

#21
Folder:
~~planning~~
ponds

#326(2)

IGN AND DEVELOPMENT OF A REMOTELY CONTROLLED
MOBILE DATA ACQUISITION SYSTEM FOR CONTINUOUS AND
LONG TERM MONITORING OF WATER QUALITY CHARACTERISTICS
IN HAWAIIAN ANCHIALINE PONDS:

WATER QUALITY CHARACTERISTICS OF KALOKO POND
- A SMALL CASE STUDY

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CIVIL ENGINEERING

DECEMBER 1996

By
D. N. Bhambare

Thesis Committee:
Gordon L. Dugan, Chairperson
Edmond Cheng
Loren D. Gautz
Clifford W. Smith

We certify that we have read this thesis and that, in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Civil Engineering.

Thesis Committee

Chairperson

Acknowledgments

I would like to acknowledge Dr. Clifford W. Smith for providing the funding for this research. Special thanks are due to Mr. Thomas Fake - GPS specialist, Ms. Laura Carter Schuster - Cultural Resources Manager, Mr. Francis Kuailani - Park Superintendent, and the park officials at the Kaloko-Honokohau National Historical Park, Kailua-kona for providing assistance to complete this study. Their assistance during the park closure due to government shut down is laudable. I would also like to thank Mr. Charles Nelson, Machinist at the Biosystems Engineering; without whose assistance many of the parts of the system would not have been possible.

Table of Contents

Acknowledgments	iii
List of Tables	vi
List of Figures	vii
List of Abbreviations and Symbols	x
1. Introduction	1
2. Literature Review	4
3. Materials and Methods	9
3.1 Introduction	9
3.2 Controls	10
3.3 Data Acquisition System	12
3.4 Instrumentation	13
3.4.1 Salinity Meter	13
3.4.2 Dissolved Oxygen Meter	14
3.4.3 Temperature Sensor	15
3.4.4 pH Meter and Oxidation Reduction Potential (ORP) Meter	16
3.4.5 Radiation Sensor	16
3.4.6 The Water Level Measurement System	16
4. Results and Discussion	18
4.1 Introduction	18
4.2 Presentation of the Data	20
4.3 Profile of Various Parameters in the Pond	22
4.3.1 Salinity	22
4.3.1.A Salinity Distribution in the Top Layer	22
During Calm Periods	22
During the High Tides	23
4.3.1.B Salinity Profile during Calm Periods	23
4.3.1.C Salinity Distribution when a High Tide was Receding	24

4.3.1.D Salinity Distribution and Profile in the Other Part of the Pond	25
4.3.1.E Salinity Distribution during Low Tides	25
4.3.1.F Salinity Distribution and Profile when Approaching High Tide	26
4.3.1.G Salinity Profile During the High Tide and Afterwards	27
4.3.1.H The Floating Profiles	27
4.3.2 Temperature	29
4.3.2.A Temperature Variation with the Depth	30
Daytime Profile	30
Nighttime Profile	30
Diurnal Variation in Temperature	31
4.3.2.B Freshwater Temperature	31
4.3.2.C Effect of Sunshine Hours on the Temperature	31
4.4 Dissolved Oxygen	32
4.4.1 Supersaturation	33
4.4.2 Depth Profile of Dissolved Oxygen	34
4.4.3 Diurnal Variations of Dissolved Oxygen	34
4.4.4 Effect of Sunshine Hours on Dissolved Oxygen	35
4.5 pH	36
4.6 ORP	38
5. Conclusion	40
Appendix A. Location Map of Kaloko Pond	76
Appendix B. Avian mortalities in the Kaloko-Honokohau National Historical Park in 1994.....	77
Appendix C. Tide Chart for the Month of November 1995	79
Appendix D. Solar Radiation During the Period of November 10-21, 1995	80
Appendix E. Design of Control Mechanisms for the Instrument Boat	81
Appendix F. Salinity Meter: Construction and Calibrations	87
Appendix G. pH and ORP Interface Construction and Calibrations	94
Appendix H. Dissolved Oxygen Meter Interface and Calibrations	103
Appendix I. Temperature Sensor Interface and Calibrations	108

Appendix J. Photographs 114

References 115

List of Tables

<u>Table</u>	<u>Page</u>
2.1 Surface and bottom temperature and salinity profile (January 29, 1988) at Kaloko pond (Chai, 1991).	7
4.1 Data logging times and their significance	19
4.2 Important information about the figures to be compared for studying the floating profile pattern.	28
4.3 Solubility of oxygen in water exposed to water-saturated air at atmospheric pressure	33
E1 Output of of column positioning system at various depths.....	86
F1 Calibration data for the salinity device	89
F2 Calibration of the conductivity cell	92
G1 Calibration of the pH and ORP interfaces	98
G2 Calibration of pH electrode	99
G3 Values of ORP buffers at different temperatures.....	100
G4 Field calibration of pH electrode	101
G5 Field calibration of ORP electrode	102
H1 Calibration values for the DO interface	103
H2 Field calibration of the dissolved oxygen sensor	104
H3 Calibration values of DO sensor for salting out coefficient	106
I1 Calibration of YSI 44003A temperature sensor	112
I2 Resistance of the thermistor to the final voltage output calibration	112

List of Figures

<u>Figure</u>	<u>Page</u>
1 Salinity distribution at 1.8 in. on November 11, 1995	43
2 Salinity distribution at 3.7 in. on November 12, 1995	43
3 Salinity distribution in the Kaloko pond at 2.73 in. depth, on November 13, 1995	44
4 Salinity distribution in the Kaloko pond at 7 in. on November 13, 1995	44
5 Salinity distribution in the Kaloko pond at 18 in. depth, on November 13, 1995	45
6 Salinity distribution in the Kaloko pond at 43.4 in. depth, on November 13, 1995	45
7 Salinity pattern in Kaloko pond just after the high tide, on November 16, 1995, at 8 in depth	46
8 Salinity pattern in Kaloko pond just after the high tide on November 16, 1995, at 9.4 in depth	46
9 Salinity profile just after the high tide, at 34.2 in. depth	47
10 Salinity profile just before the low tide, at 5.5 in. depth	47
11 Salinity at low tide in the other part of the pond at 3.7 in. depth	48
12 Salinity at low tide in the other part of the pond at 6 in. depth	48
13 Salinity [at low tide] in the other part of the pond at 20 in. depth	49
14 Salinity [at low tide] in the other part of the pond at 27.25 in. depth	49
15 Salinity profile at 7 in. depth on November 17, 1995	50
16 Salinity profile during one of the low tides at 5.8 in. depth	50
17 Salinity profile during one of the low tides at 18 in., on November 17, 1995, 18:00 hrs	51
18 Salinity profile during rising tides at 4.75 in., on November 17, 1995, 22:00 hrs	51
19 Salinity profile during rising tides at 8 in., on November 17, 1995, 22:00 hrs	52
20 Salinity profile during lowest low tide on November 19, 1995 at 26 in. depth	52
21 Salinity distribution during the minor high tide of the day, before the highest high tide, on November 20, 1995 at 10 in. depth	53

22	Salinity distribution during the minor high tide of the day, before the highest high tide, on November 20, 1995 at 13 in. depth	53
23	Salinity distribution during the lowest low tide of the month, depth 5 in.	54
24	Salinity distribution during the lowest low tide of the month, depth 7.5 in.	54
25	Salinity distribution during the lowest low tide of the month, depth 11 in.	55
26	Salinity distribution when a high tide was fast approaching, depth 13 in.	55
27	Salinity distribution during the highest high tide of the month at 3.2 in. depth	56
28	Salinity distribution during the highest high tide of the month at 13 in. depth	56
29	Salinity distribution during the highest high tide of the month at 25 in. depth	57
30	Salinity profile just after the highest high tide of the month at 5.5 in. depth	57
31	Salinity profile just after the highest high tide of the month at 15 in. depth	58
32	Salinity distribution eight hours after the highest high tide	58
33	The temperature distribution at 3.5 in. depth on November 12, 1995 at 16:00 hrs	59
34	The temperature distribution at 2.73 in. depth on November 13, 1995 at 8:00 hrs	59
35	Temperature variation at 8 in. depth on November 16, 1995, 12:00 hrs	60
36	Temperature variation at 5.5 in. depth on November 16, 1995, at 14:00 hrs	60
37	Temperature variation at 20 in. depth on November 17, 1995, at 13:00 hrs	61
38	Temperature variation at 6 in. depth on November 17, 1995, at 17:00 hrs	61
39	Temperature distribution at 18 in. depth on November 17, 1995 at 17:00 hrs	62
40	Temperature distribution at 30 in. depth on November 17, 1995 at 17:00 hrs	62
41	Temperature variation at 4.75 in. depth on November 17, 1995 at 22:00 hrs	63
42	Temperature variation at 8 in. depth on November 17, 1995 22:00 hrs	63
43	Temperature profile at 20.6 in. on November 17, 1995 at 22:00 hrs	64
44	Temperature profile at 32.8 in. on November 17, 1995 at 22:00 hrs	64
45	Temperature distribution at 8.5 in. depth, 1 hour after the sunrise	65
46	Temperature distribution at 5 in. depth on November 20, 1995 14:00 hrs	65
47	The dissolved oxygen distribution pattern at shallow depth on November 12, 1995	66

48	The dissolved oxygen pattern at shallow depth on November 13, 1995.....	66
49	The dissolved oxygen distribution at 7 in. depth on November 13, 1995 at 22:00 hrs ..	67
50	The dissolved oxygen distribution at 43 in. depth on November 13, 1995 at 22:00 hrs	67
51	Dissolved oxygen at 5.5 in. depth during a low tide	68
52	The dissolved oxygen profile at 20-24 in. depth on November 17, 1995 at 13:00 hrs ..	68
53	The dissolved oxygen profile at 6 in. depth on November 17, 1995 at 17:00 hrs	69
54	The dissolved oxygen profile at 18 in. depth on November 17, 1995 at 17:00 hrs	69
55	Dissolved oxygen profile at 4.75 in. on November 17, 1995 at 22:00 hrs	70
56	Dissolved oxygen profile at 20.6 in. on November 17, 1995 at 22:00 hrs	70
57	Dissolved oxygen profile on a normal day 1 hour after sunrise	71
58	Dissolved oxygen profile on a normal day 2 hours after the sunset	71
59	Dissolved oxygen profile at 11 in. on November 20, 1995 at 19:00 hrs	72
60	Dissolved oxygen profile at 19 in. on November 20, 1995 at 19:00 hrs	72
61	Dissolved oxygen profile at 29 in. on November 20, 1995 at 19:00 hrs	73
62	The pH variation at the surface on November 11, 1995 at 16:00 hrs	73
63	The pH profile at 5.5 in. depth during a low tide	74
64	The pH variation at 18 in. depth on November 17, 1995 at 17:00 hrs	74
65	The ORP pattern at 1.8 in. depth on November 11, 1995 at 16:00 hrs	75
66	The ORP pattern at 3.5 in. depth on November 12, 1995 at 16:00 hrs	75
E1	Circuit diagram of control system for steering.	82
F1	Calibration chart of the salinity measuring device	90
F2	Circuit diagram of the salinity measuring device	93
G1	Circuit diagram for pH, ORP, and DO interface.....	97
I1	Circuit diagram of temperature sensor	111
J1	Inside structure of the boat before it was filled with poly-urathane foam	114
J2	Propeller, winch, and steering mechanism of the boat	114

List of Abbreviations and Symbols

°C	Degrees celcius
‰	Parts per thousand, a unit for salinity measurements. (Even though in the newer standards the salinity is a unitless quantity, traditional units are used for readability.)
Ω	ohm
ELISA	Enzyme Linked Immuno-sorbent Assay
k	Kilo = 10^3
M	Molar Concentration g-mole/Liter
MB	Megabytes
MGD	Million Gallons per Day
mV	milli-volts
V	Volts
P	Power
R	resistance
r.p.m.	rotations per minute

Chapter I

Introduction

Kaloko and Aimakapa fishponds provide habitat for two endangered birds: Hawaiian coot and Hawaiian stilts. Recent outbreaks of avian botulism at these sites have reduced the population of these birds to alarmingly small numbers, (Figures in Appendix B, Morin, 1994). Current management practice relies on removing dead birds from the ponds in an attempt to prevent contamination of other species; and removing sick birds to the pens where they are treated. No attempt is made to remove the root cause of the problem i.e. preventing the development of the botulinum toxin in the waters.

Botulinum toxin is produced by *Clostridium botulinum* bacteria under anaerobic conditions and only when they are infected with a bacteriophage. The bacteria form spores under adverse conditions and these spores are known to be among the hardiest. They can survive even at 80°C, and remain viable in soil for years. Moreover, *Clostridium* bacteria are omnipresent. Monitoring for bacteria, therefore, is not a good option.

Monitoring for toxin in the pond water is extremely difficult because the concentration of toxin is very low, the toxin is unstable at ambient temperatures (believed to be autodestructible in 8 - 10 days), and the measurement of the toxin at very low levels is not possible with existing methods.

The botulinum toxin is believed to be concentrated by lower invertebrates (Personal Communication, Dr. Thierry Work, 1994, National Biological Survey (NBS)), and they form a major source of food for the birds. Monitoring toxin in the lower invertebrates is a complex process; analysis of a large number of samples from all over the pond would be required during

the outbreak period, and the toxin may not be present in measurable quantities. Only one researcher has currently developed an ELISA kit for avian botulism toxins and that method is only as sensitive as white-rat bioassays.

The outbreak of the botulism can be prevented by preventing anaerobic conditions in the ponds; or isolating the birds from the anaerobic pockets. The ponds receive freshwater from inland, and mixing with saltwater takes place through many different mechanisms. Freshwater being lighter than the saltwater floats on the latter. Temperature differences created by differential heating change the density of water at various locations and induces the convectional mixing process. Winds create waves on the surface of the water which helps the mixing process. Winds also tend to promote saturation of the top layers of the water with dissolved oxygen. This dissolved oxygen is then distributed to the depths of the ponds and used by various plants and animals. Recent evidence shows that the production of toxin is more dependent on the salinity and pH in the water (Rocke, 1996).

The ponds are formed in a depression of volcanic lava flow. They are not deep, but they contain soil sediment in the depressions which allow the benthic fauna and flora to flourish. Water level in the ponds fluctuates due to tides. During low tide, some parts of the ponds are isolated from the others, when water mixing and oxygen transfer to the bottom sediment may be poor. Also, at nights, when photosynthetic activity in aquatic plants stops, dissolved oxygen levels decrease due to respiration of aquatic plants. The anaerobic conditions developed at some parts of the ponds result in the release of hydrogen sulfide gas, which can be detected by any person who is familiar with its smell. These anaerobic conditions may be providing suitable environment for the proliferation of anaerobic organisms like *C. botulinum*.

Determining the dissolved oxygen profile, mixing of saltwater and freshwater profile, pH and temperature profile will help to understand the above problem. Anaerobic pockets of the ponds

could be marked and the birds could be prevented from feeding there, or proper mixing conditions could be created to eliminate anaerobic pockets.

In the present study, Kaloko pond was used as a model for Aimakapa pond. Most of the birds feed at Aimakapa; but it is land locked, and access to it is difficult. Kaloko pond is only few miles north of the Aimakapa pond (Site Map, Appendix A), and most of the other environmental conditions are same. Monitoring in the Aimakapa pond was postponed due to nesting season of the already rare and endangered birds.

