THE ACCURACY AND PRECISION OF ORP MONITORING IN BIO-NUTRIENT REMOVAL PROCESSES

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Abstract

It is important to have complete denitrification in the anoxic zone to provide good conditions for phosphorus removal in a bio-nutrient removal process. The objective of this research was to examine the possibility of using oxidation reduction potential (ORP) as a means of assessing the completeness of denitrification in the anoxic zone.

First, the reliability and sensitivity of ten probes were tested and evaluated. Next, ORP values in complete denitrification conditions from biological systems with different initial NO_x concentrations and denitrification rates were collected and the usefulness of these redox values was assessed.

Batch testing was used in this research. The Remote Data Acquisition and Control System, an automated data log-in system, was used to collect redox values. ORP probes were tested in quinhydrone buffer solutions. The biological systems in the anoxic tests were proportional combinations of mixed liquors from the anaerobic zone, aerobic zone, and the return sludge line of the UBC bio-nutrient removal process, so that different initial NO_x concentrations were obtained. Sodium acetate (NaAc) was added to the systems of carbon addition tests in order to achieve different denitrification rates.

The probe test results indicated that measured ORP values were linearly related to standard ORP values of the tested quinhydrone solutions. Adjustment factors were developed based on this relationship for each probe.

In the ORP vs time curves of biological batch tests, knees characteristic of the minimum first derivative were observed. At these knees, the NO_x removal efficiencies were found to be 92.6 % on average in anoxic tests, and to be 96.2 % in carbon addition

tests. Redox values at the knees had an average of -28 mv (adjusted value), with a standard deviation of ±8 mv (adjusted value). When redox values reached -44 mv (adjusted value), the lower limit of the 95% confidence interval, the biological system was still a good environment for phosphorus removal in the process.

Adjusting measured redox values is not necessary in order to achieve the conclusion about using ORP values to control a denitrification process. The -42 mv, the lower limit of the 95% confidence interval from measured redox values, is suggested to be used as a denitrification control guideline. However, probe testing is still considered necessary.

It was concluded that ORP monitoring can be used as a control tool in a denitrification process. Probe test procedures, including testing solutions, adjustment factors development, and testing frequency are recommended in the research.

Table of Contents

Abstract ii

List of Tables viii

List of Figures xi

List of Abbreviations xiii

Acknowledgements xiv

1 INTRODUCTION 1

2 LITERATURE REVIEW 3

2.1 Oxidation-Reduction Potential Measurement 3

2.2 The Application Possibilities of ORP Measurement 5

2.3 ORP as a Control Parameter in Waste Treatment Processes 6

2.4 ORP Monitoring in Bio-nutrient Removal Processes 7

3 EXPERIMENTAL DESCRIPTION 9

3.1 Research Objectives 9

3.2 UBC Bio-nutrient Removal Process Introduction 10

3.2.1 Process scheme 10

3.2.2 Process mechanism 12

3.3 Experimental Set-up 13

3.3.1 Data log-in system 13

3.3.2 QBASIC program 13
3.3.3 Batch testing apparatus 15
3.3.4 ORP probes and probe maintenance 15
3.4 Analytical Parameters and Techniques 18
3.4.1 NO_x (NO_3^- and NO_2^-) 18
3.4.2 MLSS and MLVSS 18
3.4.3 pH 19
3.4.4 Temperature 19
3.4.5 Chemical oxygen demand 19
3.5 Data Analysis Techniques 19

4 RESULTS **20**

4.1 Probe Testing Results 20
4.1.1 Introduction 20
4.1.2 Probe test 1 (March 4, 1991) 22
4.1.3 Probe test 2 (April 4, 1991) 22
4.1.4 Probe test 3 (May 7, 1991) 22
4.2 Anoxic Batch Tests (Without External Chemical Addition) 29
4.2.1 Introduction 29
4.2.2 Anoxic batch test 1 (March 11, 1991) 30
4.2.3 Anoxic batch test 2 (March 21, 1991) 34
4.2.4 Anoxic batch test 3 (March 28, 1991) 34
4.3 Anoxic Batch Tests (With External Carbon Addition) 36
4.3.1 Introduction 36
4.3.2 Carbon addition test 1 (February 1, 1991) 37
4.3.3 Carbon addition test 2 (February 7, 1991) 37

