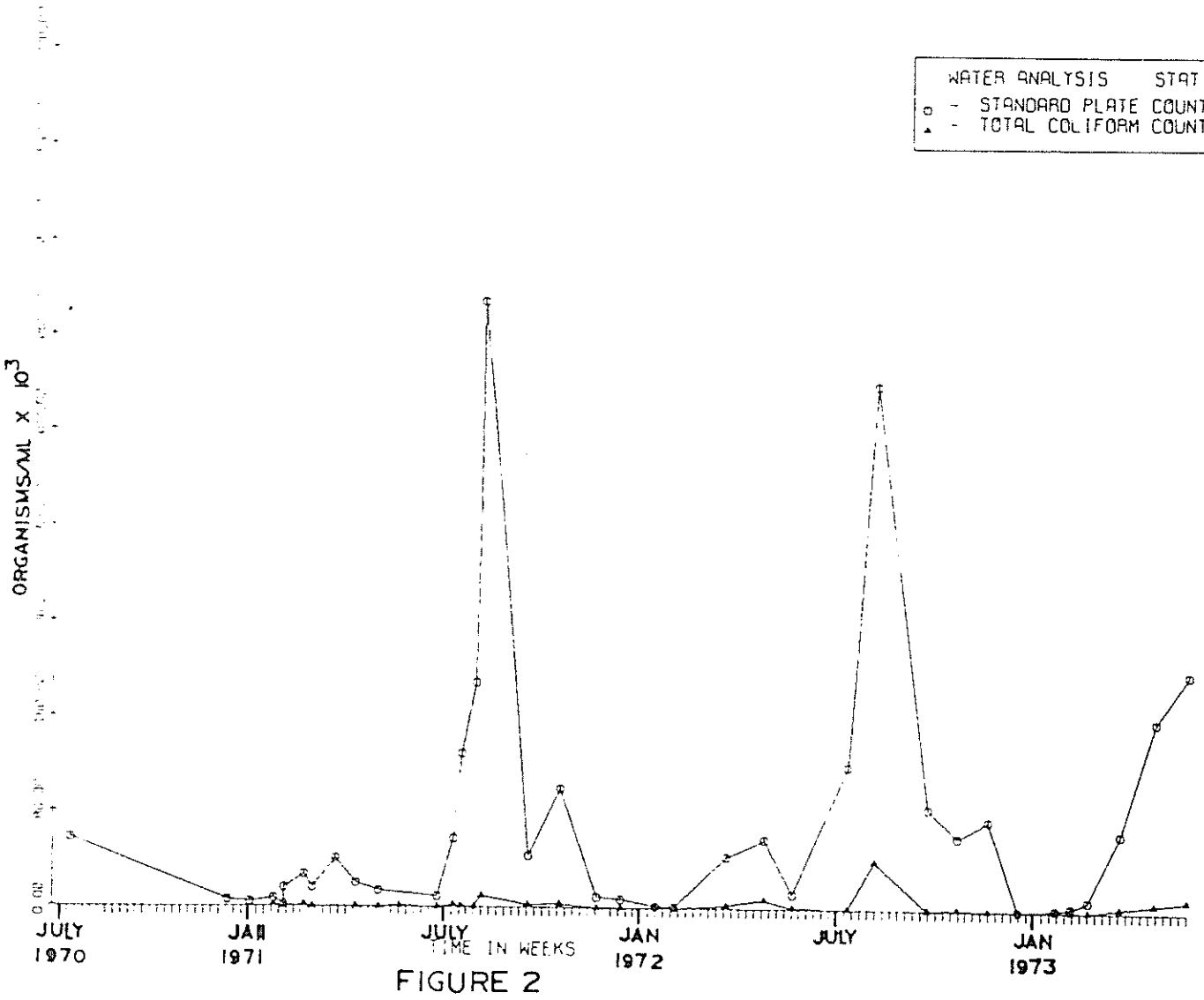

WATER ANALYSIS STATION
o - STANDARD PLATE COUNT1
▲ - TOTAL COLIFORM COUNT1
BEGINNING DATE 700717
ENDING DATE 730516
ORGANISMS/ML X 10^3
JULY 1970
JAN 1971
JULY
TIME IN WEEKS
JAN 1972
JULY
JAN 1973

FIGURE 2

various stations also appears to influence the number of bacteria in suspension. Significant correlations between sediment concentration and the fecal streptococci count was noted for 4 stations (1, 2, 3 & 7; Table X), sediment and standard plate count for 2 stations (3, 7), and between sediment the total coliform count for 2 stations (3, 7). All of the stations are for flowing water. No correlations were noted for ponded water.

Inspection of Table III listing average values for the various parameters also indicates a possible correlation between average sediment concentration and bacterial load when determined by the average standard plate count. A grouping of stations in order of decreasing concentration of sediment 2, 7, 3, 1 and 5 is also a grouping of these stations in consecutive decreasing order of bacterial concentration. This same general relationship between decreasing concentration of sediment and decreasing order of bacterial count occurs for the total coliform count, the fecal coliform count and the fecal streptococci count, however, there is some variation for the latter. However, it appears that this relationship only exists for relatively high sediment concentrations (>420 ppm). Thus, bacterial count may be dependent on sediment concentrations in highly turbid water.