Kaloko and Aimakapa ponds are very close to the sea and their water level changes according to the tidal changes in the open sea. Monitoring for the above parameters at only a few, and limited number of stations would greatly simplify the job of monitoring, but the site to best represent specific conditions needs to be ascertained. As mentioned earlier, small pockets of water may be the problem areas, which may not be visible with the naked eye. In the present study a fast, mobile recording system was developed and field tested. The results of this and similar studies would enable better planning for the permanent monitoring stations.

The specific objectives of this study are:

1. Develop a rapid mobile water quality measurement system for salinity, temperature, dissolved oxygen, pH and oxidation reduction potential at different depths in the pond,
2. Field test the feasibility of the system in actual Hawaiian conditions;
3. Record the above parameters in the pond for at least one tidal cycle (two weeks); and,
4. Analyze the collected data for ecological problems.

Chapter II

Literature Review

Measurements of water quality parameters in Kaloko pond are rare. Kaloko pond was owned by Kona Coast Development Corporation, Huehue Ranch, and Stillman Establishment.

Prehistorically, Kaloko belonged to the highest chief of the district of Kona, and, in turn, to the paramount chief of the island of Hawaii. Its produce did not make the ahupua'a or ali'i generally wealthy, but existed as a constant ready source of fish. Kaloko did provide part of the protein wealth on which the nobility depended in order to feed the retinue of priests, warriors, craftsmen, and favorites and to help in the financing of civil and martial enterprises (Kikuchi and Belshe, 1971). "Kaloko fishpond is classified as a *loko kuapa*, a fishpond constructed when the Hawaiians erected a massive sea wall across the mouth of the bay. The original sea wall was nearly 750 feet long and 35 feet wide at the top and contained nearly 150,000 cubic feet of rock. It was constructed with the seaward face at an angle of about 25° while the pond's side was around 18°. The sides facing both the sea and pond were faced with large boulders and stones angled so that they would absorb the force of the sea. The interior of the sea wall was found not to contain any traces of an earlier sea wall, but rather a rubble of large stones piled in a rather haphazard fashion. This allowed for the permeability of the wall which would absorb a wave rather than act as a solid barrier and would allow for passage of sea water at a slow rate.

...Within the sea wall there once existed two sluice gates; one now is completely destroyed while the other has been filled with stones. Both increased the drainage and circulation of the pond's water and at high tide served as harvesting points where the fish were scooped up with a net.

...Heavy seas and tsunamis have repeatedly damaged the sea wall and in 1960 and 1968 the northern portion of the *kuapa* was totally breached. ...It (Kaloko) has the largest and thickest man-made sea wall on the island of Hawaii and is the best and most impressive example on that island, even in its eroded condition", (Kikuchi and Belshe, 1971).

Their "physical description" of the pond is as follows:

"Kaloko is a natural embayment approximately 11 acres in size separated from the sea by a man-made sea wall. The main pond of has a roughly rectangular shape with an inlet on the southeast corner forming a tapering appendage.

The generalized pattern of the physical state of the pond can be described as a water body consisting of two layers. The surface layer is one characterized by a lower density, salinity, and temperature. It is a result of surface mixing between the freshwater entering the pond from numerous springs along its shore and the more saline water of the deeper pond and the open sea. This layer may be 5 to 18 inches thick. Its temperature is in the range of 20°-24°C and its salinity is in the range of 18-24‰ (parts per thousand). In the shallow back area of the pond, near the springs, the water may become almost fresh with salinities of 4-8‰ and temperatures as low as 18-20°C. The second, deeper layer is the main body of brackish water. The most abundant growth of marine plants (algae) and minute animals (zooplankton) occur in its upper portion. The temperature of this layer is in the range of 28-31°C, and the salinity is in the range of 25-29‰. For contrast it should be noted that ocean waters offshore would be in the temperature range 22-24°C, and have 33-35‰ salinity. However, there is a sufficient escape of freshwater along this coast to cause lower temperatures and lower salinities for several tens or hundreds of feet beyond the sea wall or out from the shoreline.

A third layer could probably be distinguished as that occurring very near the bottom where decomposition of the accumulated muck has depleted the oxygen and released hydrogen sulfide. However, such waters are not as well defined, readily evident, or general in their occurrence as the two main bodies already described. Measurement made near the bottom have shown oxygen concentrations about 25-33% lower than in the main or brackish layer and hydrogen sulfide concentrations above 0.2 ppm (parts per million) and occasionally exceeding 5 ppm. (Concentrations of H₂S in excess of about 3 ppm are probably injurious to young fish.)

The dissolved oxygen content of the water is a complex result of photosynthetic and respiratory activities plus the influence of temperature and pressure. It therefore shows time variations which reflect such diurnal changes as of light and temperature and cloud cover. The oxygen content should be lowest in the early hours of the morning before sunrise and highest about midday, or slightly thereafter. Measurements made at various times of the day over a two month period showed the oxygen content to be generally oversaturated, that is in excess of 8 ppm, and never dropping below 5 ppm. (The O₂ threshold for fish life in Kaloko over long periods is probably about 4-4.5 ppm. For a few hours fish can tolerate dissolved oxygen contents below 1 ppm in the water.) This indicates the high level of plant activity in the pond which releases oxygen in the photosynthetic process. That activity is also responsible for the assimilation of most of the available nutrients thus causing measurements of these materials to be low as compared with fresh seawater. Nitrogen is essentially depleted in the pond and is the limiting chemical factor in the primary productivity.

The accumulation of organic rich sediment (muck) on the pond floor was probed with rods and tubes from boats and by divers. Examination showed much of this to be partly digested algal material that had cycled at least once through the gut of fish or shrimp. This dark green bottom material continues to decompose and changes to a dark grey or black color with burial. Mixed with the muck is a portion (over 50%) of wind or water transported silt and a small but persistent admixture of coral sand. The thickness of this muck may exceed 5 feet. The maximum pond depth, to bedrock, is about 12 feet but over 50% of the pond has depths of 3 feet or less."

Only one report on file (Chai, 1991) briefly touches the subject of water quality in the recent past. He performed the measurements for salinity and temperature close to the sea wall (*makai*), approximately one third of the way across the pond (*mid-makai*), two thirds (*mid-mauka*) and as far from the ocean as possible (*mauka*) from January 28-31, 1988, along with the study and inventory of the flora and fauna of the pond. He recorded the readings at subsurface depth at all four locations, and 1.5 m at makai, 4.0 m at mid-makai, 6.0 m at mid-mauka, and 1.0 at mauka

locations. The results are shown on Table 1. He briefly mentioned the oversaturation with dissolved oxygen, but no specific numbers are provided. This study, though a small effort to represent the big picture, is a very important stepping stone to assert the need for further detailed study.

Table 1. Surface and bottom temperature and salinity profile (January 29, 1988) at Kaloko pond. (Chai, 1991).

Location	Depth	Time of Day			
		8:00 AM		3:00 PM	
		T °C	Salinity ‰	T °C	Salinity ‰
makai	Subsurface	18.2	22.3	32.0	34.0
mid-makai	Subsurface	23.5	35.5	25.5	34.5
mid-mauka	Subsurface	23.0	35.5	26.5	35.5
mauka	Subsurface	23.0	24.5	24.3	25.0
makai	1.5 m	35.0	31.2	35.0	34.0
mid-makai	4.0 m	31.7	33.5	30.0	32.5
mid-mauka	6.0 m	30.2	30.3	30.8	34.5
mauka	1.0 m	30.8	34.5	31.3	34.5

Apple and Kikuchi (1975) performed 28 measurements in 18 fishponds. Collective results show the range of dissolved oxygen from 6 to 13 ppm, for a mean of 7.9 ppm and a mode of 7 ppm. Salinity ranged from 2 to 32.4‰, pH 8 to 9, and temperature was between 18 to 31°C with mean of 24.7°C.

Maciolek and Brock (1974) conducted an exhaustive survey of anchialine ponds of the Kona coast for aquatic species of plants and animals. They studied almost 300 ponds of various sizes and depths. The water quality measurements were limited to salinity, temperature and other

visual indicators such as sedimentation. A single numbered result for each parameter was presented. From their study, the Kaloko pond had a rocky bottom, it was more than 1.5 m deep, and the main pond had a salinity of 8‰. Aimakapa pond had a sedimented bottom, was more than 1.5 m deep and had a salinity of 7.8‰.

Bienfang (1980) conducted a five-year study of water quality in the Honokohau harbor monitoring the effect of the harbor construction on the newly created water basin. This study has a limited significance for the conditions in Kaloko and Aimakapa ponds, since the Honokohau harbor basin area is totally open to the sea. Nonetheless, the site is within one mile of both the ponds and thus the freshwater can be of similar character. They indicated that the freshwater had a significant amount of nutrients in it, but due to the short residence time in the bay freshwater did not mix with the bottom layers. " ...This influx (1.5-2 MGD water) occurs at sufficient rates to produce a continual outflow at the surface, irrespective of the direction of tidal flow. Location of the predominant inputs at the back reaches of the harbor results in surface outflow of the entire basin. This process also entrains subsurface waters and thereby reduces the effects of molecular diffusion of surface nutrients to the subsurface ocean water and enhances harbor flushing rates. The flushing rates of the harbor are over six times larger than would be produced solely by tidal action."

His measurements of pH were in the 8.02 to 8.21 range, in which lower values were shown by freshwater. The dissolved oxygen values though were much lower. He reported problems with the YSI oxygen probe, and chose to do the analysis through the Winkler titration method. The values ranged from 4.53 ml O₂/liter [*sic*] back berthing basin to 5.83 ml O₂/liter in the waters near the bottom. In the front berthing basin, the dissolved oxygen values ranged were 5.44 ml O₂/liter at the surface and 5.18 ml O₂/liter in the subsurface layer. Bienfang reported that the oxygen levels in both areas and depths are near saturation concentrations for the existing temperature and salinity conditions.

Chapter III

Materials and Methods

3.1 Introduction

A mobile system to measure salinity, dissolved oxygen, temperature, pH, and ORP was constructed. It consisted of a radio controlled boat and associated electronics, Geographical Positioning System (GPS), data acquisition system (using Campbell Scientific's 21X datalogger), and the above instruments. The desired advantages of using this system are as follows:

1. compactness,
2. ease of use, as the boat can be controlled from the shore at any time of the day, and
3. specifically constructed system which included all the desirable functions.

A small double hull boat, constructed from wood and PVC foam core sheets, was filled with polyurethane foam. The keel of each hull was a piece of 2 in. x 4 in. wood, and ribs were made from 1 in. x 2 in. pine-strips. The individual hulls were 13 in. wide, 18 in. deep, and 48 in. long excluding the nose cones. Nose cones did not have any wooden supports, but they were filled solid with the foam. The wooden form was first prepared, the two sections joined, and the PVC sheets were then bent using hot air guns around the wooden forms. The sheets were then screwed down to the inside of the top edges of the boat.

The two hulls were joined together by wooden pieces of 2 in. x 4 in. sections, two at the mid-section and one at the end. Two bearings supporting the instrument column were constructed from polyethylene strips and pieces of wood, and were attached to the front cross-ties with ¼ in. x 8 in. stainless steel bolts. A bracket made from a strip of stainless steel also supported the holder for the GPS antenna. Inside the hulls four boxes made of the same PVC sheet were placed. They provided space for the two lead-acid batteries, instruments, and the GPS receiver.

An electric trolling motor (Minn Kota 12 V Turbo 35T, Transom mount) was mounted on the rear cross-tie bar. The bar also provided support for the small electric winch to raise and lower the instrument column through a set of pulleys. The winch was constructed from PVC sheets and bars. The drum has a diameter of $\frac{3}{4}$ in. and a gear-motor running at 40 r.p.m. turned it. The motor was controlled by automatic controls which is discussed in the following sections.

Commercially available Trimble Navigation GPS equipment (ProXL receiver, with MC-V datalogger) was chosen because of its ability to provide submeter accuracy. This accuracy was obtained through differential corrections by using the post-processing technique. The field (rover) files were first collected, and then they were corrected with positions of a known location (base station). The National Park Headquarters at the Kaloko-Honokohau National Historic Park has a operating base station. The datalogger could store up to 8 hours of data if positions were recorded once a second. Downloading, processing and differential correction of the position readings were done using PathFinder software from Trimble Navigation. The positions were recorded with time stamped on them. The water quality measurements were recorded with local time. The times on both the recordings were matched for obtaining the x-y positions of the measurements. The 21X datalogger and MC-V datalogger times were corrected every day. The 21X datalogger's time appeared to be drifting around 5 to 6 seconds everyday compared with the MC-V time.

3.2 Controls

The trolling motor was steered using a 4.5 r.p.m. electric motor (Grainger stock # 2L006) and a sprocket and chain mechanism. The motor could develop 50 lb-ft torque. The steering mechanism was controlled by the automatic control electronics as illustrated in the next section.

A rotary switch located in the control pod of the trolling motor provided five forward and three reverse speeds, which was operated by twisting the handle in clockwise or anticlockwise direction. The rotary switch obtained the eight speeds through a travel of more than 180 degrees. The handle was replaced by a servo so that two forward and one reverse speeds were attained. The servo (FP-S9304) was directly controlled through the receiver of the radio control unit. It had adequate torque (93 oz-inch) to turn the rotary switch, but the length of angular travel was limited to 90 degrees. In the initial trials conducted in the Ala Wai canal, it was found that these settings were adequate and no further improvement was necessary. Field practice showed that the third forward speed would have been useful, but the fourth and fifth speeds were unnecessary.

A three-channel frequency-modulated radio controller (Futaba PCM 1024) was used as a remote control unit. It operated at 75 MHz frequency allocated to the surface systems designated for cars and boats. The controls were modified to best serve the purpose of controlling the boat. Auxiliary servo control was used to switch the speeds. Throttle control and the throttle trim adjustment were swapped by changing the wires on their potentiometers; the latter's knob interface was more suitable for controlling the instrumentation column position, instead of the pistol trigger interface. The range on the servo travel was increased by adding two 2.2K resistors on the potentiometer of the trim control (Appendix E). Steering interface had an appearance of a car steering wheel and was quite suitable for its job.

The control mechanisms on these systems could be classified as a closed loop ON-OFF system. The radio controller came with its own receiver and three servos. Two of these servos were directly coupled to the potentiometers, whereby, servo position could be translated into an electrical voltage signal. A regulated 6.0 volt supply was applied to the 10k Ω potentiometers. The voltage tapped across the potentiometer was between 2.25 and 4.8 volts. It could be trimmed up or down either by trim controls on the transmitter or through manual alignment of

servo and potentiometer. The voltage signal was used to control the position of the steering or instrumentation column. Complete circuits are shown in Appendix E. Each controller uses two LM741 operational amplifiers (op-amps) to compare the controlling signal and feedback signal. Based on their magnitudes the op-amps provide error signals, switching either of the two op-amp outputs positive. This positive signal was then amplified and used to control the direction of the rotation of the motors for steering or position control. Full-bridge or 'H' type of transistor arrangement was used to switch the polarity of electric supply to the motors. Control signal was converted into a band of low and high levels by passing the original signal from the potentiometer on the servo through a potential divider. This band provided necessary stopping time for the motors, as well as immunity from noise. Op-amp arrangement was such that when the feedback signal was within the band neither of the two op-amps would give positive output.