4.3.4 Carbon addition test 3 (March 1, 1991) 42

5 DISCUSSION **44**

5.1 Introduction 44

5.2 Evaluation of Probe Testing Results 44

5.2.1 The Probe's behaviour in quinhydrone buffer solutions 45

5.2.2 Redox value adjustment 46

5.2.3 Evaluation of probe testing results 50

5.3 Redox Values for Complete Denitrification Conditions 50

5.3.1 Defining ORP values for complete denitrification conditions . . . 50

5.3.2 Measured ORP values at the knees 51

5.3.3 NO_x levels at the knees 56

5.3.4 The possibility of using ORP as a control parameter 58

5.4 The Necessity of Adjusting Measured ORP Values 64

6 CONCLUSIONS and RECOMMENDATIONS **68**

6.1 Conclusions 68

6.1.1 Probe testing experiments 68

6.1.2 The accuracy and precision of ORP monitoring 69

6.1.3 The necessity of adjusting measured ORP values 70

6.2 Recommendations 71

Bibliography **72**

Appendices 75

A Results of Probe Test 2 and Probe Test 3 75

B Results of Anoxic Batch Test 2 and Anoxic Batch Test 3 88

C Results of Carbon Addition Test 2 and Carbon Addition Test 3 95

List of Tables

4.1 Nominal ORP values of reference quinhydrone solutions 21

4.2 Buffer solutions' compositions 21

4.3 Experimental conditions for probe test 1 22

4.4 Experimental conditions for probe test 2 22

4.5 Experimental conditions for probe test 3 29

4.6 Mixed liquor combinations 29

4.7 Process characteristics on March 11, 1991 30

4.8 Experimental conditions for anoxic batch test 1 31

4.9 Process characteristics on March 21, 1991 35

4.10 Experimental conditions for anoxic batch test 2 35

4.11 Process characteristics on March 28, 1991 35

4.12 Experimental conditions for anoxic batch test 3 36

4.13 Process characteristics on February 1, 1991 38

4.14 Experimental conditions for carbon addition test 1 38

4.15 Process characteristics on February 7, 1991 42

4.16 Experimental conditions for carbon addition test 2 42

4.17 Process characteristics on March 1, 1991 43

4.18 Experimental conditions for carbon addition test 3 43

5.1 ORP values: Avg, Std and SD (probe test 1) (mv) 46

5.2 Adjustment ratios (probe tests 1 to 3) 48

5.3 Measured ORP values at the knees (DM, AT1) (mv) 54

5.4 Measured ORP values at the knees (DM, AT2) (mv) 54
5.5 Measured ORP values at the knees (DM, AT3) (mv) 55
5.6 Measured ORP values at the knees (DM, CA1) (mv) 55
5.7 Measured ORP values at the knees (DM, CA2) (mv) 55
5.8 Measured ORP values at the knees (DM, CA3) (mv) 55
5.9 Measured NO_x at the knee position (AT 1-3) 56
5.10 Measured NO_x at the knee position (CA 1-3) 56
5.11 Initial NO_x levels and removal efficiencies (anoxic tests 1-3) 57
5.12 Initial NO_x levels and removal efficiencies (carbon tests 1-3) 57
5.13 Adjusted ORP values at the knees (DM, AT1) (mv) 58
5.14 Adjusted ORP values at the knees (DM, AT2) (mv) 59
5.15 Adjusted ORP values at the knees (DM, AT3) (mv) 59
5.16 Adjusted ORP values at the knees (DM, CA1) (mv) 59
5.17 Adjusted ORP values at the knees (DM, CA2) (mv) 59
5.18 Adjusted ORP values at the knees (DM, CA3) (mv) 60
5.19 Avg and Std at the redox knees (AT 1-3 and CA 1-3) 60
5.20 NO_x (adjusted ORP value is -12 mv, AT1) 61
5.21 NO_x (adjusted ORP value is -28 mv, AT3) 62
5.22 NO_x (adjusted ORP value is -44 mv, AT1) 62
5.23 NO_x (adjusted ORP value is -44 mv, AT2) 62
5.24 NO_x (adjusted ORP value is -44 mv, AT3) 63
5.25 NO_x (adjusted ORP value is -44 mv, CA1) 63
5.26 NO_x (adjusted ORP value is -44 mv, CA2) 63
5.27 NO_x (adjusted ORP value is -44 mv, CA3) 63
5.28 NO_x (measured ORP value is -42 mv, AT1) 65
5.29 NO_x (measured ORP value is -42 mv, AT2) 65