The number of bacteria suspended in both ponded and flowing waters in the study area is quite high ($>10^4$ and $>10^3$ SPC/ml respectively, Table III). This is in marked contrast to waters such as streams from mountain watersheds, which are most often the subject of water research and may contain as few as 50 total bacteria/ml. The most plausible explanation for this high concentration of viable bacteria may be a result of the high

concentration of suspended sediments in flowing water and available nutrients in flowing and ponded water. It is probable that the majority of bacteria in a flowing water system are bound by adsorption to particulate matter (20). Thus, an increase in suspended solids may likewise cause an increase in the suspended bacteria concentration. The high count is not directly a result of refuge use of the water as the plate count for the water supply (station 9) is quite high (average SPC 3.5×10^4/ml). However, water flowing through the refuge does show an increased number of cells. Water leaving the refuge (station 7) has an average SPC of 1.5×10^5/ml. This may be a reflection of population growth in the water and not a contribution of bacteria as a result of refuge use.

Use of the Rio Grande water for refuge purposes does not appear to detrimentally effect water quality when evaluated by its bacteriological populations.

The State of New Mexico sets the standard for fecal coliform bacteria in the Rio Grande Basin encompassing the study area at 50/ml (arithmetic average). All waters sampled with the exception of station 5, the permanent swamp, exceed this concentration (Table III). The average fecal coliform value for water used as the water-fowl habitat (station 4) exceeds the state standards but is less than the canal water flowing through the refuge which ultimately receives this water. The highest value (Table III) is in the water of station 2 not used by the refuge.

It is likely that the source of fecal contaminants at station 4 is the water used to fill the pond. This water is obtained from the ditch sampled at stations 1, 3, and 7.

Figure 3 indicates that the highest values for the bacterial counts determined occur early in the season during ponding. The counts decline during the period of waterfowl use probably as a result of settling and death of the bacterial cells. There is no evident trend in increase of any of the bacteriological parameters in the pond during the waterfowl use period.

On February 5, 1973 the canal receiving the effluent from station 4 was sampled twice above and below the incoming effluent. The result of the effluent was to increase the average standard plate count from 1.3×10^3 to 5.1×10^3/ml, the average total coliform count from 1.9×10^2 to 3.5×10^2/ml, the fecal streptococci count from 0.4 to 1.6/ml, and decrease the fecal coliform count from 5 to 2.6/ml. It is believed that the dumping of the pond water does not further degrade the quality of the receiving water when determined by the usual microbiological water quality parameters.

The average fecal coliform count for refuge incoming water is 187/ml (station 9) and increases slightly to 212/ml (station 7; Table III). The average fecal streptococci count also increases in the water during its passage through the refuge from 11 to 15.6/ml (Table III). This increase may represent growth of the respective populations rather than addition of fecally polluted water. It has been demonstrated that these usually accepted indicators of fecal pollution are capable of growth in other river water environments (21).

E. Physical and Chemical Parameters (Excluding Nitrogen Analyses)

The overall effect of the refuge on the physical and chemical parameters considered (excluding nitrogen analyses which will be