3.3 Data Acquisition system

Initially, a data-acquisition system based on National Instruments' DAQCard 700 PCMCIA type of datalogger with a Compaq Contura Aero 4/25 subnotebook computer was developed. It would have provided on board computation power, as well as, about 40 MB of storage space. The whole system was designed around this arrangement. However, this approach was abandoned due to the loss of the computer and unavailability of a suitable replacement. The data acquisition system in its entirety was replaced by a Campbell Scientific 21X datalogger with SM192 storage module. This system was much better in terms of sampling and noise rejection, but it lacked the former's sophistication of on-board processing, refined display, and almost infinite data storage capacity. The computer system would have directly shown the readings of dissolved oxygen, salinity, temperature, pH, ORP, sampling depth, radiation, water level, etc. directly by performing all the necessary computations and corrections to each of the readings; e.g. salinity is a function of conductivity and temperature, dissolved oxygen depends on salinity and temperature.

With the 21X datalogger, all the voltage signals from the instruments were recorded and the processing was done afterwards on a personal computer. The 21X datalogger was programmed to record the above eight parameters for every second only when the instrument column was lowered below a certain, presettable level; otherwise it was made to record radiation and water level every minute averaged from the readings taken at each second.

Sampling over every second was decided because the conditions in the pond could change quite rapidly. Two high tides and two low tides occur every day, and within a span of six hours the high water level changes to low water level. The entire pond had to be sampled as fast as possible to produce as true as possible picture of the entire system at a given time. Many commercial systems were deemed inadequate, as the maximum sampling they allowed was one reading every 3 minutes, and they did not have any provision to accept additional signals like the depth at which measurements were being performed. Cost was also a decision making factor. So, instead of a ready-made system, the instrument system was built from individual meters. All components were robust and continuous measurement type, -entirely suitable for field experimentation.

3.4 Instrumentation

3.4.1 Salinity meter

Instead of using a commercial, recording type salinity meter, a salinity meter made from individual components was used to save expenses. It consisted of YSI 3310 field type of conductivity probe, a square wave oscillator, and a filter. The output of the device has very little AC component and noise in it, and its response is quite rapid. It is directly calibrated from the YSI meter, and is accurate enough within $\pm 5\%$ of the conductivity reading. The exact

mechanism to ascertain the level of accuracy is not stated in the information booklets. It is difficult to believe that the path of ion currents only determines the accuracy of the system. It would be possible to machine the conductivity cell to much closer tolerances, if a linear relationship between conductivity measurement accuracy and machining accuracy is known. The meter uses different frequencies for detecting a fouled conductivity cell. So frequency dependence of accuracy is out of the question. The electrodes used are made from pure nickel coated with black electro-deposited platinum, the surface area of which must determine the resistance offered at the liquid-solid interface. It would have been impractical to measure the surface area of such a coating, however, a rough estimate of it may be indicative of the accuracy in measurement. The control of such a parameter is not feasible, and beyond the scope of this research, hence a thorough calibration procedure using gravimetric measurements and primary standard solute of potassium chloride was not carried out. There is a good reason to believe that the $\pm 5\%$ range of accuracy is readily achievable, especially when a highly repeatable system is involved.

Calibration and data analysis of the salinity readings are illustrated in Appendix F. Field calibrations using 0.1 M solution of KCl were performed to check the accuracy of the system.

3.4.2 Dissolved Oxygen Meter

A commercially available dissolved oxygen meter (YSI model 57) was used for the project. Its 0-135 mV output was amplified by a high input impedance amplifier, similar to those used for pH and ORP signal amplification, to a level of 0-5V. The meter applies temperature correction directly to the readings, but for salinity corrections the dial has to be set for an appropriate level. This problem was solved by recording the readings at a dial setting of 0 salinity and correcting them afterwards based on the equations recommended by the Standard Methods (AWWA, 1995). The salting out coefficient for the oxygen-permeable membrane was obtained from

calibrations. The instrument had another trivial problem of using two C-cell batteries and thus requiring adjustment of the red-line (voltage input to the meter) by manually turning the knob. The power supply was replaced by a regulated power supply using a LM317 adjustable voltage regulator. It provided a constant voltage of 1.25 volts to the meter, thereby eliminating the need to adjust the red-line frequently. The meter was calibrated frequently in the field (Appendix H). Instead of changing the settings on the meter, drift was recorded and proper corrections were applied to the results.

3.4.3 Temperature Sensor

YSI 44003A precision thermistor was used as a temperature sensing element. Its time constant in still air is 9 seconds, whereas in well stirred oil it is 1 second. AWWA recommends thermistors due to their fast response times, and this was the fastest sensor available from Newark Electronics. It is assumed that the time constant in the salt water would be around 2 seconds, and in 8 to 10 seconds it will show the correct temperature reading. Thermistors change their resistance according to the temperature. Their response is mostly nonlinear - better represented by exponential relationship. They also need to be lightly loaded in an electrical sense, as they warm up if excess current is passed through them. Otherwise, they are accurate and can be replaced in the circuits without making adjustments. The element used was accurate within $\pm 0.2^{\circ}\text{C}$. Important design considerations, circuit diagram, and calibrations are shown in the Appendix I.

3.4.4 pH Meter and Oxidation Reduction Potential (ORP) Meter

Ingold® Xerolyte type pH and ORP electrodes were used in this experiment. They have gelled electrolyte and can operate at up to 100 psi (6.7 atmosphere) pressure. The pH electrode (InPro 4500) had very high (500 M Ω) output resistance. In order to correctly measure the voltage

developed by the electrodes in response to the pH and ORP stimulation, the measurement system had to have a very high input resistance. An interface using TL082 BIFET op-amp and LM741 as an amplifier was developed. It had input resistance in the order of $10^{12}\Omega$, i.e. more than 1,000 times the output resistance of the electrodes. The circuit also provided a virtual ground for the measurement of these signals, which was very important for avoiding the fouling of reference half-electrodes by ground loops in those two sensors. The circuit and operating principle is illustrated in Appendix E.

3.4.5 Radiation Sensor

A quantum (sensitive in the photosynthetically active radiation only) photo-sensor, made by Lambda Instruments Corp., was used on the boat. It provided an voltage output which could be recorded by the datalogger. However, the discontinuous readings obtained during the experiment forced to abandon the radiation data. Instead, the readings for total radiation recorded at the weather monitoring system of Natural Energy Laboratories of Hawaii (NELH) are used. NELH site is about 5 miles north of the ponds and has almost the same weather conditions.

3.4.6 The Water Level Measurement System

It was assumed that the water level in the pond would reflect the changes in the tide level in the open sea to the same extent, which is about 3 feet. Given a margin of one foot on either side for the setup, the sensor was designed to measure up to 5 feet of change in the water level. The tradeoff for this increased range and the very nature of the float and pulley design resulted in offset errors up to +1 in. to -1.5 in. depending on the rising or falling levels, when measured under the laboratory conditions. In the field the waves might have reduced this error. But, the radio controller using two channel AM signals showed much more noise in the field, even when

the other FM unit was switched off. This noise could be removed by statistical means, such as modal values, averaging, and selection of the band of continuous readings showing least amount of noise. The choice of noise-reduction method varied for each plot. This method produced fairly good readings, but rising and falling patterns could not be established, whereby the delay between the low/high tide in the open sea and its corresponding low/high water levels in the pond could not be established. This was a significant handicap since it was initially planned to perform the measurements when the water level in the pond was at its true maximum or true minimum. Ultimately, when the FM unit went out of service, the AM unit was used to control the boat, and a simple calibrated post was erected for level measurement. Level readings from November 19 onward are manual readings, and are much more accurate but discontinuous. The scales for the water level in the pond and the tide level in the ocean are totally independent of each other. Right now, there exists no means of matching these scales.

Chapter IV

Results and Discussion

4.1 Introduction

Sampling in the pond was done to represent the various states of the tidal cycle. A tidal chart, as shown in the Appendix C was used as a guide to decide the sampling times. The sampling times during the period of November 11 - 21, 1995 are shown in table 1. File names reflect the date and time of sampling, e.g. RG112105 indicates that the sampling was done on November 21, starting in the 05:00 hours –it does not necessarily mean the logging was stopped in the same hour. In the subsequent discussions while indicating the source file, the prefixes RG (for Rover files, GPS corrected, with datalogged values) were sometimes dropped and additional suffixes like sampling depth and one of the five letters –s for salinity, t for temperature, p for pH, o for ORP, and d for dissolved oxygen were added.

Afternoon sampling times on November 11 and 12 represent relatively calm periods of the day; on those days the highest high tides of the day occurred more than eight hours earlier, and the approaching second high tide was much smaller. On the next day (November 13, 1995), sampling was done during the period 8:17 - 9:16 hours, when highest high tide of the day was occurring. This highest high tide was much smaller than the highest high tide of the month recorded on November 21. On the same day, from 22:34 to 23:09 hours, another calm period of the tidal cycle was recorded. It also shows the conditions during night time. November 13 is a special day for analysis as a brief cloudy period existed on November 12th.

During the next two days, the instruments were calibrated, and all the batteries were charged. November 14 to 19 was a relatively normal period of tidal cycles. Sampling on November 16 was

done just after the high tide and just prior to low tide. On November 17 the two high tides of the day were of equal magnitude. On that day, sampling was done approximately two hours after peak tide, at the lowest low tide of the day, and on the approach of the high tide during the night. Information from these two days should complement each other.

November 18 was a full of problems day; the three channel remote control unit stopped working, and the two channel unit, which was dedicated for transmitting information from water level sensors to the datalogger on the boat, took a day to reconfigure. On November 19th, which represent onset of the highest high tide of the month, sampling was done at the peak of the minor high tide, and the major low tide of the day. Afternoon (13:56 - 14:36 hours) recordings on this day resulted in sampling at erratic depths. The data is available, but it is not plotted. It should resemble the recordings of November 16th at 12:00 hours and November 17th at 13:00 hours.

From November 19th onward, in a period of 28 hours, sampling was conducted 7 times. This was one of the most critical periods of the month. Early morning hours of November 22 would have provided a second set of readings for the highest high tide of the month. The experiment was scheduled to stop after that. On November 20th, sampling was done around 8 am, 3 pm, 8 pm, midnight, 3 am of the next day, 5 am, and 11:30 am. Sampling during 3:20 to 3:50 on November 21 recorded the highest high tide of the month. After all this extensive sampling, the instrument column positioning system malfunctioned, and the experiment was halted.

4.2 Presentation of the Data

It is impractical to display the vast amount of the data numerically. Instead, the data is mostly presented in graphical format. While analyzing the graphs, individual readings of salinity, pH, ORP, DO, and temperature were plotted for different sampling depths for each sampling session.

This resulted in reviewing more than 330 individual graphs. Harvard ChartXL software was used to plot the graphs. The original data is stored in Microsoft Excel format. Harvard ChartXL can access the Excel data without importing it.

The graphs are plotted with the boundary-map of the Kaloko pond. The graphs are pseudo 3-D plots. They are known as three dimensional vector graphs, but after printing on plain paper they resemble a 2-D plot with vertical bars. The base of the bars is the path taken by the boat in the pond. Sampling depth is indicated by the height of the individual bars at that particular location. Plotting for approximately the same sampling depths greatly enhances the presentation and analysis of the information, but it results in a separate graph for each depth. The value of the parameter being displayed is indicated by the color of the bar. Plotting for approximately the same sampling depth results in a narrow range of values to be displayed which can be more precisely distributed over the band of 12 colors. This approach is much better for displaying the values compared to that of using heights of the bars. It is little difficult to see small differences in heights of bars, especially when arranged on a curved trajectory. The legend on the side of the graph helps to understand the range of the values being displayed. Only the most important graphs are displayed for the sake of brevity and convenience.

The graphs are further divided into 20 m X 20 m squares along the grid lines. The axes of the graphs represent northing and easting in meters measured with respect to the Old Hawaiian datum. These squares are numbered alphabetically along the east-west direction, and numerically along the north-south direction. In this system, square K1 represents the southernmost tip of the pond. This is a point where the boat was usually docked for instrument calibrations, data-retrieval and all other major activities due to its proximity to access roads. The boat was usually harbored near a rock in the square P1.

4.3 Profile of Various Parameters in the Pond

4.3.1 Salinity

Salinity measurements help to construct the picture of the sources of fresh water, mixing of salt water and fresh water, and general stratification in the pond. Records for salinity ranged from 11.5‰ to 31.5‰. Higher levels of salinity were found at greater depths. Generally, the pond was sampled at depths of no more than 36 inches. Records taken on November 13 around 10:30 pm, at the depths of 28.3 and 43.4 inches showed the highest salinity as stated. (Figures 5 and 6). However, 31.44‰ salinity in the top layer was measured on November 11th, which is very close to the recorded maximum. Variation in salinity was maximum in the top layer. The term salinity distribution in the following discussion means its variation in the horizontal plane at a particular depth, and the term salinity profile means the variation with depth along the path considered.

4.3.1.A Salinity Distribution in the Top Layer

During Calm Periods

Measurements done on November 11th and 12th reflect a period of calmness. Major high tides of the day occurred more than eight hours earlier, and a long enough calm period helped to establish a pattern of salinity. The measurements were taken on the onset of minor high tides of the day, and slowly rising waters might have very little influence on the established pattern. There is an open channel flow between the pond and the sea. The discharge point to the sea is around the square D4. The sources of freshwater are clearly noticeable from Figure 1 and Figure 2. Also worth noting is the variation in the salinity readings and general pattern of salinity. Salinity gradually increases from east to the north-west part. Figure 1 shows a little higher range of salinity than Figure 2. The explanation for this would be rather complex. The difference in the major high tides on those days was around an inch only. Slight difference in the time might have

caused that. More discussion on this follows in section 4.3.1.E, Salinity Distribution During Low Tides.

During the High Tides

Figure 3, which is the representation of conditions during high tide on November 13, 1995, shows how the general pattern was rearranged. Overall salinity then was not only higher, but highly variable. One more source of freshwater is noticeable in the squares J1-K1 or the southmost part of the pond, and repeated measurements around this part show that the pattern during high tide is not steady but rapidly varying. Even though this source was discharging into a small bay, rushing seawater must have made its way into it. To develop the correct representation of the pond during high tides, much faster equipment should be used.

4.3.1.B Salinity Profile during Calm Periods

Salinity increases with depth, although less rapidly, and at depths greater than 12 inches it is surprisingly uniform all over the pond. Below 20 inches it rarely varies more than 1 part per thousand anywhere in the pond. Actual levels depend on other factors like tide level and resultant water level in the pond. Depths shallower than 12 inches, however, do show the local variations, like proximity to the sources of freshwater, closeness to the discharge point, path along the freshwater flow, etc.

Figures 4, 5, and 6 show the salinity pattern on November 13 during night hours (22:34-23:09 hours). At this time, the minor high tide of the day was just over and the water was slowly receding for the smaller low tide of the day. The measurements were mainly concentrated in the J1-I9 corridor, which was directly next to the location from where the boat was controlled. The figures indicate that the pond is highly stratified, especially at deeper depths. Point to point variation in the salinity was very very small. Salinity is mainly dependent on the depth.

However, even then, the deeper depths did show the proximity-effects of freshwater sources. At a depth of 7 in. the salinity ranged from 25.96‰ to 27.01‰ (Figure 4), at a depth of 18 in. it ranged from 30.143 to 30.707‰, and at the depth of 28 in. it ranged from 31.054 to 31.318‰. At a depth of 43.4 in. it was amazingly uniform - ranging between 31.251 to 31.525‰ only (Figure 6). It is evident that the freshwater being lighter than the salt water floats on it and discharges into the ocean. This sheet of freshwater may not be thicker than 7 in. during calm periods. Mixing may not be taking place rapidly. Otherwise the depths of the ponds would have shown wider ranges of values. Slower diffusion of freshwater in the saltwater explains the stratification of the layers over such a large area.