5.30 NO_x (measured ORP value is -42 mv, AT3) 65
5.31 NO_x (measured ORP value is -42 mv, CA1) 66
5.32 NO_x (measured ORP value is -42 mv, CA2) 66
5.33 NO_x (measured ORP value is -42 mv, CA3) 66

List of Figures

3.1 UBC bio-nutrient removal process 11

3.2 Data log-in system scheme 14

3.3 Batch test apparatus 16

3.4 ORP probe 17

4.1 Probe test 1.1 (pH 4.03): (A) Probes (1-5). (B) Probes (6-10). 23

4.2 Probe test 1.2 (pH 6.30): (A) Probes (1-5). (B) Probes (6-10). 24

4.3 Probe test 1.3 (pH 7.06): (A) Probes (1-5). (B) Probes (6-10). 25

4.4 Probe test 1.4 (pH 7.78): (A) Probes (1-5). (B) Probes (6-10). 26

4.5 Probe test 1.5 (pH 8.78): (A) Probes (1-5). (B) Probes (6-10). 27

4.6 Probe test 1.6 (pH 9.85): (A) Probes (1-5). (B) Probes (6-10). 28

4.7 Anoxic batch test 1.1 (ratio 0) 31

4.8 Anoxic batch test 1.2 (ratio 1) 32

4.9 Anoxic batch test 1.3 (ratio 2) 32

4.10 Anoxic batch test 1.4 (ratio 3) 33

4.11 Anoxic batch test 1.5 (ratio 4) 33

4.12 NO_x test results (anoxic test 1) 34

4.13 Carbon addition test 1.1 (control) 39

4.14 Carbon addition test 1.2 (20 mg/L) 39

4.15 Carbon addition test 1.3 (40 mg/L) 40

4.16 Carbon addition test 1.4 (60 mg/L) 40

4.17 Carbon addition test 1.5 (80 mg/L) 41

4.18 NO_x test results (carbon addition test 1) 41

5.1 Measured ORP values vs pH (probe test 1) 47

5.2 Measured ORP values vs standard ORP values (probe test 1) 49

5.3 Anoxic test 1.1: first derivatives vs time 52

5.4 Anoxic test 1.1: first derivatives vs time (Avg 5) 53

5.5 Anoxic test 1.1: first derivatives vs time (Avg 10) 53

List of Abbreviations

AT: anoxic test

Avg: average

CA: carbon addition test

COD: chemical oxygen demand

DM: the derivative method

DO: dissolved oxygen

min: minute

MLSS: mixed liquor suspended solid

MLVSS: mixed liquor volatile suspended solid

NO_x: a comprehensive measure of both NO_3^- and NO_2^-

ORP: oxidation reduction potential

SD: standard value

Std: standard deviation

UBC: the University of British Columbia

VFA: volatile fatty acid

Note: in this thesis the term "redox value" means the same as "ORP value".

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Chapter 1

INTRODUCTION

It is important to remove nitrogen and phosphorus from municipal and industrial wastewater, especially when the wastewater is discharged into inland water systems such as lakes and rivers; nitrogen and phosphorus are major elements which are responsible for excessive growth of aquatic plants and algae, or eutrophication. Eutrophication can have detrimental effects on aquatic life and the usefulness of the water resource. Among the currently employed methods of nitrogen and phosphorus removal, the biological method has advantages over chemical methods, as it has fewer chemical requirements and lower sludge production. The biological method is often more cost effective (US EPA, 1975).