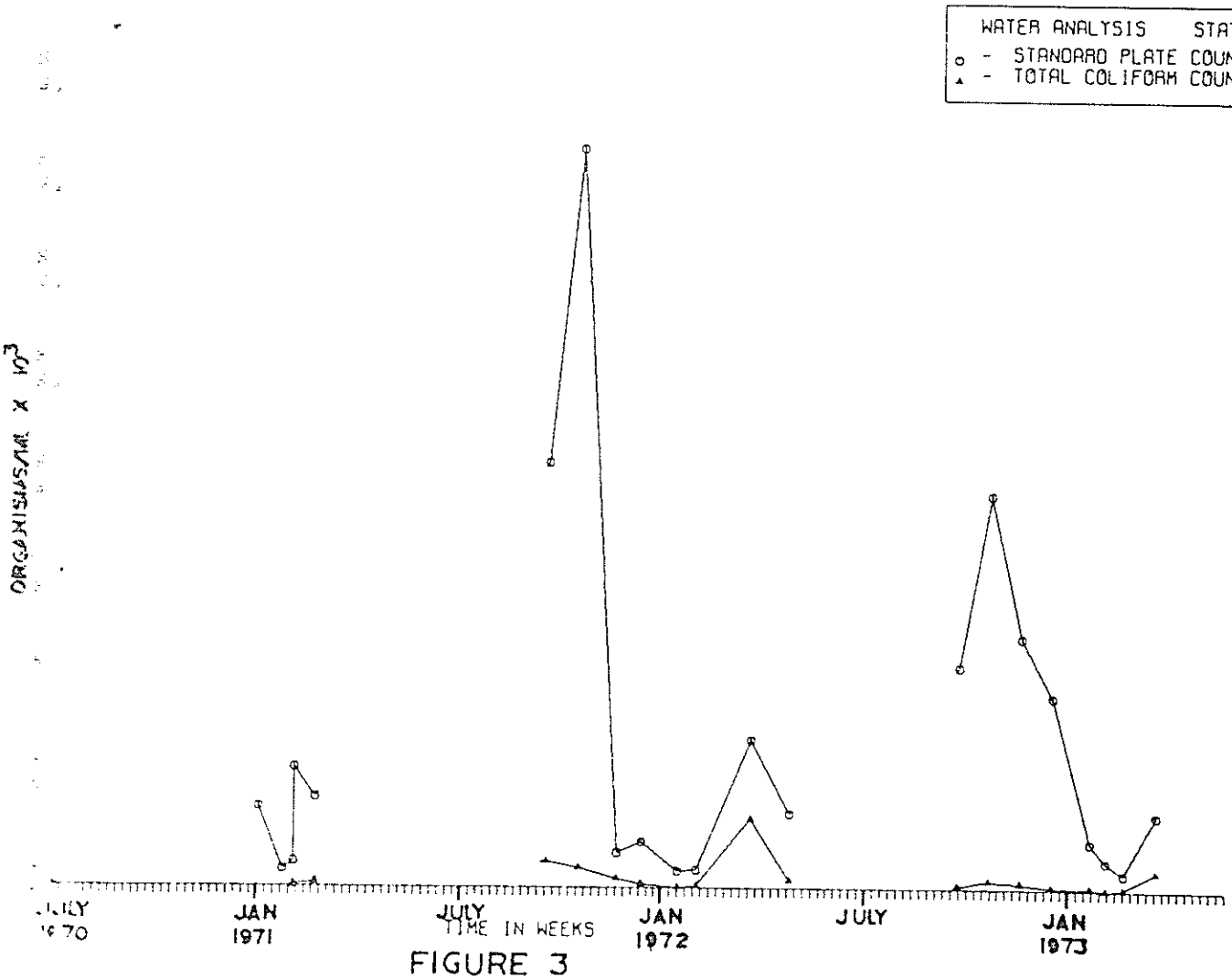

WATER ANALYSIS STATION
o - STANDARD PLATE COUNTS
▲ - TOTAL COLIFORM COUNTS
BEGINNING DATE 700717
ENDING DATE 730516
ORGANISMS/ML X 10^3
JULY 1970
JAN 1971
JULY
TIME IN WEEKS
JAN 1972
JULY
JAN 1973

FIGURE 3

treated separately) can best be observed by comparing station 9 (entering water) with station 7 (leaving water) in Table III. The most significant changes occur as increases in values for specific conductance, total dissolved solids, sediment, chemical oxygen demand, and total phosphate. The sediment value rises because water is often diverted from the Bureau of Reclamation Channel which is flowing faster than the irrigation drain water and has the highest sediment mean (more than 1000 ppm higher than the next nearest value). Since the sediment carries many adsorbed species with it, the values of COD and total phosphate rise accordingly. The rise in total dissolved solids (reflected in higher values for specific conductance and for most of the cations and anions) was probably due to the rise in the temperature of the water as it moved through the refuge. The entering water had average temperatures of 16.3°C at station 2 and 16.8°C at station 9. The average temperature had risen to 17.7°C by station 3, 18.3°C by station 1, and finally to 19.1°C at station 7 when the water left the refuge.

The waters ponded in stations 4, 5, & 6 are considered separately since their characteristics are quite different from the flowing water. For instance, the total dissolved solid (TDS) values in the ponds range from 1174 - 1523 ppm whereas all the values for flowing waters are less than 1000 ppm. Also, the sediment values are very low in the ponds (average < 200 ppm) while the flowing waters all have values > 1000 ppm. By referring to Table III, the values for selected parameters of 4, 5, and 6 during periods of waterfowl use can be compared. The BOD value is significantly higher in 4 than in 5 and 6. This could occur

because 4 is allowed to grow grass during the summer months and then is flooded and the decaying vegetation can provide nutrients. In line with this explanation is a slightly higher COD value for 4 and also a higher standard plate count meaning a greater concentration of organisms.

Another difference between 4 and No's 5 and 6 is the higher values for dissolved and total phosphate. The year-round ponds are apparently in an equilibrium state with respect to the phosphorus cycle whereas the phosphorus values in 4 reflect the fact that the water in 4 originates as surface water with similar phosphorus concentrations. For instance, water passing by station 3 was diverted into station 4 and the dissolved and total phosphate values were .33 and 2.9 ppm respectively while the same values for station 4 were 0.30 and 2.3 ppm.

It is of interest to note that evaporation causes the average TDS value in #4 (1523 ppm) to exceed the state of New Mexico limit of 1500 ppm. However, when the pond waters are mixed with flowing surface water, the dilution lowers the values below violation (see discussion of water release on page 11).

F. Mercury Analyses

Mercury analyses of both water and fish samples taken in the refuge were conducted both because of the recent concern over mercury in the environment and because very little data of this type exists for New Mexico's waters.

Two general trends were observed in the fish analysis data in Table VII. The larger and most carnivorous fish (bass) contained the most mercury and approached but did not exceed the F.D.A. limit of 0.5 ppm mercury. It can be seen by the tissue

Table VII

Total Mercury in Fish in the Bosque Refuge

Type	weight-g	micrograms of mercury	ppm
Channel catfish	47.6112	5.21	0.11
Bullhead catfish	69.7093	13.10	0.19
Carp	201.6721	86.72	0.43
Bass	233.2710	103.42	0.47

Table VIII

Mercury Content of Selected Tissue of Channel and Bullhead Catfish

Channel Catfish

tissue	weight-g	micrograms of mercury	ppm
Liver	1.0938	0.34	0.31
Kidney	0.1801	0.39	2.16
Muscle	2.8607	0.20	0.07

Bullhead Catfish

Liver	2.3070	0.25	0.11
Kidney	0.6870	0.68	0.99
Muscle	2.7410	0.38	0.14

analysis (Table VII) that 14% of the mercury in the channel catfish and 9% of the mercury in the bullhead were contained in the liver and kidney. The amount of mercury in muscle tissue which would be eaten is therefore less than that reported for the total fish.

There were no trends in the mercury analysis data (Table IX) for the water that could be related to the type of water. The total mercury values were about 2-3 ppb with about equal distributions between "inorganic" and "organic" mercury. It appears, however, that even these waters that are relatively free from industrial pollution contain significant and detectable mercury levels.

G. Data Plots

There were three reasons for designing the computer program to plot the data in terms of concentration of a parameter vs. time or concentration of one parameter vs. another parameter. First, the large amount of data would have made hand plotting a tedious process. Second, by plotting vs. time, seasonal changes could be observed and anomalous values could be more easily recognized than by going through the larger number of data sheets. Third, the plots of parameter vs. parameter were necessary to determine the validity of correlations as will be described later. Two representative plots are included in this report (Figures 4 and 5) for illustration purposes.