4.3.1.C Salinity Distribution when a High Tide was Receding

The measurements done around noon on November 16th, (Figure 7) show that at a depth of 8 inches, when a small high tide was receding, the salinity values in the top layer ranged from 15.116 to 24.049‰ from east side to west side. These measurements were carried out within one hour after the high tide and show an interesting pattern. It appears as if a thin curtain (at least 8 in. deep) is being pulled to the sea. Ocean side still shows appreciably lower salinity (compared to assumed salinity of at least 32‰ for the ocean water at Kona) and supports the above assumption. Further on, measurements near the southeast source (Figure 9) showed that the freshwater did not penetrate to 34 in. depth in that area either, which is consistent with earlier postulation of a thin layer. Figure 8, indicating a small portion of the 9.4 in. depth shows that the freshwater curtain there was at least 9.4 in. deep. From Figure 6, the salinity near that location was around 18‰.

Conditions around the noontime on November 17, 1995 (Figure 15) were almost the same as that of November 16. Both measurements were carried out on the receding phase of the high tide, and the water level in the pond was 18 and 19.45 in. when tide level was around 16.5 and

14.4 in. respectively. It is quite similar to Figure 7. The ranges of values are also comparable, and support the conclusion drawn earlier.

4.3.1.D Salinity Distribution and Profile in the Other Part of the Pond

Figures 11, 12, 13, and 14 show the conditions in the other part of the pond on November 16 during a low tide. The pond was divided by ancient Hawaiians for raising fishes for the *ali'i* (chiefs). This part does not have a direct contact to the sea. A big chunk of volcanic rock on the north-west side of the pond provides a mostly impervious barrier to the seawater. Salinity stratification is quite visible through the figures. Source of the freshwater is not clearly identifiable; but the freshwater must be flowing in at a number of places. At this time, the salinity at 3.7 in. and 6 in. depth was mostly around 17‰, at 20 in. depth it ranged from 26.224 to 27.399‰, and at 27.25 in. it was between 26.918 and 28.050‰.

4.3.1.E Salinity Distribution during Low Tides

Figures 10 to 14 show the conditions on November 16th, around 5 pm in the afternoon, one hour before the major low tide of the day. Water level in the pond was still relatively high (18.07 in.), but the water in the ocean must have been receded dramatically (tide level 3 in.). A distinctive band in the northern part of the pond was visible, and the instrument boat was navigated through it. Figure 10 shows the general conditions therein. The boat occasionally swerved outside the band, but nonetheless it shows quite low salinities along the route. Even oceanside showed salinity as low as 19‰ at 5.5 inch depth. The northern freshwater source indicated a salinity reading near 12‰. Salinity in the remaining part of the pond at this time was less than 25 and more than 20‰.

Figure 16, representing salinity on November 17, around 18:00 hours represents the conditions very much similar to that of Figure 10. During both times the low tide was rapidly approaching. However, on November 17th, the water in the pond was lower by 1.5 inches. Figure 16 has some of the areas not shown in figure 10. The values of salinity are comparable, however, a completely unexpected pattern is visible in the southeast part. At a depth of 5.82 in., the salinity actually increases in an area farther from the sea. It is quite possible that the freshwater curtain being pulled does not have uniform thickness, and simply the freshwater coming in from the south-east source could not keep up with the water drawn to the ocean by the low tide. Salinity distribution at the 28 in. depth (Figure 17), at that time, however, was fairly uniform. The pattern was broken at some places by the sources of freshwater. There might be a tiny source of freshwater in the square N2.

Figure 16 can also be compared to Figure 15, which represents the conditions four hours before on the same day. General pattern of salinity is very similar. It shows that the salinity pattern once established after the high tide remains same until the next high tide.

During the lowest low tides on November 19 and 20, 19:00 hours, from Figures 20, and 23, 24, 25, salinity profile can be constructed. Figure 23 has quite a resemblance to the Figures 1, 2, 7, and 10; and fits in the freshwater blanket postulation. A shallower depth on November 19th at 19:00 hours showed the uneven pulling of the curtain (Figure not shown).

4.3.1.F Salinity Distribution and Profile when Approaching High Tide

What happens when a high tide approaches is an interesting but rather complex situation. It is clear now, that the measurements in the narrow corridor provided limited information regarding this event. Measurements on November 17, 22:00 hours, Figures 18 and 19 for 4.75 in. and 8 in. depths; and on November 21, 00:00 hours, (Figure 26 for 13 in. depth) were mainly

performed in this corridor due to night time conditions. A consistent pattern from Figures 18 and 19 is not evident. Figure 26 shows higher salinity around square I6 and about 1‰ less salinity in square J3. At 21.7 in. depth, the salinity as usual, showed a narrow range of 29.163 to 29.425‰, and at 34.3 in. it ranged from 29.393 to 29.550‰ (Figures not shown). The later two depths showed slightly less values. Overall, the destruction of general pattern takes place, and it is very difficult to correctly picture the top layer; the bottom layers, however, do retain their uniformity.

4.3.1.G Salinity Profile During High Tide And Afterwards

During the highest high tide of the month (November 21, 03:00 hours, Figure 27), surface waters at 3.2 in. depth showed relatively high salinities of 27.235 to 28.443‰. A meaningful pattern from the short segment could not be established. Salinity in the J2 square was minimum, but nearby in K1 square it was maximum. It showed mostly an increasing trend from south to north. Around the same time, at the 25 in. depth (Figure 29), the salinity showed a narrow range of 30.002 to 30.284‰. From Figure 30, the regular salinity pattern in the top layer was not established after two hours. The depths of 15 in. (Figure 31) and 25.6 in. (figure not shown) however were fairly uniform, but quite different from the top layer. Eight hours after the highest high tide, the usual salinity pattern was established as seen in Figure 32.

4.3.1.H The Floating Profiles

The salinity distribution during a short time frame at a particular depth is fairly uniform throughout the pond. The greater depths show as little as 0.25‰ variation in salinity throughout the pond. The corridor, as mentioned earlier, is even better to compare the results since the same locations were sampled over and over again. It will be interesting to know what happens when a floating sampling station records the values.

Figures 22 and 26 can be compared as both show the salinity profile at 13 in. depth. Figure 21 supports the values and pattern shown in Figure 23, but for 10 in. depth. Important information regarding these and other figures is shown in the following table.

Table 4.2. Important information about the figures to be compared for studying the floating profile pattern.

Figure #	22	25	26	28
Date	11/20/95	11/20/95	11/21/95	11/21/95
Time	14:45	20:08	00:10	03:35
Water level in the pond (in.)	17.5	16.5	15.8	30.75
Tide level (in.)	14.4	-2	18.0	28.8
Measurement depth (in.)	12.5-13.5	10.7-11	13	13.25

Sometime after 19:00 hours (Figure 25) the lowest low tide of -2 in. occurred in the open sea. At the midnight hours the water level in the pond was quickly rising in anticipation for the highest high tide of the month which was due at 3:00 am (Figure 26).

The ranges of salinity values visible in Figures 22 and 26 are quite comparable. Figure 22 shows a wide excursion to the east and ignoring the low values encountered along that path most of the values are comparable. Figure 25, which shows salinity distribution at 10.7 - 11 in. depth when the lowest low tide is occurring, also shows quite comparable range. Figure 28 is considerably different than either of these figures. At that time the highest high tide was occurring, and it is possible that the ocean waves directly break above the stonewall and distribute their energy in the pond. Salinity at the surface (Figure 27) is quite high, as it also is at 13 in. depth. From the above observations it is possible to say that the salinity distribution at a particular depth from the surface of the pond remains very much the same, unless a very high tide comes. During the low tide levels, the water level in the pond varies very little, which approximately corresponds to the salinity profile at a particular depth.

4.3.2 Temperature

Temperature is a very basic environmental indicator. In this investigation it also provided the basis for corrections for temperature dependent measurements such as dissolved oxygen and salinity. Temperature is the measure of energy in a system. It is a well known fact that various biological systems only work well within certain temperature ranges. Generally, the rate of thermophillic reaction doubles for every 10°C rise in the temperature. Many of the thermophillic systems reach their maximum potential around 35°C. The primary source of thermal energy input is solar radiation. A narrow band (400 - 700 nm) of solar radiation is used for photosynthesis, and infrared portion (700 nm to 3.0 μm) of it raises the temperature of the water. Plant and animal metabolism releases energy stored in food, which in turn results into temperature rise. Evaporation occurs at all times and results in removal of thermal energy from the surface of the water. Radiation may also contribute to a small amount of energy removal. Generally, fluids transfer thermal energy by convection. This convection process is dependent on density differences and results in mixing. If for some reason this process is hindered, unusually high temperatures may develop and the bio-systems can suffer. Reduction in the dissolved oxygen is one of the most important effects of elevated temperatures. Cooler temperatures are generally beneficial for the growth of aquatic fauna.

The temperature in the Kaloko pond was measured in the 28-31°C range. Surface water temperatures were usually lower, but some spots reached 32°C as shown in Figure 46, for November 20th, 14:00 hours at the 5 in depth. It is especially true with the water freshly emerging out of the soil. The sudden rise in temperature may be due to the proximity of the bottom surface, which is very efficient in absorbing the radiation. Surface temperatures at morning hours on normal days were also quite high, – figure 45, which shows the temperatures at the 8.5 in. depth, about one hour after the sunrise, to range between 26.2 to 29.9°C, with most at the higher range.

4.3.2.A Temperature Variation with the Depth

Daytime Profile

Daytime temperature profiles can be seen in figures 38, 39, and 40, which shows data gathered on November 17 at 17:00 hours. It is evident that the deeper depths have higher temperatures. Surface temperatures at 5.82 in. ranged from 27.4 to 29°C. At the 18 in. depth the temperature was between 30.1 and 31.4°C; and at 30 in. depth it ranged between 31.1 and 32°C. The temperature increases quickly up to a depth of 18 in., and then it increases slowly. During daytime a profile of hot-cold-hot profile was not observed, instead it always appears to be cold-hot-hotter from top to bottom.

It appears that the sunlight penetrates through all the depths and the plants tethered to the bottom of the pond use it to synthesize the food. Lower surface temperatures mean the infrared heat is minimally absorbed there, and also the photosynthetic activity is lower. The bottom layers for these very reasons show higher temperatures.

Nighttime Profile

Nighttime temperature profile for almost the same environmental conditions as above can be seen in the Figures 41 through 44 based on November 17, 22:00 hours' data. Comparing figures 38 and 41, surface temperatures appear to be about 2°C lower compared to the daytime temperatures. During this night time, temperatures at the 8 in. and 4.75 in. depth are almost same. The heat stored in the deeper layers appears to be, either not lost - which is unlikely, or is replenished by respiration when it was lost. Compare figures 39 and 43 for 18-20 in. depth, and figures 40 and 44 for 30-33 in. depth. Even the measurements on November 19th, and 20th showed very comparable ranges. Like salinity, temperature also shows very little spatial variation at deeper depths.

Diurnal Variation in Temperature

Temperatures recorded on November 17, at 13:00 (Figure 37), 17:00 (Figure 39) and 22:00 hours (Figure 43) at the 18-20 in. depth would be helpful to determine the diurnal variation of temperature. A central spot such as J3 or K3 can be chosen for analysis which is away from the sources of fresh water. This depth would have been little affected by warm/cold freshwaters at the surface or rapid cooling by winds and evaporation.

Analysis shows that the temperatures around J3 squares were approximately 30.6, 30.2, and 30.7°C, which indicates that the temperatures remain the same unless major changes in radiation take place.

4.3.2.B Freshwater Temperature

Freshwater appears to be colder, but it quickly heats up after entering the pond. This may be due to shallow depths where solar radiation is quite efficiently absorbed. From figure 36, a profile through the path of freshwater to the sea, it appears that the freshwater did not have enough time to warm up. During a minor high tide, as shown in figure 35 and figure 7 when temperature and salinity patterns match, it is evident that the water has adequate time to warm up. A slight anomaly between salinity and temperature patterns, as shown in figures 38 and 16, must have been attributed by shallower depths.

4.3.2.C Effect of Sunshine Hours on the Temperature

Solar radiation has a dramatic effect on the temperature. Usual surface temperatures ranged around 27-29°C. However, a brief cloud cover on November 12 (Appendix D, Solar Radiation During the Period of November 10-21, 1995), lowered the temperatures dramatically to the 23-25.5°C range as shown in Figure 34 for RG111308. On November 11th, the surface temperatures were between 28.3 and 29.5°C (figure not shown), and on November 12th, at

16:00 hours, the surface temperatures were 25.8 to 28.0°C - but mostly above 26.5°C (Figure 33). Surface temperatures on November 13th increased to 25.5 to 26.5°C due to the clear weather, but the deeper depths show about 2°C less temperatures compared to the other normal days. Intermediate data is not available, but after three days the temperatures at the depths were normalized. The cloud cover on November 12 reduced the energy input to the pond by 25% only, but the effects were measurable and highly noticeable. Extended periods of cloud cover could not be studied due to the short study period.

4.4 Dissolved Oxygen

Aerobic biological reactions depend on the amount of dissolved oxygen in the water. One important reaction is the respiration for most of the higher organisms. Extended periods of lower (<4mg/L) dissolved oxygen may impair and/or prove fatal to many organisms. The facultative anaerobic organisms, which can tolerate lower dissolved oxygen levels, may even thrive because of the reduced competition for food and decreased predation from higher organisms, and thus may promote other environmental problems in the system, such as algal bloom and fish kills. Having appreciable levels of oxygen in the water results in a healthy aerobic system. An aerobic system is much more efficient in consuming mineral nutrients in the water, and the end-products of it are not as objectionable as that of anaerobic systems. Odors and appearance are some of the most objectionable results of the anaerobic systems from a human point of view. Low dissolved oxygen content also means less photosynthetic activity, which in turn leads to a buildup of nutrients in the pond.

During the period of investigation, the dissolved oxygen ranged from 4.44 (Figure 48, RG111308) to 13.07 mg/L (Figure 61, RG112019-29.5 in.), but most of the times it was above 8 mg/L. A slight reduction in radiation resulted in a large reduction in the dissolved oxygen content.

Spatial variation of dissolved oxygen in the depths appears to be an intriguing phenomenon. It is a function of photosynthetic activity and respiration, which in turn are related to depth to the pond bottom.

4.4.1 Supersaturation

The measured values of dissolved oxygen in the pond appear to be higher when compared to the values of equilibrium concentration of dissolved oxygen at atmospheric pressure for various levels of salinity, as shown in the table below. The table is obtained from Standard Methods for the Examination of Water and Wastewater (AWWA 1995). It appears that the pond is supersaturated with oxygen up to almost 200%. The pond, however, does not appear to be eutrophied. On normal days, the night time dissolved oxygen concentration rarely goes below the equilibrium concentration. Also, the dissolved oxygen profile is fairly uniform, DO increases with depth, and it appears that the deeper depths are not anoxic at all.

Table 4.3. Solubility of oxygen in water exposed to water-saturated air at atmospheric pressure. Values of dissolved oxygen are in mg/L.