People have studied biological nutrient removal processes from different aspects such as nutrient removal mechanisms (nitrification, denitrification, and phosphorus removal), process alternatives, and process controls. One current area of research interest is the development of automated control systems for bio-nutrient removal processes. In a process such as that shown in Figure 3.1, the aerobic zone is nitrate rich because of the nitrification. When denitrification is required, it is necessary to recycle the mixed liquors from the aerobic zone to the anoxic zone, because denitrification will occur in the anoxic zone. It is important to have good control of the denitrification process in the anoxic zone to guarantee that no significant quantity of nitrate is recycled from the anoxic zone to the anaerobic zone by the anoxic recycling line. Nitrates could jeopardize the favourable conditions necessary for phosphorus removal in the process. It is generally realised that detection of nitrate concentrations in the anoxic zone is an important step in overall

process control.

Since nitrate probes are very expensive and are far from problem free when used in sewage treatment plants, indirect measures of nitrate presence are potentially useful. Previous research indicated that oxidation reduction potential (ORP), or redox value, might be able to be used as a control parameter. ORP probes are sensitive to the nitrate couple, commercially available and inexpensive.

The first part of this research involved the testing of individual probes for suitability. ORP probes were tested in quinhydrone buffer solutions and evaluated by comparing the measured values to the standard values of each buffer solution.

In the second part of this thesis, biological systems were used in batch tests to investigate the possibilities of the redox measurement in a bio-nutrient removal process. The effect of different initial nitrate levels and different denitrification rates on redox values, in complete denitrification conditions, were studied.

As a result of the data generated, testing procedures for ORP probes were recommended.

Chapter 2

LITERATURE REVIEW

2.1 Oxidation-Reduction Potential Measurement

Oxidation-reduction potential measurement determines the ratio of oxidants to reductants within a solution. It is different from pH measurements because it is non-specific with respect to any one compound. What the ORP electrode pairs test is the prevailing net potential of a solution. This measurement makes it possible to determine the ability to oxidize or reduce a given species in the solution (ASTM, 1983).

Equation (2.1) is used to describe the oxidation reduction potential of a process solution:

$$E_m = E_0 + \frac{RT}{nF} ln \frac{A_{ox}}{A_{red}} \tag{2.1}$$

E_m = the measured oxidation reduction potential relative to a reference half cell (mv).

E_0 = a constant that is dependent to the choice of reference electrode (mv).

R = universal gas constant (8.314 joules/deg - mole).

T = absolute temperature (^oC + 273.15).

n = number of electrons involved in the process reaction.

F = Faraday constant (96,464 joules/volt).

A_{ox} and A_{red} = activities of the oxidants and reductant participating in reactions.

More detailed redox theory can be found in Petersen (1966), Bates (1973), Broadley (1990), and Wareham (1992).

Wareham (1992) described typical bacterial electron and energy transport chains, and gave a good picture of the redox measurement from the microbial level. His description indicated that the external ORP value directly reflected the activity of the biological materials in the system at the cellular level. His belief in the correlation between a particular ORP value and a given bacterial population agreed with the work of Whitfield (1969).

The ORP electrode actually consists of an indicating electrode and a reference electrode. The indicating electrode is made of a noble metal; platinum, gold, and silver are among the commonly used. This electrode is constructed in such a way that only the noble metal is in contact with the test solution. The contact area should be about 1 cm^2 (ASTM, 1983). A reference electrode can use a calomel, silver/silver chloride, or other electrodes which have a constant potential. Descriptions of how ORP probes function are presented in ASTM (1983), Coleman (1987), and Wareham (1992).

According to ASTM (1983), ORP electrodes generally are not subject to solution interference from colour, turbidity, colloidal matter and suspended matter, and so are ideally suited to applications in wastewater treatment processes where the above interferences are commonly encountered with nitrate probes.

Temperature and pH will change the measured ORP of an aqueous solution. In most situations, temperature correction is not done because of its minimal effect and complex nature. Variations in pH are taken into consideration only when the oxidation reduction reaction involves either hydrogen or hydroxyl ions.

ASTM (1983) recommended ORP electrode cleaning procedures, and suggested that as much as a 10 mv difference between the experimental readings and the published standard solution values would be acceptable.

2.2 The Application Possibilities of ORP Measurement

The application possibilities of ORP measurement have been researched by Rohlich (1948), Hood (1948), Eckenfelder and Hood (1951), and Nussberger *et. al* (1953).