The seasonal effect of water temperature on dissolved ions can be seen using sodium analyses vs. time in flowing water (Figure 4). Cooler temperatures reduce the solubility and the converse is observed for warmer waters during the summer months.

Table IX

Mercury Analysis-Refuge Waters
Inorganic-ppb*

St. #	11-17-71	1-15-72	6-14-72	1-29-73	2-5-73	2-14-72	3-15-73	5-16-73	Ave.
1	1.3	2.0	0.0	4.8		.6	1.4	4.9	2.1
2	0.0	0.0	4.2	2.6		.4	0.6	1.3	1.2
3	1.1	0.0	0.0	2.7	1.6	1.0	0.4	1.3	1.0
4	0.4	0.0		2.5		1.1	0.0		0.8
5	0.0	0.0	3.2	5.3		1.3	0.4	1.7	1.7
6	0.0	0.0	0.0	2 8	2.1	2.2	0.5	1.0	1.1
7	0.7	0.0	0.0	2.3			0.6	0.9	0.8
9	---	---	---	2.2		1.5	0.0	0.7	1.1

Organic-ppb*

St. #	1-29-73	2-5-73	2-14-73	5-16-73	Ave.
1	0.0	---	0.5	0.0	0.2
2	0.0	---	0.1	0.0	0.0
3	1.5	1.3	---	0.2	1.0
4	2.2	---	1.0	---	1.6
5	2.7	---	1.6	---	2.2
6	2.7	1.0	1.1	0.5	1.3
7	1.6	---	---	0.7	1.8
9	2.6	---	---	0.0	1.3

* Detection limit is 0.1 ppb so values of 0.0 should be interpreted as < 0.1.

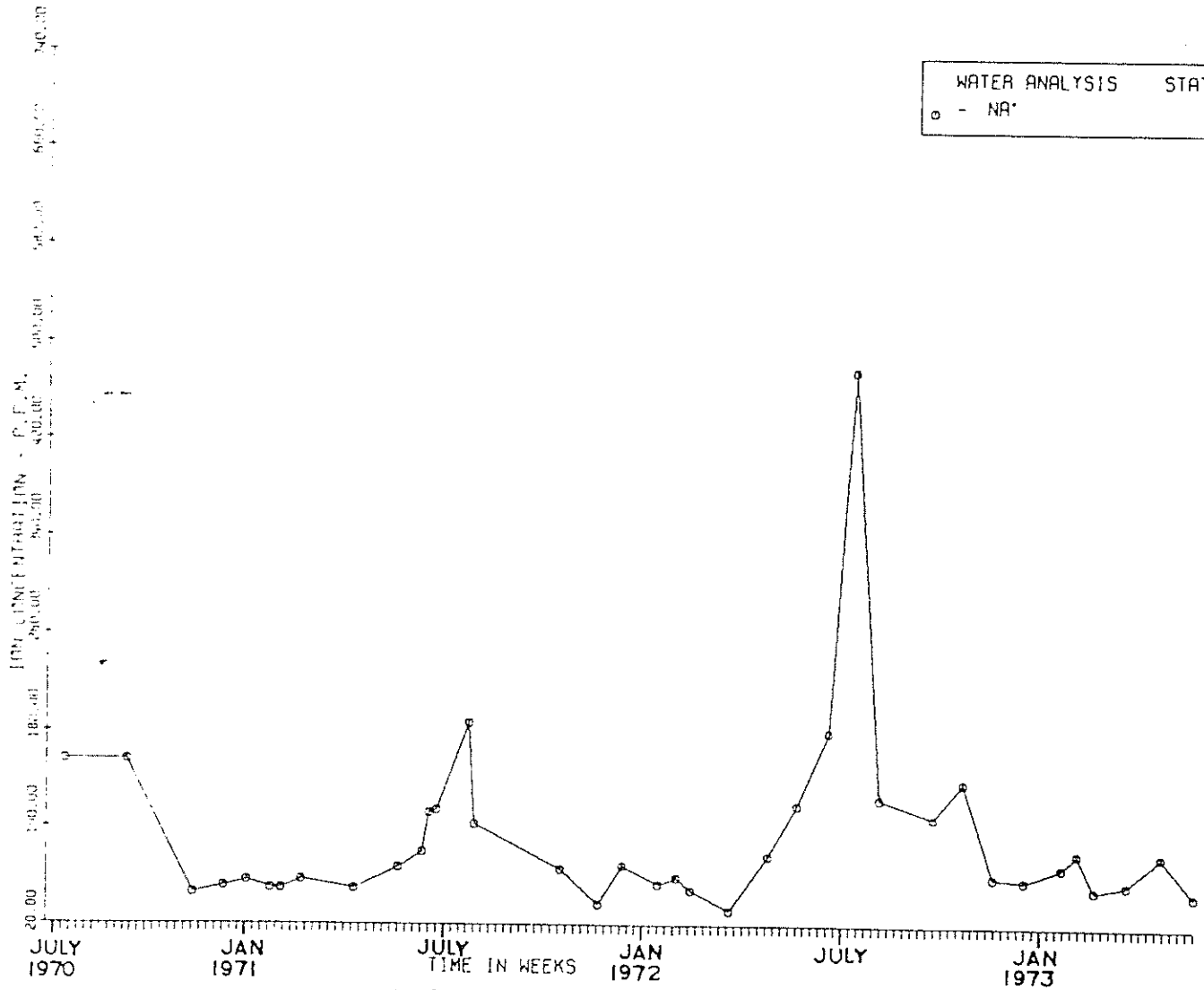

WATER ANALYSIS
o - NA+
STATION
2
BEGINNING DATE 700717
ENDING DATE 730516
JULY
1970
JAN
1971
JULY
JAN
1972
JULY
JAN
1973
TIME IN WEEKS