(Salinity = 1.80655 x chlorinity)

Chlorinity	0	5	10	15	20	25
Salinity	0.00	9.03	18.07	27.10	36.13	45.16
Temperature(°C)						
25	8.263	7.850	7.457	7.083	6.728	6.390
26	8.113	7.711	7.327	6.962	6.615	6.285
27	7.968	7.575	7.201	6.845	6.506	6.184
28	7.827	7.444	7.079	6.731	6.400	6.085
29	7.691	7.317	6.961	6.621	6.297	5.990
30	7.559	7.194	6.845	6.513	6.197	5.896
31	7.430	7.073	6.733	6.409	6.100	5.806
32	7.305	6.957	6.624	6.307	6.005	5.717

4.4.2 Depth Profile of Dissolved Oxygen

Dissolved oxygen increases with respect to depth. Salinity and temperature also increase with depth. The equilibrium concentration of dissolved oxygen at a particular partial pressure of oxygen decreases with increased temperature and increased salinity. This clearly leads to the conclusion that oxygen is of photosynthetic origin, which is more predominant in the lower depths of the pond. The reason for this may be the nutrients that are mainly derived from the soils, or leached up from the soils, support the autotrophic flora. The day of November 20th would be one of the normal days in the pond; though the major high tide was becoming successively bigger, the solar radiation was at its normal level for almost a week. From figures 59, 60, and 61, it appears that the northern part of the pond had a little lower oxygen, but it is still in the supersaturated range. At the 5 in. depth, at the same time, the northern part showed relatively high values (Figure 58). This could be the result of floating plants in the north side, or the oxygen rich freshwater must have been flowing from the areas where vegetation growth was rich. The stratification of dissolved oxygen is quite evident, at the deeper depths as the dissolved oxygen attains nearly constant levels. Comparing figures 52 and 54, new information about spatial variation is evident. It appears that during daytime, the dissolved oxygen at a given depth below the water surface seems to be more at the places where the bottom is closer to the water surface. The Kaloko pond can be considered as a shallow pond and sunlight must be reaching the full profile.

4.4.3 Diurnal Variations of Dissolved Oxygen

Comparing figures 52 and 54, it appears that during the daytime on November 17th, as the day progressed, the dissolved oxygen levels rose. At 18 to 20 in. depths, the DO increased from 9.1 to 10.1 mg/L in square K3. During nighttime the dissolved oxygen at the surface slightly

decreased. Comparing figures 53 and 55, dissolved oxygen within the 6 in. depth decreased by 0.3 mg/L. The spot in square J2 which showed maximum DO in the afternoon, showed minimum DO. Comparing figures 54 and 56, DO in square J3 at the 20 in. depth remained almost the same (10.3 mg/L) four hours after the sunset.

The day of November 17 showed a little lower values of dissolved oxygen. From figure 57, which shows dissolved oxygen profile just one hour after sunrise on November 20, the DO levels are surprisingly high, 11.6 to 12.2 mg/L. Compared to values shown in figures 58 to 61, it appears that the dissolved oxygen decreased very little. Figures 57, 59, and 60 represent almost same sampling depths, same water level, but they differ in the sampling time. Considering that by this day, the cycle of daily variation in DO is well established, it appears that the diurnal DO variation is quite low.

4.4.4 Effect of Sunshine Hours on Dissolved Oxygen

The temperature showed a positive relationship with the dissolved oxygen. Consider the fact that the equilibrium concentration of dissolved oxygen decreases with increasing temperature. Higher temperatures can also be associated with increased absorbance of solar radiation, which, in turn, is linked to higher levels of oxygen through photosynthesis. During night time, the temperature remained very much the same, but dissolved oxygen was slightly reduced.

Direct effect of reduced sunshine can be seen through figures 47 and 48. On November 12, solar radiation was about 25% lower, but comparing figures 47 and 53 (which represents a normal day of the solar radiation), it appears that reduced sunshine did not have immediate effect on the dissolved oxygen. On both days, the DO at surface appears to be between 8.45 and 9.0 mg/L. On the next day, on November 13th, in the morning, the DO was at least 1 mg/L less. The day's radiation helped to increase this level as seen in figures 49 and 50, which

prevented the DO levels going below the saturation mark. However, the effect of longer periods of cloud cover could be devastating. From figures 47 and 48 it appears that the southeast part of the pond, which produces more oxygen during normal days consumes more oxygen during cloudy days. Some of the locations are particularly vulnerable, as the DO at some spots reached as low as 4.4 mg/L due to a 25% reduction in insolation. The areas of low DO take longer to recover from effects of reduced radiation. Compare figures 49 and 50 with 55 and 56, and 59 and 60, which show conditions in the early night hours of 19:00 to 22:00. On November 13th, the northern part of the pond had higher DO (8.24 and 10.7 mg/L) compared to the southern part; four days after the north and south sides showed almost similar concentrations of 9.9 and 10.6 mg/L; and three days after then, on November 20th, the southern side had more DO than the northern side, almost 12.40 and 12.06 mg/L. DO in the northern part on that day, however, was around 11 mg/L. This shows that the southern part is more vulnerable to the effects of reduced sunshine, and it takes longer to recover.

Figure 51 shows the dissolved oxygen profile through the visible band when a low tide was occurring. The levels appear to be low. The residence time of water in the pond must be responsible for this behavior.

4.5 pH

pH in the pond appears to be fairly constant. It ranged mainly between 8.5 and 8.7. Considering the logarithmic scale on which pH measurement is based, a difference of 0.2 pH unit amounts to $10^{0.2} = 1.585$ times or 58.5% increase/decrease in the hydrogen ion activity. However, higher readings, as high as 9.030 on November 16th at 16:00 hours in H10 (northern source) region, and lower readings (8.133 on November 13th at 08:00 hours) were recorded. On November 16, at 16:00 hours when a low tide was occurring, the measurements around H10 region indicate the pH of the northern source. The freshwater band, which was visible at this time, showed lower

values of pH in the initial path to the sea, but after the central portion it showed almost the same pH as other parts of the pond. This information is not readily discernible from figure 63 since the range of values displayed is relatively high. Higher soil pH combined with water pH in the range of 7.5 to 8.5 are considered conducive to the production of botulinum toxin.

pH did not show variation according to depths. The pattern was sometimes directly proportional to the temperature, and sometimes inversely proportional to it. The pH readings were not corrected for temperature as the temperature does not vary much, and the error in reporting the uncorrected pH values is 0.003 per pH unit deviation from pH 7.0, per °C deviation from 25°C (Bates, 1973). e.g., at 29°C, for the 8.5 pH reported, the error would be no more than 0.018. Assuming that the electronics did not generate appreciable errors in the measurements, (temperature alone can not explain the variation in the pH readings as observed) it means chemical changes occurring in the water are reflected in the pH readings. However, owing to such small differences, exact interpretation stays beyond the scope of this investigation. In future experiments, the pH interface circuit should be modified to better amplify the alkaline pH range. When eutrophication in rivers occurs, the daytime pH can increase in excess of 10 and nighttime pH could drop to less than 8.5. In this situation, eutrophication is not evident.

Measurement of pH has another limitation too. The submersible pH electrode showed a slow response. e.g. from calibrations done on November 15th, 1995, when pH electrode was switched from pH buffer 4.0 to pH buffer 10.0, it took few seconds to show 3.291volts (pH =10.22), but almost 5 minutes to reach to 3.169 v (pH = 10.08). Buffer capacity of the pond water should also be an important consideration.

4.6 ORP

Oxidation Reduction Potential roughly represents the status of organic systems. The exact interpretation of the ORP values in complex biological systems is very difficult, even the comparison between two values is a daunting task. ORP is a result of electron activity. It can also be interpreted as a measure of the ease with which a substance either absorbs or releases electrons (Ingold® 1982). ORP values vary with temperature and pH, and these values are required to be reported along with the ORP values. As pH is a measure of the activity of hydronium ion only, the ORP depends on all the ions - metallic and non-metallic, in the solution. "The redox potential measures the competing processes of electron donation (reduction) and acceptance (oxidation)... Below -200 mV processes are strictly anaerobic, between 0 and -200 mV they show transitional character and positive mV-values indicate aerobic processes. A direct comparison of values can only be valid for the same redox pairs, ionic strengths and pH values. The pH value has always to be given" (Rump and Krist, 1992)

The values measured in the Kaloko pond ranged from 421.2 mV to 870 mV on November 13th. Most of the times the values were around 575 mV. ORP is the highly variable parameter measured in the pond.

ORP values show greatest variation in the top layers as shown in Figures 65 and 66. The distribution is not uniform and also it is a highly localized phenomenon. ORP values should be analyzed with care as the calibrations performed in the field did not tally. The calibrations for ORP were done on November 15th and 21st. On November 15th, the readings for ORP buffers were around 100 mV off. On November 21st, the reading for 462 mV buffer was 467 mV, which is quite close considering the large temperature coefficient of the ORP buffers. Considering all the data collectively an interesting trend is evident. For an unknown reason, the ORP readings increase, and then they suddenly drop down. From November 11th till 13th, the readings

increased successively, and from November 16th to November 20th, they also increased successively. The November 21 readings were lower for no known reason. The probe was calibrated on the same evening, and the calibration was all right. No accumulation of debris on the probe was observed.

Chapter V

Conclusion

The overall system worked adequately in the field. Rough pond bottom conditions caused many problems while navigating. Shallow spots where volcanic a`a rocks were protruding could not be avoided while controlling the boat from the shore. The boat picked up speed when travelling in a straight line, which caused the boat to lodge on the shallow, difficult to see a`a ledges. Freeing the boat from such incidences took a lot of effort. While controlling the boat from a kayak in the northern section of the pond, the three channel radio controller was accidentally dropped in the salt water and stopped working. The two forward speeds on the boat were slightly inadequate and a third forward speed would have been great help to scan the pond in a short period of time.

Navigation through shallow waters was a significant problem, but it is an urgent necessity. Either an on-board rescuing mechanism or computerized navigation should be devised. The second approach is much more difficult but will prove immensely helpful for long term unmanned monitoring. It will help to sample the specific sites in a well planned manner.

From the salinity measurements it is apparent that the amount of freshwater going to the ocean through the pond is small. When high tides approach, the fresh water layer appears to be pushed inward. It may be due to the small difference between ground water level and the water level in the pond. The higher tidal waters simply block the passage of the freshwater to the sea. When the tides recede, the freshwater blanket appears to be pulled out of the pond from the east to northwest direction. There could be two factors behind the uneven pulling: the discharge path for the surged water lies nearby of that point, or the freshwater source in the north is much bigger than the source in the southeast side. The second cause is more feasible and helps to explain the increase in salinity in the southeast corner at low tides. During the periods of high tides, rapid mixing of salt water and freshwater must be taking place in the pond and the nutrients from

the freshwater being mixed with the water in the pond. Should the blanket of freshwater keep flowing over the saltwater at all times, the freshwater would be effectively discharged to the sea, without transferring much of its nutrients in the pond. It is also possible that the salt water may intrude in the loose volcanic soil around the pond during high tides. Further study is required to answer these questions. The present equipment is adequate for this study, only the water level measurement system should be updated. By recording salinity distribution in the shallower depths, in as short a time period as possible, the correct picture of the situation can be captured.

From the dissolved oxygen measurements carried out in the pond, it is evident that the photosynthetic activity in the pond is quite vigorous. The pond could have lot of primary producers. The consumers of the oxygen in the pond are less, which is evident from the diurnal variation of the dissolved oxygen. It may also be possible that the fauna in the pond is diurnal (active during the day only). In the event of the short cloud cover the dissolved oxygen levels decreased and required considerable time to recover. It has been observed that the dissolved oxygen levels in the pond rose up to 13 mg/L. The problem areas in the pond may be near the southeast side, since this part showed maximum changes in dissolved oxygen during the day. The question of "What will happen when extended periods of cloud cover occur over the pond?" is still unanswered.

The temperature profile in the pond is always cold-hot-hotter, and it never becomes hot-cold-hot. It can be linked to the salinity profile. Also the autotrophic plants are suspended in the body of the water and not floating on the surface. Had the water been muddy, or the algae floating on the surface the hot-cold-hot pattern could have been seen. Also the daily change in the temperatures is quite low unless a reduction in solar insolation takes place. Solar insolation has a dramatic effect on the temperature and dissolved oxygen in the pond.

The overall pH in the pond appears to be normal. pH varied in the low alkaline range, 8.3 to 8.5. The soil around the pond may have a slightly high pH, which could be up to 9.0.

Eutrophication in the pond is not evident. Eutrophication is evident when night time dissolved oxygen becomes quite low. On normal days, even during night times the dissolved oxygen remained in the supersaturation range. pH during nighttime did not drop, nor did it increase during the daytime.

In case of ORP measurements, either the probe was faulty, or genuinely the cycle of rise and sudden fall in ORP is taking place in the pond. This observation needs careful study. ORP was one of the parameters which showed high spatial variation in the pond.

The location of a long term monitoring station in the pond depends on its purpose. Freshwater monitoring stations should be within the top 12 inches of the surface. The monitoring for dissolved oxygen and temperature should be located below 12 inch depth. The southeastern portion of the pond showed much more variation in the level of dissolved oxygen, and this spot should be the focus for long term monitoring.

Recommendations for future studies:

In this study, the overall equipment performed its purpose well. The size of the pond, and the rocky shores and shallow spots made the operation a tedious job. These obstacles could be dodged in the future by demarking the shallow spots with buoys and floats. The speed of the boat could be increased to cover more area in a shorter time period; however, the accuracy of pH measurements would be compromised. The present system for salinity measurements is quite adequate. In the future studies, if the particular pond has open access to the sea, the measurements should be performed more in the shallower depth, as the deeper depths may not show much variation. If the pond does not have open flow to the sea, then the freshwater layer

may be relatively deep, and the measurements should be performed at deeper depths.

Appendix A

Site Map of Kaloko-Honokohau National Historical Park

Appendix B

Avian Mortalities in Kaloko-Honokohau National Historical Park in 1994

Appendix C

Tide Chart for the Month of November 1995

Appendix D

Solar Radiation During the Period November 10-21, 1995

Appendix E

Design of Control Mechanisms for the Instrument Boat

A three channel radio controller (Futaba PCM 1024) was used to control various functions of the boat. Initially, it was thought that servos would be powerful enough to steer the boat, and change the speeds. But the construction of the trolling motor required to develop a powerful steering mechanism. Instead of providing a rudder for steering, the propeller and motor assembly was designed to turn. The important parts of the steering and instrument column positioning system are shown in Appendix J. The control mechanisms on steering and instrument column positioning system could be classified as a closed loop ON-OFF systems. For changing the speeds the FP-S9304 servo provided by the manufacturer was used. It had about 98 oz-inch. of torque. The torque for turning the rotory knob on the speed controller was measured by winding a string on the handle and hanging successively larger weights to it. The required torque was not more than 50 oz-inch, and thus the servo had sufficient torque for performing the intended function.

The radio controller came with its own receiver and three servos. Two of these servos were directly coupled to the potentiometers, whereby, servo position could be translated into an electrical voltage signal. A regulated 6.0 volt supply was applied to the 10k Ω potentiometers. The voltage tapped across the potentiometer was between 2.25 and 4.8 volts. It could be trimmed up or down either by trim controls on the transmitter or through manual alignment of servo and potentiometer. The voltage signal was used to control the position of the steering or instrumentation column. Complete circuits are shown on the following page. Each controller uses two LM741 operational amplifiers (op-amps) to compare the controlling signal and feedback signal. Based on their

circuit diagram

magnitudes the op-amps provide error signals, switching either of the two op-amp outputs to positive. This positive signal was then amplified and used to control the direction of the rotation of motors for steering or position control. Full-bridge or 'H' type of transistor arrangement was used to switch the polarity of electric supply to the motors. Control signal was converted into a band of low and high levels by passing the original signal from the potentiometer on the servo through a potential divider. This band provided necessary stopping time for the motors, as well as protection from turning the motor in forward and reverse direction when noise was present. Op-amp arrangement was such that when the feedback signal was within the band neither of the two op-amps would give positive output.