Rohlich (1948) questioned the usefulness of exact potentials in aerobic and anaerobic zones because the measured ORPs were quite different from one treatment plant to another, and among probes used in the same tank of a given plant, but he believed that ORP vs time curves could be useful in operational control of a sewage treatment process.

Nussberger (1953) generated some ORP-time curves for various activated sludge systems. He intended to use them as guidelines to indicate whether the process was underloaded or overloaded, underaerated or overaerated. He concluded that ORP measurement provided a tool to control aeration in the activated sludge process and to control the sewage addition volume at each point in a step aeration process.

In a discussion of the paper by Grune and Chueh (1958), Eckenfelder (1958) mentioned that in experiments to control chlorination of a wastewater containing sulfides, sulfites, and thiosulfates, a sharp break in the ORP-time curve was observed when all the sulphur compounds were oxidized. This is a supportive observation for possible ORP application in automated control systems.

O'Rourke *et. al* (1963) investigated the use of ORP for aiding in the adjustment of the air supply to the point of greatest need during periods of heavy organic loads. In this case, the ORP electrode was used in the aeration basin.

Harrison (1972) argued that overall redox potential was of little value in studies of growing microbial cultures because of the complexity of the biological system.

The use of ORP has also been researched in the field of fermentation. Because of the difficulties in measuring the very low DO (dissolved oxygen) concentrations in an aerobic microbial fermentation process by the use of DO probes, ORP probes have received more

attention as a measurement tool to get information about the system. Kjaergaard (1977) concluded that the redox potential was significantly dependent on the concentration of dissolved oxygen. He also pointed out that it was not possible to "put forward any general laws concerning the exact changes that take place in the redox potential during microbial growth, but the qualitative changes are well known".

Radjai *et. al* (1984) noted, in his research on optimizing the production of amino acids such as homoserine, lysine and valine, that specific ORP values generally corresponded to the optimum production rate of the amino acid.

2.3 ORP as a Control Parameter in Waste Treatment Processes

The application of ORP as a control tool in waste treatment processes has been discussed by several researchers.

Poduska and Anderson (1981) noted a high positive ORP value ($\geq$ +100 mv) when there was an effective control on hydrogen sulphide odours developed in lagoons storing aerobically digested sludge. A platinum redox electrode with a pH/millivolt meter was used in their research.

Eilbeck (1984) found that the detection of the redox breakpoint (a marked increase of about 400 mv) was helpful in deciding chlorination dosage rates to achieve residual chlorine in the wastewater treatment effluent. He used a gold electrode measured with reference to a saturated KCl calomel electrode.

Watanabe *et. al* (1985) found that ORP was an effective index for controlling the methanol feed rate to achieve a good denitrification rate in a biological single sludge pre-denitrification process. The results indicated that by maintaining an ORP of -150 $\pm$ 15 mv (the electrodes used were not identified in the paper) to manipulate the methanol feed rate, the effluent NO_x was maintained below 1 mg/L with variations in the influent

flow rate and influent concentrations of NO_x and COD (chemical oxygen demand).

The research of De la Menardiere *et. al* (1991) was conducted at a full scale activated sludge system in France. The plant consists of two tanks in series, a non-aerated tank followed by an aerated tank. There is a sludge recycle from the secondary settler to the non-aerated tank. It was found that in the non-aerated tank, when ORP values were in the range of -230 to -100 mv (referring to a conventional hydrogen electrode), phosphate release was at a high level of 60 mg/L (as PO_4^-), while an absence of nitrate was observed. In the aeration tank, "correct setting of ORP regulation limits has proved an essential operation parameter to ensure good simultaneous C, N, and P removal".

ORP's application in aerobic sludge digestion systems was researched by Peddie *et. al* (1988). It was observed that the ORP profile was reproducible with the cycled operation of alternating aerated and non-aerated conditions in the aerobic digesters. The slope changes of the ORP profile clearly defined the range of aerobic and anaerobic respiration and fermentation.

Wareham (1992) used the distinctive breakpoint occurring in the ORP-time profile and correlated it to nitrate disappearance to control his aerobic/anoxic sludge digestion system. He also used the ORP breakpoint to control the addition of sodium acetate to the reactor in his biological phosphorus removal experiments.