FIGURE 4

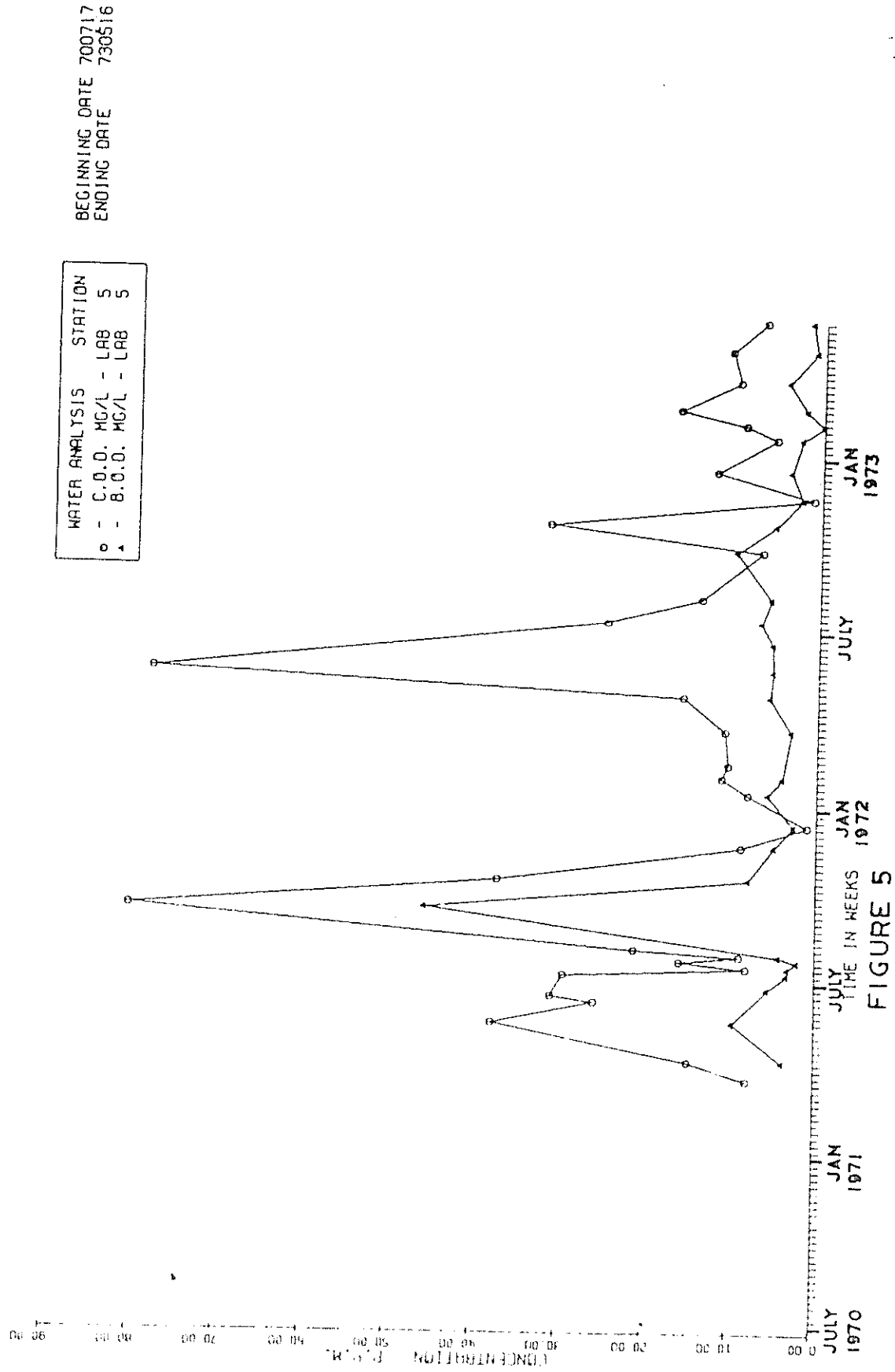

BEGINNING DATE 700717
ENDING DATE 730516
WATER ANALYSIS STATION
o - C.O.D. MG/L - LAB 5
▲ - B.O.D. MG/L - LAB 5
JULY 1970
JAN 1971
JULY
JAN 1972
JULY
JAN 1973
TIME IN WEEKS
FUNCTION

FIGURE 5

Several parameters can be plotted vs time on the same graph (Figure 5). This serves the purpose of observing increases or decreases of supposed interrelated parameters. For instance, COD and BOD are plotted on Figure 5 and although a few of the rises and falls occur together, the COD values are much more erratic and no general trend can be observed. It should be pointed out however, that COD values may be highly susceptible to sampling procedures and several large pieces of organic material may contribute to an abnormally high COD.

II. Data Correlation

One of the aspects of this study involved an attempt to perform linear regression analyses on the data and thereby obtain correlation coefficients for the parameters to check their interrelationships. A computer program available in the subroutine library of the New Mexico Tech Computer Center was modified to accept the data format of this study. The computer then generated correlation coefficients for all parameters for each station vs all other parameters for that given station. Since there were 30-40 variables for each of 8 stations, the number of correlations checked was approximately (35)x(35)x(8), or almost 10,000. From this data, the more highly correlated (correlation coefficients >0.6) parameters were listed and collected. Table X is a listing of parameters which correlate for 3 or more stations.