The voltage difference between the high and low control signal was about 0.3 volts. This depended on the stopping time required for the motor, the play in the steering column, and the noise in the circuits. Since these circuits were used along with the radio controller, they showed appreciable amount of noise, especially at a close range, which could not be taken out. With the values as shown in the circuit, the steering column could be positioned within 10° and the instrument column could be positioned within $\frac{1}{4}$ inch of the intended values. This positioning was considered adequate, especially steering control did not show any undesirable shortcomings, the play in the steering was not noticeable. For a much better control, use of unity amplifiers on the control and feedback signals located very close to the potentiometers is recommended. It will put very very light load on the main potentiometer, giving perfectly linear relationship between servo position and the follower system; and most importantly, it will allow to put out some current on the control and feedback wires. This current will reduce the noise in those lines, thereby allowing much accurate positioning. In that case, use of a potentiometer for adjusting the difference between high and low control signals is recommended.

The power amplifiers on the column positioning system were little different from the steering system. The steering motor required only 200 mA current to operate and its stalling current was

approximately 600 mA. The small signal transistors, 2N2222 and PN2907, could not handle this current. Theoretically TIP32, a PNP power transistor built to handle 3 A current, should have been adequate, but it heated up and blew repeatedly during initial testing. So it was replaced by TIP42, which was able to handle 10 A, and it provided troublefree service. The NPN power transistor, TIP31 also provided trouble free service. These transistors however, have very poor current amplification(β). TIP31, manufactured by Texas Instruments, had β of 42. TIP42, manufactured by Motorola showed $\beta > 100$ for the amount of current used by the motors. Due to low β , high base current was required, and additional transistor amplifiers were used as shown in the circuit. Though the LM741 could have provided this current, very conservative approach of lightly loading them was adapted. Present settings drew less than 1 mA from the op-amp. Also the Light Emitting Diodes (LEDs) provided 1.7 V voltage drop when initially the circuits were being developed for unipolar power supply. Together with the transistors' 0.6 V base to emitter voltage drop it provided 2.3 Volt drop to take care of 2 V low signal put out by the op-amps. This approach did not worked, nonetheless, the LEDs provided visual indication for the working of the comparators.

The power components for the instrument column positioning system are considerably different. The motor for the winch needed 1.2 A to operate and its stall current was more than 4 A. In that circuit, a high amplification, high current darlington transistor (TIP101) eliminated the base drive circuit for NPN side, but the TIP42 transistor required much more base current. About 120 mA current could be obtained through 100 Ω resistor, but they were heating up quite rapidly, so it was replaced with a bulb which could carry 120 mA at 12 V. While developing this system, the components available on hand were used. I would recommend using SPST relays with the op-amps. Relays would be much better to handle the near-short circuit starting currents for the motors. Relays would be much more reliable too. Only limitation is that they are expensive compared to transistors for unknown reason. Some of the relays come in with a bistable switch

type arrangement so that they operate only when the minimum rated voltage is applied to their coils. This feature would be very important to make the circuit operate from a single power supply. Ensuring that the negative power supply is not disconnected is a rather tedious job. If the negative supply is removed from the above circuit, both the sides (forward and reverse) of transistors operate simultaneously creating a short circuit. A fast blowing fuse before the power supply to the transistors would provide the required safety. In the current circuit, a fuse was provided before all the components, but it proved a little handicap to pinpoint the malfunctioning between transistors and comparators. A power cutoff before the transistors would have lighted up both the LEDs indicating that the comparator is faulty. Another reason for faulty comparator signal is break in the wires to the potentiometers.

Output signal for the column positioning

The feedback signal for the column positioning system was used to record the position of the instrument column in the water. This sensor consisted of a ten-turn 1,000 Ω potentiometer and ten groove pulley of about 2 in. diameter. A spring obtained from a tape return mechanism of a tape-measure was used for rewinding the fine kevlar string on the ten groove pulley. The rectangular column was marked with inch marks. Normal water line when the boat was fully loaded was noted. The calibration of the column position and the voltage output signal is as follows. Note the values of position shown indicate the inchmarks at the top of the bearing. The water line is at -10.625 in. measured from the top of the bearing.

Table E1. Output of column positioning system at various depths.

Position (in.)	Output (V)
12	1.106
18	1.547
24	1.995
30	2.467
36	2.958
42	3.474
48	4.019
54	4.610

$$\text{Position (in.)} = 12.02348 \times (\text{Voltage output}) - 0.329$$

Appendix F

Salinity Meter: Construction and Calibrations

Operating principle

Conductivity, k , is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement.

Conductance (G) is defined as the reciprocal of resistance. Conductance of a solution is measured between two spatially fixed and chemically inert electrodes. The arrangement of electrodes and spacers is known as conductivity cell. To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current signal. The conductance of a solution is directly proportional to the electrode surface area, A , cm^2 , and inversely proportional to the distance between the electrodes, L , cm . The constant of proportionality is, k , such that:

$$G = k (A/L)$$

is called "conductivity." It is a characteristic property of the solution between the electrodes. The units of k are $1/\text{ohm-cm}$ or $\text{mho per centimeter}$. Conductivity is customarily reported in micromhos per centimeter.

Commercial meters measure the quantity of electrical current flowing through the cell either directly or indirectly. The direct measuring types would have to measure the alternating current, which is relatively difficult. Indirect types would measure the a.c. voltage developed across some fixed resistor due to this a.c. current, or measure the direct current (d.c.) voltage which is obtained by rectifying the a.c. voltage. Measurement of d.c. voltage is comparatively easy. YSI 33 meter was measuring the a.c. current directly, hence it did not have a d.c. voltage recorder

output. Adding a recorder output to the commercial meter might have compromised its accuracy and the meters are relatively expensive for this kind of experimentation. YSI model 33 costs around \$711, the one with recorder output (YSI model 32FL) would have costed \$1,706. These meters consume lot of electricity and the battery voltage has to be monitored. Considering all these factors, it is better to construct the meter from components. The YSI conductivity cell was used, since it is not possible to construct the cell easily. The conductivity cell has a cell constant of 5 cm^{-1} .

The improvised meter applies a highly symmetric square wave on the conductivity cell, in series with a known, precise resistor - $47\Omega \pm 1\%$. Conductivity cell consists of two black-platinum plated pure-nickel electrodes separated by a fixed distance. Current passing through the conductivity cell varies depending on the conductivity of the solution the cell is dipped in. Higher ion concentration enables to conduct more electricity. The amplitude of the applied square wave is constant as it is obtained through a regulated power supply. The current passing through the conductivity cell as well as through the fixed resistor, creates a voltage difference across the fixed resistor. Square wave is used to avoid electrolysis of the salt solution and ionic deposition of platinum layer from one electrode to the other. For this very reason, highly symmetric square wave is necessary. It could be obtained either through using very close tolerance parts, as done in the commercial meters, or by using a binary divider circuit as used here.

The voltage developed across the conductivity cell was then filtered through a small germanium diode, which had very low forward voltage drop (<0.3 volts). The output then was passed through a simple RC filter. A large ($100 \text{ k}\Omega$) resistor across the $10\mu\text{F}$ capacitor provided discharge path when the applied a.c. square wave was of smaller magnitude. Theoretical time constant of this filter was about 1 second for falling signal, however, it was noticed that the device responded to the change in salinity quite rapidly, usually within a part of a second. Field observations of the data showed that the meter had very low noise output, and the results were highly reproducible.

The device was then calibrated against YSI 33 salinity meter in different concentrations of table salt, by using the same probe. Same way, the effect of inserting the conductivity cell into the holder plate was also studied, and it was verified that it had no effect on the final results. The calibration data and graph is shown below:

Table F1. Calibration data for the salinity device.

Meter conductivity	Device voltage	Device conductivity	Conductivity % error	Salinity meter	at 28°C	
					Salinity device	Salinity % error
14000	4.31	14388	-2.77	7.59	7.82	3.00
16700	4.21	17216	-3.09	9.19	9.50	3.36
20400	4.09	20764	-1.78	11.42	11.64	1.95
25000	3.94	25458	-1.83	14.26	14.55	2.01
28500	3.84	28762	-0.92	16.46	16.63	1.01
31400	3.76	31515	-0.37	18.31	18.39	0.40
34900	3.66	35105	-0.59	20.57	20.71	0.65
38000	3.58	38105	-0.28	22.60	22.67	0.31
40300	3.52	40434	-0.33	24.13	24.21	0.37
44200	3.43	44065	0.31	26.73	26.64	-0.34
48000	3.35	47440	1.17	29.31	28.93	-1.30
51500	3.27	50966	1.04	31.71	31.35	-1.16

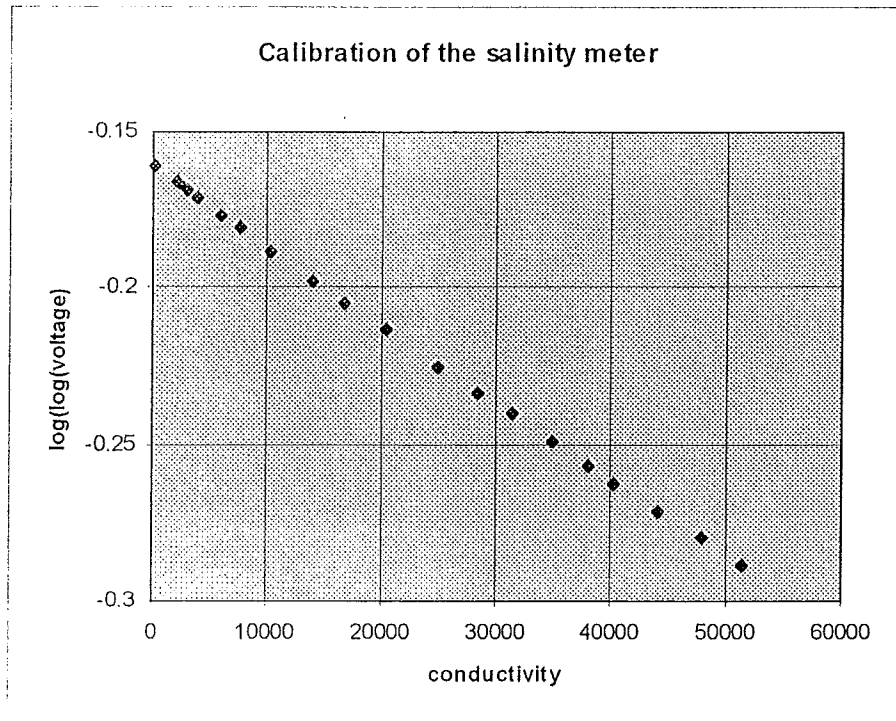


Figure F1. The calibration chart of the salinity measuring device.

From the data it is clear that $\log(\log(\text{voltage}))$ vs conductivity is very close to a straight line, r^2 values are beyond 0.999.

The relationship between the voltage measured and conductivity is

$$\text{conductivity} \left(\frac{\mu\text{mho}}{\text{cm}} \right) = \frac{\log(\log(\text{voltage measured})) + 0.1617924}{-2.4876 \times 10^{-6}}$$

The table also shows the error values represented as a percent deviation from the actual values - as measured from the values obtained by the meter, resulting from this curve fitting. The maximum percent error in the measurement of conductivity from this setup is not more than 2% within the range of 14.5 to 32.

Calculation of salinity values from the conductivity values

Salinity values depend on the conductivity values, temperature, and pressure. A method described in the Standard Methods for the Examination of Water and Wastewater (AWWA, 1995) is used. The protocol is as follows:

In situ measurements produce quantity R which is the ratio of the in situ conductivity to the standard conductivity at $S = 35$, $t = 15^{\circ}\text{C}$, $p = 0$ bars (where p is the pressure above one standard atmosphere).

R is factored into three parts -

$$R = R_p \cdot r_t \cdot R_t$$

R_p is pressure correction factor, r_t is temperature correction factor. R_t is the quantity on which salinity is determined.

Thus,

$$R_t = \frac{R}{(R_p \times r_t)}$$

$R_p = 1$, when no pressure correction applied, since the pressure was not appreciably different from 1 atmosphere, always less than 3 feet of water compared to 32 feet for atmospheric pressure.

r_t is given by a formula:

$$r_t = C_0 + C_1 t + C_2 t^2 + C_3 t^3 + C_4 t^4$$

$$\text{where } C_0 = 0.676\,609\,7$$

$$C_1 = 2.005\,64 \times 10^{-2}$$

$$C_2 = 1.104\,259 \times 10^{-4},$$

$$C_3 = -6.9698 \times 10^{-7}, \text{ and}$$

$$C_4 = 1.0031 \times 10^{-9}$$

Conductivity of standard sea water at 15°C is defined as $42,914 \mu\text{mho/cm}$.

Thus

$$R_t = \frac{\text{conductivity measured}}{42,914 \times r_t}$$

and

$$\begin{aligned} \text{Salinity} = & a_0 + a_1 R_t^{0.5} + a_2 R_t + a_3 R_t^{1.5} + a_4 R_t^2 + a_5 R_t^{2.5} \\ & + \left[\frac{t - 15}{1 + 0.0162(t - 15)} \right] \times (b_0 + b_1 R_t^{0.5} + b_2 R_t + b_3 R_t^{1.5} + b_4 R_t^2 + b_5 R_t^{2.5}) \end{aligned}$$

$$\begin{array}{ll} \text{where } a_0 = 0.0080, & b_0 = 0.0005 \\ a_1 = -0.1692 & b_1 = -0.0056 \\ a_2 = 25.3851 & b_2 = -0.0066 \\ a_3 = 14.0941 & b_3 = -0.0375 \\ a_4 = -7.0261 & b_4 = 0.0636 \\ a_5 = 2.7081 & b_5 = -0.0144 \end{array}$$

Calibrations:

Table F2. Calibration of the conductivity cell. (All calibrations were performed on the same KCl

solution prepared on 7/22/95)

Place	Std. solution	Date	Reading	Conductivity
Lab	0.1 M KCl	7/23/95	with the YSI 33 meter	14,000 $\mu\text{mho/cm}$
Lab	0.1 M KCl	10/13/95	4.38 volts	12,473 $\mu\text{mho/cm}$
Field	0.1 M KCl	11/9/95	4.281 volts	15,196 $\mu\text{mho/cm}$
Field	0.1 M KCl	11/15/95	4.35 volts	13,315 $\mu\text{mho/cm}$
Field	0.1 M KCl	11/21/95	4.32 volts	14,111 $\mu\text{mho/cm}$
temp 2.275 volts (28.6°C)				

The conductivity of 0.1 M KCl at 25°C should be 12,890 $\mu\text{mho/cm}$ (AWWA, 1992). The conductivity 13,000 $\pm$ 500 $\mu\text{mho/cm}$ equals to 7.467 $\pm$ 0.310 ‰ salinity at 25°C.

Circuit diagram

Appendix G

pH and ORP Interface Construction and Calibrations

In the original scheme, it was assumed that the pH and ORP electrodes could be directly connected with the data acquisition system. Many of the budding instrumentalists would be thinking on the same line, and therefore writing the next sections is absolutely necessary.

All modern pH electrodes have very high output resistance. This resistance comes from the glass interface. In the early days of pH instrumentation attempts were made to make the glass membranes as thin and porous as possible, which often resulted in compromises being made with accuracy and robustness. During those days the voltage measurements across such a high resistance, which is in the region of 500 M Ω , were very difficult to perform. Quite often the procedure involved setting up a null point (matching the voltages of two points) using a very accurate potentiometer and very sensitive galvanometer, which often took almost 15 minutes to complete. For further information about the subject matter please refer to the text "Determination of pH: Theory and Practice" by Bates R. G. (1973).