The most highly correlated pair of parameters was dissolved oxygen and temperature. We know that as the temperature rises, the solubility of a gas decreases and every station except 6 bore out this correlation. Station 6 was anomalous for dissolved

Table X

Listing of Parameters with Correlation Coefficients 0.6 for Three or More Stations*

Parameters	Station Numbers	Parameters	Station Numbers
Temperature-Dissolved Oxygen	1,2,3,4,5,7,9	S.P.C. vs C.O.D.	3,7,9
C.O.D. vs F.S.C.	1,3,9	S.P.C. vs T.A.C.	2,3.5,6
C.O.D. vs Kjeldahl Nitrogen	1,3,9	S.P.C. vs F.S.C	3,4,7,9
Sediment vs Kjeldahl Nitrogen	1,2,3,7	S.P.C. vs Kjeldahl Nitrogen	3,7,9
Sediment vs Conductance	1,2,3,4,5,6,7	S.P.C. vs F.S.C.	2,4,9
Sediment vs F.S.C.	1,2,3,7	S.P.C. vs Kjeldahl Nitrogen	3,7,9
Sodiium vs Chloride	1,2,4,5,6,9	S.P.C. vs F.C.C.	2,4,9
Sodium vs Dissolved Solids	1,4,5,6,9	F.S.C. vs Kjeldahl Nitrogen	1,2,3,7,9
Chloride vs Conductance	1,2,4,5,6	T.A.C. vs Kjeldahl Nitrogen	1,3,4
Chloride vs Dissolved Solids	4,5,6.9	T.C.C. vs C.O.D.	3,5,9
Dissolved Solids vs Conductance	1,4,5,6	T.A.C. vs Total Phosphate	2,5,7,9
Bicarbonate vs Conductance	1,4,6,7	T.C.C. vs F.S.C.	3,6,7
Calcium vs Sulfate	3,4,5,7		

*See Table III for explanation of abreviations

oxygen in that it was often supersaturated with oxygen especially in the summer. The reason for this was unclear, but the high values for DO seemed to coincide with heavy algae growth in the water and photosynthesis may have produced these excess quantities of oxygen.

Three other highly correlated sets of parameters which are related were sodium and chloride vs specific conductance with seven and six stations respectively correlating and also, as a result sodium vs chloride with six of the eight stations correlated. These cases are discussed because for this approach to be relied on, one would hope to have the more obvious correlations verified.

There was no set of parameters which had high correlations for all of the sample stations although the examples discussed in the previous paragraph were very close to being 100% correlated. It might be expected that correlations could occur in groups in relation to the type of water sampled. For instance, sample stations 1, 3, 7, and 9 were located along the same irrigation drain system. Stations 4, 5, and 6 were all standing water, but 4 may have been anomalous due to its intermittant nature and the fact that the waterfowl were concentrated there. Station 2's water was different than any of the other flowing waters since it was flowing relatively unaltered through the Bureau of Reclamation Channel.

A further check on the correlations was to plot parameter vs parameter as in Figure 6. These sets of parameters had very high correlation coefficients, yet the plots show that most of the data was grouped together at the origins of the axes with only one point at very high values. It cannot be known whether the