In those golden days, other methods which involved direct measurement of the voltage developed across such a high resistance were also being improved. This method fundamentally measures the ultrasmall current passing through the measurement circuits. The primary requirement for such a system would be an amplifier with very high input resistance. The potential (electromotive force, e.m.f.) of any system is the voltage measured across infinitely large resistor. The potential developed across the pH electrode would be acting on the series combination of the input resistance of the amplifier and the output resistance of the pH electrode (same as the resistance of glass bulb). The potential is thus divided between these two resistances, the magnitude being proportional to their values. Theoretically we should be

measuring the potential of the electrode, but in practice it was a measurement of the voltage developed across it. The voltage measured across the pH electrode is the difference between the potential developed and the potential drop (product of resistance of glass bulb and the current through it) across the glass bulb. It is evident that to correctly measure the potential developed due to pH chemistry, the input resistance of the measurement circuit should be 100 to 1000 times more than the resistance of the pH electrode.

Ordinary electronic multimeters have input resistance in the order of 50 M Ω , the National Instruments DaqCard 700 data acquisition card has input resistance 1,000 M Ω , and the Campbell Scientific's 21X datalogger also has the input resistance of that order. Clearly, these systems should not be connected to the pH electrode without a suitable interface. The interface should have input resistance of 1 T Ω (1 terra-ohm = 10^{12} ohms) and output resistance not more than 1 M Ω .

Immediate thought was to get the commercially available interfaces. And they were expensive, considering that they were not budgeted originally. Also, additional space and electricity requirements should also be considered. Obtaining a commercial interface was the easiest but expensive way, but the other not so easy way involved making these interfaces.

Development of semiconductor devices, and the developments especially in the area of operational amplifiers (Op-amps) put the devices which have input resistance of 1 T Ω , and linear amplification in the range of million times into novice hands. Radio Shack® sells TLO82 for around \$2.50, which is a dual package of BiFET (field effect transistor on the input side and bipolar junction transistor for high output current on the output side) op-amp. It has the input resistance of 1 T Ω . This op-amp is known as general purpose op-amp due to its drift characteristics, but National Semiconductor Data Books recommend it for instrumentation work.

This transistor was used in the following circuits because of its availability, and its drift of few micro-volts per °C, would not have mattered in the pH measurements. pH electrodes put out 59 mV signal per pH unit deviation from 7.0 pH, thus requiring very little amplification, -only 14.7 for bringing 0.3 volts signal to 5 volts level in the present case. Drift of few tens of micro-volts in this small amplification should not be a major consideration. For larger amplification, other amplifiers designed especially for the instrumentation job should be considered.

The three op-amp arrangement for instrumentation as shown in Figure G1 (Jung, 1988) is a standard arrangement and many textbooks will show its benefits; Points worth mentioning here are:

1. the arrangement provides a virtual ground thereby protecting the reference electrode of the pH or ORP system.
2. the amplification can be easily changed by changing the R3 resistor, and
3. the tolerance for R1, R2, and R3 resistors is not very low, common 1% tolerance resistors can be used.

One major requirement for this circuit though is the package of ratio-matched resistor network. It determines the common-mode rejection ratio (CMRR) or noise elimination capability of the amplifier. In the present setup, the 0.05% ratio matched (Beckman type 694-3-R10K-B) resistors were used. The resistor networks were obtained from Arrow Electronics for \$4 a piece, and with \$25 minimum order they were the most expensive elements of the circuit. Mail order electronic supply stores like JDR Microdevices, and Jameco Electronics did not sell the resistor networks, but they sell TL082 for less than a dollar.

Another arrangement using commercially available instrumentation op-amps, which is an integrated one chip substitution for the same circuit except the amplification resistor R3, could not be followed through due to terse specifications offered in the sales catalogs and shortage of

time. Nonetheless the price would have been almost the same. The third op-amp is a commonly available LM741. OP07 is recommended, but LM741 is quite sufficient.

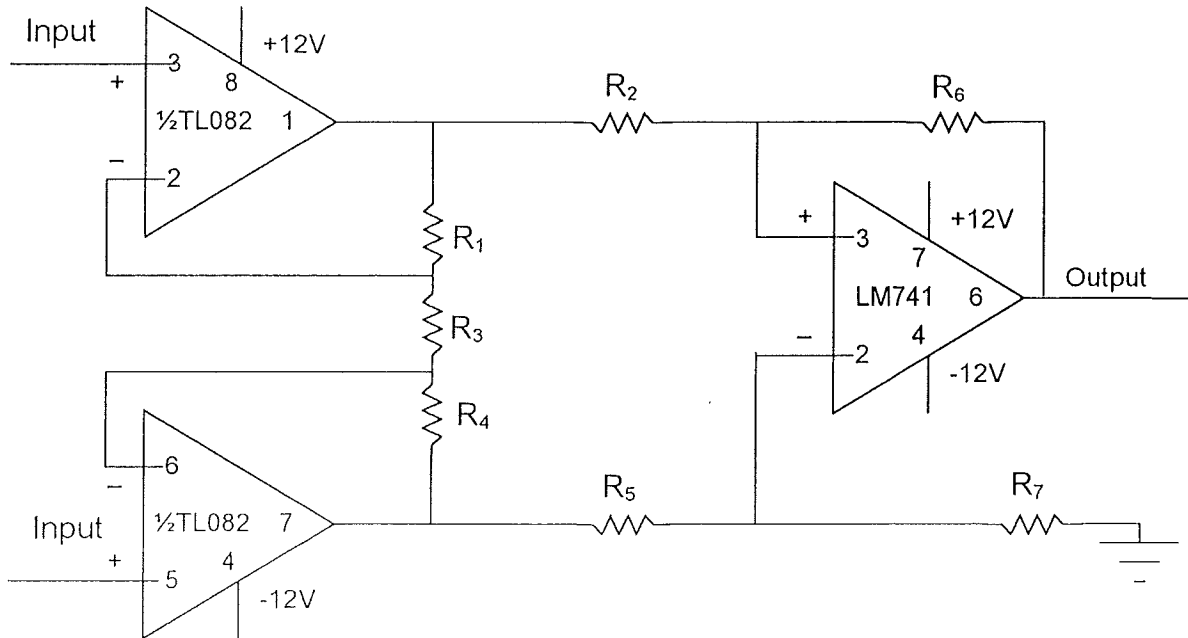


Figure G1. Circuit diagram for pH, ORP, and DO interfaces.

Resistances R2, R6, R5, and R7 determine the amplification of the last stage as well as the CMRR. R1, R3, and R4, together with the above resistors determine the amplification of the device. R1 and R3 should be of same value.

$$\text{Gain} = \left(1 + \frac{2R_1}{R_3} \right) \left(\frac{R_6}{R_2} \right)$$

The following values were chosen for pH and ORP interface:

	R1=R4	R3	Gain
pH	15K	2.2K	14.636
ORP	2.2K	2.2K	3

Actual values of offset and amplification were obtained by calibration as shown below:

Table G1. Calibration of the pH and ORP interfaces.

pH Interface		ORP Interface	
Input(volts)	Output(volts)	Input(volts)	Output(volts)
0.297	4.345	1.796	5.39
0.022	0.318	1.565	4.70
0.065	0.954	1.359	4.08
0.114	1.666	1.151	3.46
0.162	2.37	0.963	2.89
0.200	2.92	0.771	2.31
0.240	3.51	0.556	1.676
0.302	4.42	0.348	1.050
0.355	5.20	0.149	0.453
-0.355	-5.22	-0.001	0.000
-0.294	-4.32	-0.518	-1.558
-0.237	-3.48	-1.020	-3.06
-0.194	-2.85	-1.204	-3.61
-0.142	-2.09	-1.376	-4.13
-0.092	-1.35	-1.583	-4.75
-0.043	-0.63	-1.796	-5.39
-0.001	-0.023	0.00	0.0021

Regression analysis of above data:

pH:

$$\text{output} = 14.66333 \times \text{input} - 0.0065 \quad r^2 = 1$$

ORP:

$$\text{output} = 3.001655 \times \text{input} + 0.001834 \quad r^2 = 1$$

Calibrations of pH and ORP sensors

Calibration of pH sensor

The pH electrode was calibrated in the lab using pH buffer solutions manufactured by Fisher Scientific. The following values are derived from few hundred readings for each pH buffer. The

voltage values shown are calculated using the relationship developed for the pH interface as shown above.

Table G2. Calibration of pH electrode.

pH 10	voltage	pH 7	voltage
Max	0.13464	Max	-0.04784
Min	0.130312	Min	-0.05184
Average	0.132389	Average	-0.0498
Std dev	0.001171	Std dev	0.00101

pH 4	voltage	pH 7	voltage
Max	-0.21267	Max	-0.05084
Min	-0.21933	Min	-0.05517
Average	-0.21636	Average	-0.05316
Std dev	0.00127	Std dev	0.00113

Regression analysis:

$$\text{pH} = 17.19302 (\text{voltage at pH electrode}) + 7.766624 \quad R^2 = 0.9993$$

Calibration of ORP in the Lab

The ORP electrode was calibrated using ORP buffers made by mixing standard pH buffer solutions and sufficient amount of quinhydrone powder. Quinhydrone is sparingly soluble in water, and recommended amount for the buffer is 4 grams for every 500 mL solution. The buffers have to be made fresh every time, and they had large temperature coefficient as shown in the following table:

Table G3. Values of ORP buffers at different temperatures.

Temperature (°C)	pH 4.0 + quinhydrone (mV)	pH 7.0 + quinhydrone (mV)
20	470	295
25	462	285

The readings from 285 mV buffer were always inconsistent, but the 462 mV buffer was repeatable. Calibration of the ORP electrode was absolutely important since different concentration of electrolytes in the ORP electrode produce different offset voltages and the electrolyte in the present electrode had a gelled consistency. Calibration of the ORP electrode is based on only one standard (one point calibration).

Amplification and offset of the ORP interface is already determined as shown above. From one point calibration, i.e. 778 mV output for 462 mV buffer, the offset of the ORP electrode is 203 mV. Thus, ORP is calculated as:

$$\text{ORP} = \frac{\text{Voltage output at the interface}}{3} + 203 \text{ mV}$$

Field calibrations of pH and ORP sensors

Field calibration of pH, though a simple procedure of dipping the electrode in the 7.0, 4.0, and 10.0 buffer solutions and recording the voltage output of the interface, took lot of time. The solutions were kept in a the trunk of the car, and were colder than the surrounding. When they were brought out for calibration, the readings appear to take lot of time to stabilize. And, temperature measurement was also difficult. The data acquisition system with computer could have made this job extremely simple. It could have shown two parameters simultaneously. Even writing down the readings displayed on the voltmeter into a notebook, took considerable time and effort. It involved walking on rough surfaces, since the notebook was kept some distance away from the water. For this reason, the calibration of pH in the field was treated merely as a way to detect terrible malfunction of the electrode. Note also the temperature coefficient which was insignificant for 8.5 pH, would amount to 0.05 pH units for measurements at 30°C, for pH 10.

Table G4. Field calibration of pH electrode.

Date	Time	pH buffer	voltage read	Approx. pH
11/9/95	16:30	10	2.200	10.35
		4	-3.011	4.240
11/15/95	09:26	10	2.012	10.133
		4	-3.169	4.058
		7	-0.557	7.120
11/21/95	18:00	10	2.160	10.301
		4	-3.048	4.200
		7	-0.410	7.293

Field calibration of ORP was little troublesome. The ORP buffer had to be freshly prepared everytime. It consisted of mixing sufficient amount of quinhydrone in pH buffers 7.0 and 4.0, to make it supersaturated. Quinhydrone is sparingly soluble in water, and the particles float on the surface. Dipping the ORP electrode with watertight protective housing in the buffer solution was a little clumsy procedure, the quinhydrone particles used to stick all over the electrode and housing and might have been a hinderance for giving correct readings. Also, the ORP buffers used had very high temperature coefficient. ORP electrode was calibrated in the field only twice as shown below:

Table G5. Field calibration of ORP electrode.

Date	Time	ORP buffer	Voltage output (mV)	ORP reading (mV)
11/15/95	10:20	pH 4+QH	998	535
		pH 7+QH	521	376
11/21/95	18:00	pH 7+QH	385	331
		pH4+ QH	797	468

(QH – Quinhydrone)

Appendix H

Dissolved Oxygen Meter Interface and Calibrations

The dissolved oxygen meter put out a 0 to 115 mV signal. To make it compatible with other inputs to the data acquisition system, i.e. to better exploit the resolution of the data acquisition system, this output had to be amplified to 0 to 5 volt range. Requirements for the amplifier were almost same as the pH and ORP interfaces, the interface had to have more than 50K input resistance and it should interpret the signal with virtual ground. An interface as shown in Appendix G was constructed, but R1, R3, and R4 values were chosen as 10 k Ω , 470+100 Ω and 10 k Ω . With these values, the interface had an amplification of 36.087. The calibration of the dissolved oxygen meter was much simpler. The meter put out same amount of output signal for the same values displayed, i.e. the meter processed the current from the sensors, applied temperature corrections and offsets and then put out the same signal that was delivered to the display. Field calibration procedure then consisted of recording the values of DO displayed on the meter for air saturated water.

Table H1. Calibration values for the DO interface

DO displayed (mg/L)	Interface output (V)
10	4.91
9	4.47
8	4.02
7	3.57
6	3.11
5	2.66
4	2.21

$$D.O. = 2.2168896 \times \text{voltage} - 0.901627875$$

The recommended replacement period for the membrane on the DO sensor was two weeks. And since it was not damaged in the field operation, the same membrane provided service for the period of investigation. The DO meter was calibrated in the field as shown below. It is evident that the meter drifted a little initially but achieved a steady state. This drift was taken into account while adjusting the readings.

The following table shows DO calibrations in the field (Actual DO values are the theoretical air saturation values given by Manufacturer and AWWA, based on temperature and 0‰ salinity).

Table H2. Field calibration of the dissolved oxygen sensor.

Date	Time	Temp °C	Displayed DO	Actual DO	Difference
11/9/95	16:20	25.5	8.18	8.185	0.005
11/15/95	09:26	24	8.1	8.42	0.32
11/17/95	17:10	27.5	7.6	7.9	0.30
11/21/95	18:00	22.5	8.35	8.66	0.31

It is clear from the above calibration that the recorded DO readings were low by approximately 0.31 mg/L for an average value of 8.33 mg/L during November 15th to 21st. This correction amounts to 3.7%, and all the readings were multiplied by 1.037 to compensate for this drift. Unfortunately, the drift on November 11th was difficult to predict. The readings for November 11th, 12th, and 13th were also corrected by 1.037 factor based on following assumptions:

1. Either the calibration on November 9th is in error, or
2. The drift occurred quickly after the probe was put into service on November 9th, 95, and thus the readings from November 11th onward should be corrected by the same amount.

Corrections for salinity: salting out coefficient

Standard Methods for the Examination of Water and Wastewater (AWWA 1992) suggests the following procedure for correcting DO measurements in saline waters:

"Membrane electrodes are commercially available in some variety. In all these instruments the 'diffusion current' is linearly proportional to the concentration of molecular oxygen. The current can be converted easily to concentration units (e.g., milligrams per liter) by a number of calibration procedures. Membrane electrodes exhibit a relatively high temperature coefficient largely due to changes in the membrane permeability. The effect of temperature on the electrode sensitivity, ϕ (microamperes per milligram per liter), can be expressed by the following simplified relationship:

$$\log \phi = 0.43 m t + b$$

where, t = temperature °C

m = constant that depends on the membrane material, and

b = constant that largely depends on membrane thickness.

If values of ϕ and m are determined for one temperature (ϕ_0 and t_0) it is possible to calculate the sensitivity at any desired temperature (ϕ and t) as follows:

$$\log \phi = \log \phi_0 + 0.43 m (t - t_0) \quad \dots\dots\dots (A)$$

To use the DO membrane electrode in estuarine waters or in wastewaters with varying ionic strength, correct for effect of salting-out on electrode sensitivity. This effect is particularly significant for large changes in salt content. Electrode sensitivity varies with salt concentration according to the following relationship:

$$\log \phi_s = 0.43 m_s C_s + \log \phi_0 \quad \dots\dots\dots (B)$$

where, ϕ_s, ϕ_0 = sensitivities in salt solution and distilled water, respectively,

C_s = salt concentration (preferably ionic strength), and

m_s = salting out coefficient.

If ϕ_0 and m_s are determined, it is possible to calculate sensitivity for any value of C_s ."

Though not stated explicitly, from equations (A) and (B) it is clear that the two effects have additive effect on the sensitivity (ϕ) of the membrane. The meter was able to apply the temperature corrections automatically, hence only the salinity corrections were to be applied. The meter was designed to manually apply the salinity corrections by setting a dial scale for proper salinity. However, the manufacturer refused to provide the values of salting out coefficient. It was calculated by the following procedure.

The DO sensor was dipped in a freshwater bottle, and the DO reading was recorded for 0 ‰ salinity. Then the dial for salinity was set for the other value and the new DO reading was quickly recorded. The dial was set again for 0 ‰ salinity and the original reading was confirmed. This procedure was repeated for a number of samples. From a number of data points, the set of points that showed very little variation for DO readings for 0‰ salinity were chosen. Since the meter was designed to compensate for temperature effects, parameters in equation (B) only to be worked out.

Table H3. Calibration values of DO sensor for salting out coefficient. (Note: This calibration was done in the field instead of controlled lab conditions.)

Salinity (‰)	DO (mg/L)	Salinity (‰)	DO (mg/L)
0	6.825	0	6.9
25	5.8	30	5.5
30	5.7		
35	5.6	0	6.72
		25	5.7
0	7.175		
5	6.9	0	6.95
10	6.7	25	5.95
15	6.58		
20	6.45	0	6.95
		20	6.15
0	7.2		
25	5.8	0	7.1
		20	6.4
0	6.8		

Since, the DO reading $\frac{35}{5.55}$ displayed is directly proportional to the membrane sensitivity (ϕ), DO readings can be used in equation (B) instead of ϕ .

From the above data, the relationship between displayed and corrected reading is as follows:

$$\log \left[\frac{\text{correct DO}}{\text{DO without salinity correction}} \right] = -0.00247 C_s - 0.003094$$

where, C_s is salinity in ‰.

The complete equation for calculating the DO from voltage recorded is as follows:

$$\text{DO (corrected)} = 10^{((\log(2.216889 \times \text{Voltage} - 0.0901628) \times 1.0372) - 0.00247 C_s - 0.003094)}$$

where, Voltage is in volts,
 C_s is salinity in ‰,
 DO is in mg/L

Appendix I

Temperature Sensor Interface and Calibrations

The temperature sensor was built using YSI 44003A precision thermistor. It had a resistance of 1000 Ω at 25°C. The resistance changed non-linearly with temperature. Important information about the thermistor is shown below:

Interchangeability: $\pm 0.2^\circ\text{C}$ from 0 to 70°C

Max. Operating Temperature: 100°C. (Extended operation on continued cycling above 50°C will cause the thermistor to eventually exceed tolerances.)

Time Constant, Max: 1 sec. in well-stirred oil, 10 sec. in still air

Dissipation Constant, Max: 8 mW/°C in well-stirred oil, 1 mW/°C still air

Storage Temperature: -80°C to $+50^\circ\text{C}$

The design procedure for temperature sensors using thermistors is given by Wobschall (1987).

Design of non-inverting amplifier is given by Rosenstein and Morris (1985).

From pilot calibrations as shown below it was found that the resistance of the element varied from 2000 Ω to 400 Ω for a temperature range of 7°C to 52°C. Dissipation constant is an important factor that should be taken into account while designing circuits for thermistors. It is the amount of power dissipated which will raise the internal temperature of the element by 1°C.

The tolerance on the element is $\pm 0.2^\circ\text{C}$, and to stay within this limit the dissipation should not exceed 0.2 mW at 25°C. Lower temperatures would have more dissipation, but since the element is submerged in the water, approximately 0.4 mW dissipation should be alright.

Dissipation is the product of current and voltage across a resistive element.

$$P = V \times I = V^2/R$$

$$V = \sqrt{(PR)}$$

$$V = \sqrt{(2 \times 10^{-4} \times 1000)}$$

$$V = 0.447 \text{ V}$$

Maximum voltage will be developed when the thermistor's resistance is at its maximum. This happens at the minimum temperature, and the choice of lower limit of temperature measurement is little difficult. Rather than choosing the upper and lower limits of measurements, the values of individual components were decided for 25°C to have the output in the center of the measurement range, and then the limits of temperature measurements were calculated. Measurement range was set at 0-5 volts. Thus the 25°C reading should give approximately 2.5 V output. The values of precision resistors on hand were limited. From the resistor pairs of the values available, an amplification (or gain) of 5.71 was chosen. That would limit the voltage developed across the thermistor at 25°C to 0.438 volts. The following calculations show the voltage developed across the thermistor when it is connected in series with a resistor R_s .

$$\frac{1000}{(R_s + 1000)} \times 6.0 = 0.438 \text{ V}$$

$$R_s = 12,689 \Omega$$

A combination of 10 K Ω and 2.2 K Ω resistor (12.2 K Ω total) for R_s will develop a voltage of 0.455 volts when connected in series with 1 K Ω (thermistor at 25°C) when a 6.0 V regulated voltage is applied, and that should be alright.

Note that the temperature vs resistance curve of the thermistor is non-linear, and it is very close to exponential curve. The op-amps amplify the voltage linearly. Allowing more range for the thermistor's resistance variation would be a better choice. Magnifying a small non-linear voltage with large amplification would not be a good decision.

The values of temperature that can be measured with this setup are as follows:

The minimum temperature that can be measured will be limited by the input range of the data-acquisition system, which is chosen to be 5 volts. Maximum allowable input range for Campbell Scientific's 21X datalogger is ± 5 v, it can be ± 10 volts for National Instruments DAQCard 700 but there also ± 5 volt range was chosen, because the power supply on the boat was chosen to be 12 volts, and amplifying to 10 volt level would not be a wise choice, especially when the voltage regulators need few volts of voltage-drop. Moreover, resolution on the DAQCard 700 was independent of the range chosen.

For a maximum 5 V output from the temperature sensor, and with 5.71 amplification factor, maximum voltage on the thermistor should be less than 0.876 V. And this voltage will be developed when the thermistor has a resistance of R_T :

$$\frac{R_T}{(R_T + 12,200)} \times 6.0 = 0.876 \text{ V}$$

$$R_T = 2,085 \Omega$$

The thermistor will develop 2,000 Ω at 7°C. The power dissipation at this temperature would be:

$$P = \frac{V^2}{R}$$

$$P = \frac{(0.876)^2}{2000} \text{ W}$$

The power dissipation at 7°C is 0.38 mW, which is almost twice as much allowed for the still air; but the sensor will be used in water and this power dissipation should be alright.

The maximum measurable temperature is little difficult to access. The thermistor should not be subjected to repeated measurements over 50°C. Its resistance at that temperature would be

around $400\ \Omega$. The voltage developed across it would be $0.19\ \text{V}$ and after amplification the output will be $1.087\ \text{V}$.

The complete circuit diagram of the temperature measurement system is as shown below:

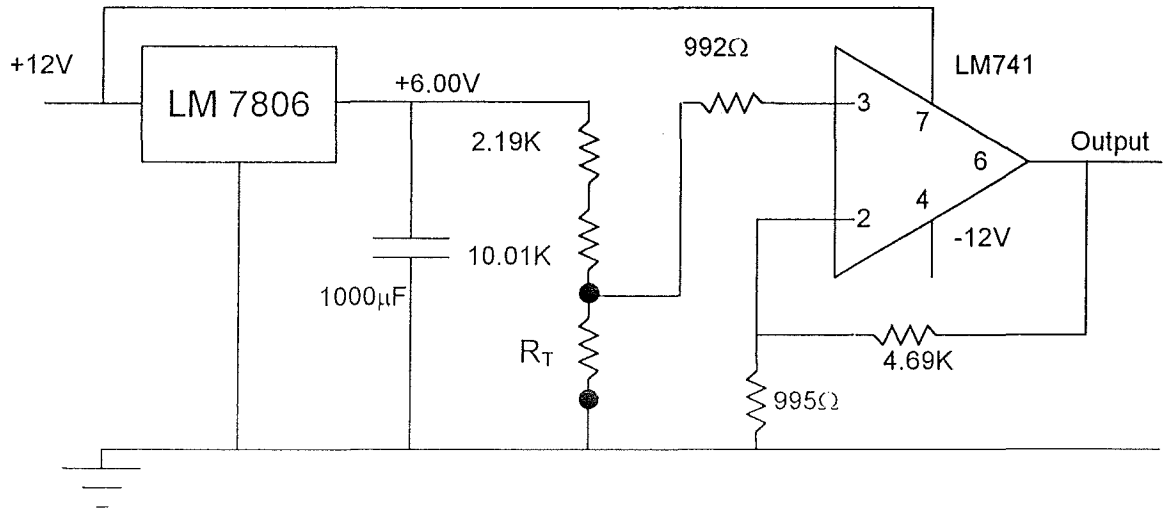


Figure 11. Circuit diagram of temperature sensor.

The thermistor was calibrated in a mixture of hot water and ice-cold water in the temperature range of 3°C to 50°C using a common, mercury-in-glass type lab thermometer. The scale of the thermometer was graduated in 1°C interval. The accuracy of the thermometer is not known. The readings for resistance versus temperature were obtained. For comparison, resistances at closeby temperatures supplied by the manufacturer are shown. Due to the uncertainty in the lab thermometer, the values provided by the manufacturer are used for final calibration.

Table I1. Calibration of YSI 44003A temperature sensor.

Temperature °C	Resistance Ω (Measured)	Temperature °C	Resistance Ω (YSI literature)
3	2,380	3	2384
5	2,170	5	2192
8	1,920	8	1936
11.8	1,650	12	1647
15	1,460	15	1462
20	1,200	20	1206
23.5	940	24	1038
26.5	940	26	963.9
27.7	900	28	896.3
34.2	710	34	724.1
39.4	600	39	609.7
42.5	540	42	551.2
49.5	425	49	438.6
50	420	50	424.8

Temperature to resistance relationship (from manufacturer's data)

$$\text{temp.} = \frac{[\ln(\ln(\text{Resistance})) - 2.066573]}{(-0.0053395776)}$$

Table I2. Resistance of the thermistor to the final voltage output calibration

Resistance (Ω)	Voltage developed at R_T (V)	Voltage output (V)
0.8	0	0
208	0.101	0.589
230	0.113	0.644
328	0.159	0.911
430	0.207	1.184
533	0.255	1.458
638	0.303	1.728
730	0.344	1.965
829	0.388	2.2

(Table I2 continued)

Resistance (Ω)	Voltage developed at R_T (V)	Voltage output (V)
926	0.43	2.45
1000	0.461	2.62
1996	0.857	4.88
1917	0.829	4.72
1818	0.792	4.51
1718	0.754	4.29
1623	0.716	4.08
1518	0.676	3.85
1422	0.637	3.62
1325	0.597	3.41
1222	0.555	3.16
1125	0.514	2.93
1023	0.471	2.68
996	0.46	2.62

Resistance to voltage relationship

$$\text{Resistance} = 0.002431563(\text{voltage}) + 0.1400690 \quad R^2 = 0.999$$

thus, output voltage vs temperature relationship is:

$$\text{temp.} = \frac{\ln\left(\ln\left(\frac{V - 0.1400690}{0.002431563}\right)\right) - 2.066573}{-0.0053395776}$$

where temp. is in $^{\circ}\text{C}$,
voltage is in V.

Appendix J

Photographs

Figure J1. Inside structure of the boat before it was filled with poly-urathane foam. Four boxes of the PVC sheets were used to hold two batteries and the instruments. Note the square bearings for instrument column.

Figure J2. Propeller, winch, and steering mechanism of the boat.

References

- American Water Works Association. 1992. Standard Methods for the Examination of Water and Wastewater. 18th Edition. Published by American Health Association, American Water Works Association, and Water Environment Federation.
- American Water Works Association. 1995. Standard Methods for the Examination of Water and Wastewater. 19th Edition. Published by American Health Association, American Water Works Association, and Water Environment Federation.
- Apple R. A. and W. K. Kikuchi. 1975. Ancient Hawaii shore zone fishponds: an evaluation of survivors for historical preservation. Prepared for National Park Service, Honolulu, Hawaii.
- Bates R. G. 1973. Determination of pH: Theory and Practice. John Wiley and Sons, New York.
- Bienfang P. K. 1980. Water Quality Characteristics of Honokohau Harbor: a subtropical embayment affected by groundwater intrusion. Pacific Science 34(3) 279-291.
- Chai D. K. 1991. An Inventory and Assessment of Kaloko Pond, Marsh, and Anchialine Pools at Kaloko-Honokohau National Historical Park, North Kona, Hawaii. Report on file at National Park Services, Hawaii.
- Hawaiian Tide and Moon Calender. 1995. Published by Hawaiian Resources Company Ltd., 94-527 Puahi St., Waipahu, HI 96797.
- Ingold® Electrodes Inc. 1982. Redox Measurement: Principles and Problems. Ingold Electrodes Inc., 261 Ballardvale Street, Wilmington, MA 01887.
- Jung W. G. 1988. IC Op-Amp Cookbook, Third Edition. Howard W. Sams & Co., A Division of Macmillan, Inc., Indianapolis, Indiana.
- Kikuchi W. K. and J. C. Belshe. 1971. Examination and evaluation of fishponds on the Leeward coast of the island of Hawaii. Prepared for Hawaii County Planning Commission, Hilo, Hawaii.

- Maciolek J. A., and R. E. Brock. 1974. Aquatic survey of the Kona coast ponds, Hawaii island. University of Hawaii, Sea Grant Advisory Report AR-74-4.
- Morin M. P. 1994. Avian Botulism Report. Report on file at National Park Services, Hawaii.
- National Semiconductor Corporation. 1988. Linear Databook, Volume 1, section 2 pp. 594-602.
- Rocke, T. 1996. Making Wetlands Safe from Avian Botulism. Science News, Vol. 149. p. 5.
- Rosenstein, M. and P. Morris. 1985. Modern Electronic Devices: Circuit Design and Application. Reston Publishing Company, Inc. A Prentice-Hall Company, Reston, Virginia.
- Rump H. H., and H. Krist. 1992. Laboratory Manual for the examination of Water, Wastewater and Soil. Second Edition. VCH Publishers Inc., New York, NY
- Wobschall Darold. 1987. Circuit Design for Electronic Instrumentation: Analog and Digital Devices from Sensor to Display, Second Edition. McGraw Hill Book Company, New York, NY.