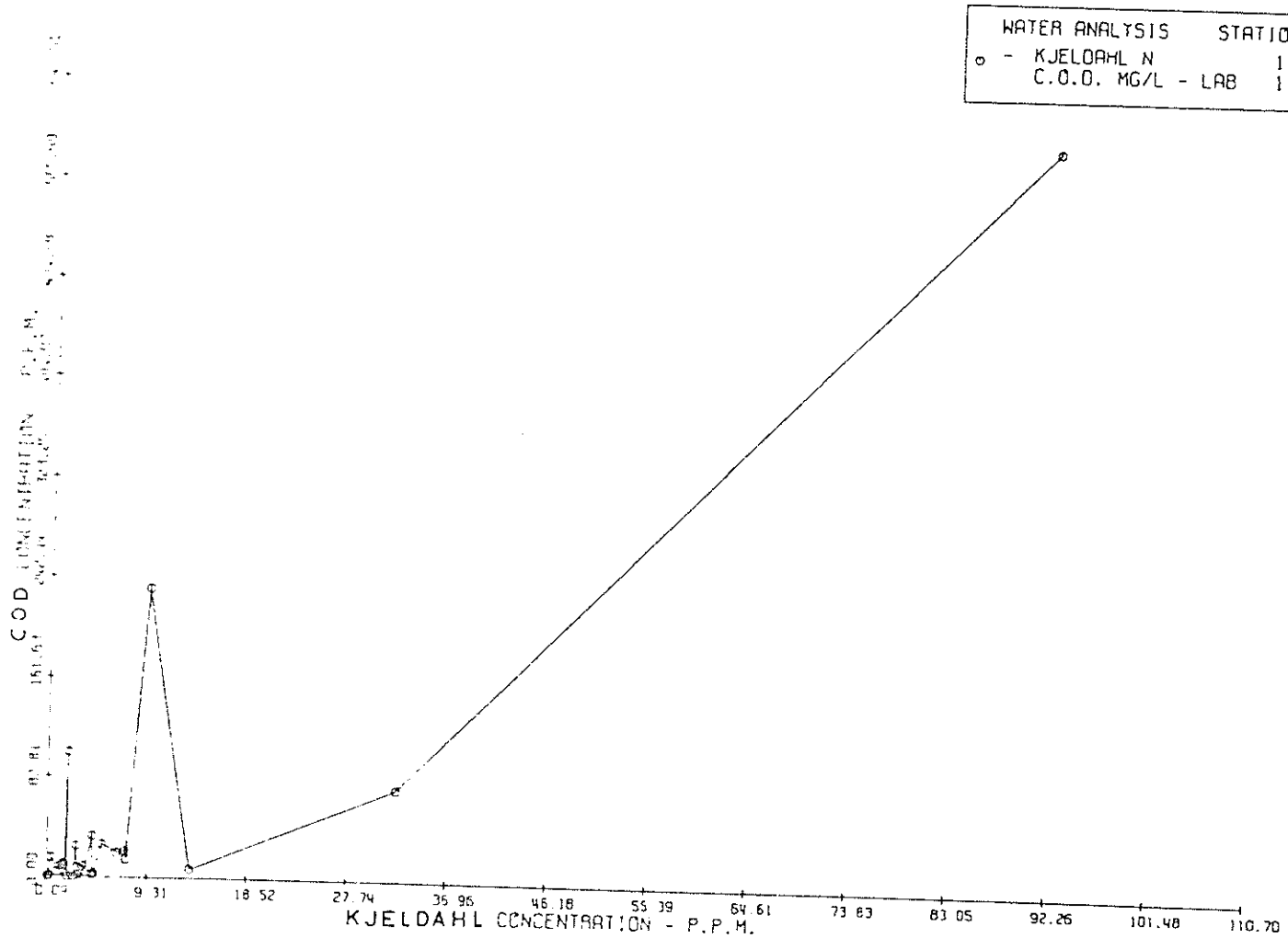

WATER ANALYSIS STATION
o - KJELDAHL N 1
C.O.D. MG/L - LAB 1
BEGINNING DATE 700717
ENDING DATE 730516
COD
9.31
18.52
27.74
35.96
46.18
55.39
64.61
73.83
83.05
92.26
101.48
110.70
KJELDAHL CONCENTRATION - P.P.M.

FIGURE 6

correlation is linear over the entire range without having data points between the extreme high and low values. There are several reasons for the inability to draw solid correlation conclusions at this stage. It is possible that an insufficient quantity of analysis data was available even though the study was conducted over a three year period. Also, the correlations may not be straightforward linear relationships and may require non-linear and/or possibly multiple regression analysis to establish their validity. It is beyond the scope of this study to carry the statistical analysis further.

Of perhaps as much interest as the correlated data was the lack of expected correlations to occur. For instance, there were only two of the stations (2 and 6) which had correlation coefficients greater than 0.6 for COD vs BOD even though it seems to be generally accepted that these parameters should be correlated since they both are a measure of oxygen demand. We were very dissatisfied with the BOD analysis in general since it seemed to be subject to many influences (i.e. temperature, poisonous material in the water, air leakage into BOD bottles). There was no observed correlation for BOD vs any plate count for more than one station, but COD was correlated to fecal streptococci count, total coliform count, and standard plate count for three stations each (Table X). It is felt that the COD is the better indication of oxygen demand potential if microbiological species are present.

The utility of this approach to find correlations could be immense in terms of water quality evaluation and water monitoring. If high correlation could be established and equations developed, many analyses could be eliminated by using the equations and

calculating parameters whose analyses are more difficult and time-consuming in terms of a more easily measured parameter. It may also be that a particular correlation only holds at a specific sampling point or section of flowing water due to intervening external influences such as high agricultural use or industrial waste dumping. That correlation will then still be useful if always used at that point for monitoring purposes. It is hoped that this approach will be used in analysis of other data collected over long time periods in the highly sedimented waters in the southwest to verify relationships established in this study and in other waters as well.

I. Evaluation of Pond Sampling Methods

In any sampling procedure, obtaining a representative sample can be a difficult problem. All of the sampling areas involving flowing waters in this study were narrow, relatively shallow, turbulent and fast-flowing which allowed the water to mix well. However, the ponded areas could have been subject to stratification. Also, the pond water at station 4 (Figure 7) was periodically replenished by the diversion of irrigation drain water. It was felt that these two effects should be checked.

Data collected at the fishing pond (station 6) from the surface and within a few inches of the bottom is presented in Table XI. The average depth of the pond is about 2-3 feet and there appears to be virtually no difference between the surface and bottom analyses.

On two separate dates both the pond edge (normal sample site) and approximate pond center were sampled in station 4. Evaporation in the ponds lowers the water level and concentrates dissolved

Figure 7. Dr. J.A. Brierley (back to camera) and Dr. D.K. Brandvold in process of collecting water samples in high-water fowl-use Station #4. Note waterfowl in background.

solids. When water is added to replenish that lost by evaporation, the rate of mixing is quite slow. It can be seen by examining Table XII that on 1/29/73, the center of the pond had higher concentrations of all parameters tested except the nitrogenous species indicating that water had been added recently and mixing was slow. However, on 2/5/73 there was virtually no difference between the center and edge so that in less than a week the pond was again relatively homogeneous. It was hoped that by always sampling at the same point at a given site that relative changes in composition of the ponded waters would not occur.

Table XI

Selected Analyses for Samples Collected Near Surface and at Bottom of Station 6 - 3/15/73.

Parameter	Surface	Bottom
pH	8.54	8.42
Temp-C°	9.9	9.5
Conductivity-ohm^{-1}	4120	4120
Dissolved oxygen	7.6	8.2
Total Phosphate	0.66	0.42
Nitrate-as NH_3	0.23	0.34
Chloride	688	695
Kjeldahl Nitrogen-as NH_3	3.37	3,11
Standard Plate Count	8.5×10^3	3.1×10^3
Total Colifirm Count	2.0×10^2	3.3×10^2

Table XII

Selected Analyses for Samples Collected Near Edge and near Center of Station 4.

	1/29/73		2/5/73	
Parameter	Center	Edge	Center	Edge
Dissolved Solids	2724	1944	820	804
Calcium	112	81	87	89
Sodium	720	542	169	157
Kjeldahl Nitrogen-as NH_3	3.1	1.6	---	---
Dissolved Phosphate	0.35	0.05	---	---
Nitrate-as NH_3	0.60	0.40	---	---
Standard Plate Count	1.3×10^4	1.2×10^3	---	---
Total Coliform Counts	74	57	---	---

IV. Conclusions

Determination of the effect of a large migratory bird population on a water system was the primary objective of the study. It appears that the waterfowl do not increase significant amounts of nitrogen compounds, a major factor in eutrophication processes. The uric acid which the waterfowl excrete is insoluble in the water of the mid-Rio Grande. It appears to collect in the sediment of the waterfowl ponds. The uric acid may be broken down when the ponds are drained and the resultant nitrogen products absorbed by the plants which develop. Thus, the waterfowl may in effect enhance crop productivity of the area. No other chemical species were noted to have been affected by the waterfowl populations.

The water quality of the waterfowl pond habitat and the canal receiving the pond effluent is not affected by the large bird population when evaluated by the standard microbiological parameters. However, the canaled Rio Grande water quality does not meet the state standard for maximum allowable fecal coliform bacteria. The high number of fecal coliform bacteria is not a result of refuge use, but is determined by various up-stream factors not defined in this study.

The flowing water in the refuge has a very high suspended sediment load. This necessitated modifications of some procedures for water analysis. The high sediment concentration appears to increase concentrations of various chemical species and microbial populations in flowing water probably by a process of adsorption. The high sediment load makes it difficult to compare results of this study with other water studies which usually deal with low

turbidity waters. It may be that the accepted water quality standards do not apply to these types of waters and should be reevaluated.

In the future, waterfowl habitat ponds should be monitored before release of water. Particular attention should be paid to salinity as evaporation and perhaps leaching increases the concentration of dissolved salts. Knowledge of the salt concentration will permit an operator to control the rate of effluent flow to allow sufficient dilution of salts in order to prevent salinity related problems. In addition, Kjeldahl-Nitrogen and COD should be monitored as indicators of potential eutrophication and oxygen deficit problems. Perhaps uric acid will remain in solution in water of other waterfowl habitats and in this case should be monitored as an indicator of a pollution problem, i.e. a potential source for oxidized forms of nitrogen such as nitrite and nitrate.

The data correlation study shows promise of utility in relating parameters and determination of quality. However, no conclusions can be drawn at this time due to the limited scope of this study and the need for more complete data from long term, short interval, monitoring.

V. Recommendations

A consequence of this study was to discover additional problems and undefined phenomena related to this environment. The following is a presentation of topics for future research.

The fate of the excreted uric acid should be defined. This will comprise a soil study following pond drainage for determination of uric acid concentrations. Subsequently, the course of the breakdown should be followed, identifying break-down products, the catalysts responsible for degradation and the kinetics of degradation.

An unusual feature of the flowing waters in this area is the high concentration of suspended sediment and concomitant large sediment surface area. This undoubtedly presents an environment for many surface-related reactions and which might involve phosphate equilibria. In addition, microbial populations are bound by adsorption to sediments in aquatic systems and are most active in this association. Thus, the nature of the association, the microbial activities, the kinetics of microbial activity should be studied for this type of environment as it has been largely ignored in aquatic studies.

Study of correlations among various descriptive parameters of the aquatic environment should be continued in detail. This may lead to discovery of a limited set of parameters that may be used to define water quality. In addition, these limited number of parameters may be such that analyses can be performed in a minimum time since the limiting factor in heading off or identifying pollution problems seems to be getting the analyses done quickly.

No significance could be attached to usual microbiological parameters of water quality for this environment. Additional research should be performed to isolate, identify and associate any exotic types of bacteria with waterfowl habitats.

VI. Bibliography

1. Standard Methods for the Examination of Water and Waste-Water, 12th Ed., American Public Health Association, Inc., New York, N.Y., 1966, p. 244.

2. Ibid. p. 424.

3. Ibid. p. 261.

4. Ibid. p. 234.

5. Ibid. p. 290.

6. Ibid. p. 205.

7. Ibid. p. 87.

8. Ibid. p. 510.

9. W.R. Hatch and W.L. Ott, "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectroscopy" Anal. Chem., 40, 2085 (1968).

10. H.L. Golterman (Ed), Methods for Chemical Analysis of Fresh Waters, Blackwell Scientific Publications, Oxford, England, 1970, p. 76.

11. B.L. Oser (Ed), Hawk's Physiological Chemistry, 14th Ed. McGraw-Hill, 1965, p. 1326.

12. T.L. Willrich and G.E. Smith (Ed), Agricultural Practices and Water Quality, p. 111, Iowa State University Press, Ames, Iowa, 1969.

13. Sigma Technical Bulleton #680, Sigma Chemical Company, St. Louis, Missouri.

14. Standard Methods for the Examination of Water and Waste Water, 12th Ed., American Public Health Association, Inc., New York, N.Y., 1966. p. 218.

15. Ibid. p. 592.

16. Ibid. p. 597.

17. Ibid. p. 618.

18. D.G. Stuart, G.K. Bissonnette, T.D. Goodrich, and W.G. Walter, "Effects of multiple use on water quality of high-mountain watersheds: bacteriological investigations of mountain streams", Appl. Microbiol. 22, 1045 (1971).

19. Ibid.

Bibliography (cont'd)

20. C.E. Zobell, "The effect of solid surfaces upon bacterial activity", J. Bacteriol. 46, 39. (1943).

21. C.W. Hendricks, "Enteric bacterial growth rates in river water", Appl. Microbiol. 24, 168 (1972).