2.4 ORP Monitoring in Bio-nutrient Removal Processes

The development of biological nutrient removal processes resulted in a significant increase of interest in ORP research. Comprehensive literature reviews of bio-phosphorus removal have been presented by Siebritz *et. al* (1983), Comeau (1984, 1989) ,and Rabinowitz (1985). The information related to nitrogen removal such as biological nitrification and denitrification can be found in U.S. EPA (1975), and Metcalf and Eddy Inc. (1979).

A significant piece of work about the usefulness of ORP monitoring in the bio-P removal process was done by Koch and Oldham (1985). Based on a series of laboratory batch experiments, the correlation between a breakpoint in redox-time curves and the end of denitrification activity was found. They also discovered a second breakpoint in the ORP-time curve indicating the end of aerobic activity. ORP values observed from this research were reported over a range of -40 to -140 mv (using a platinum sensor with an Ag/AgCl reference electrode) for complete nitrate disappearance conditions. More precise ORP values in complete denitrification conditions were not concluded in the report.

Koch *et. al* (1988) also conducted ORP monitoring in a continuous flow bio-nutrient removal process. Efforts were made to look for relationships between ORP values and nitrate concentrations in the anoxic reactor, and ortho-phosphate concentrations in both anoxic and anaerobic reactors. Several relationships were formulated between ORP and dissolved oxygen, nitrate and phosphate concentrations. However, only qualitative conclusions were given at the end of the paper.

This thesis investigated the approach of using measured ORP values as a control tool in a bio-nutrient removal process.

Chapter 3

EXPERIMENTAL DESCRIPTION

3.1 Research Objectives

The purpose of this research was to investigate the method of using ORP monitoring to assess the completeness of denitrification in the anoxic zone of a bio-nutrient removal process (such as the one shown in Figure 3.1). Since the collected ORP values represent the characteristic combination of both the probe individuality and the tested chemical or biological system, examinations of probes and their applications in monitoring a biological denitrification process are both conducted.

The first objective of this research was to determine if a probe's individual characteristics need to be considered when the ORP values collected from biological batch tests were evaluated.

A group of ten probes were tested in a series of quinhydrone buffer solutions whose standard redox values were pre-determined, and were different. The measured redox values were compared with the standard values to determine the significance of the probes' individual characteristics. The necessity of adjusting the measured redox values is discussed in conjunction with the evaluation of the biological batch results.

The second objective of this research was to determine if ORP values collected from batch tests can be used as indicators of the biological denitrification process. The batch tests were designed to stimulate the biological system in the anoxic zone. Mixed liquors from the aerobic zone, anaerobic zone, and sludge return line were all present in the

batch test system. The initial nitrate concentrations and the denitrification rates in the tested batch system were designed to be variable. Their impact on ORP values tested in complete denitrification conditions are used as an approach to assess the application possibility of ORP monitoring.

3.2 UBC Bio-nutrient Removal Process Introduction

3.2.1 Process scheme

The biological mixed liquor used in experiments was collected from the bio-nutrient removal process of the UBC pilot plant. Figure 3.1 shows the process configuration.

The pilot plant is situated close to the UBC campus, in Vancouver, B.C.. The influent sources include student residences, campus housing, and the university sports centre. The wastewater is pumped into two plastic storage tanks, each with a capacity of 9000 L. Sodium bicarbonate was added daily to the storage tanks to increase sewage alkalinity by about 100 mg/L (as $CaCO_3$) , because wastewater in the Vancouver area is low in alkalinity (80 - 120 mg/L as $CaCO_3$), and hence poorly buffered.

The influent first passes into an upflow fermenter with a flow rate of 2.5 L/min. The fermenter has a volume of 400 L. No solids wasting or mixing was conducted in the fermenter during the time when experimental work was performed for this thesis. The fermented effluent is then fed into the anaerobic zone of the bio-reactor. The 2500 L volume rectangular bio-reactor is divided into three zones. They are an anaerobic zone (1/7), an anoxic zone (2/7), and an aerobic zone (4/7).

There is a mixed liquor recycle from the anoxic zone to the anaerobic zone which is performed at a flow rate of 2.5 L/min. Volatile fatty acid (VFA) is added into the anaerobic zone to enhance the bio-phosphorus removal. The VFA feeding rate is 7 mL/min.

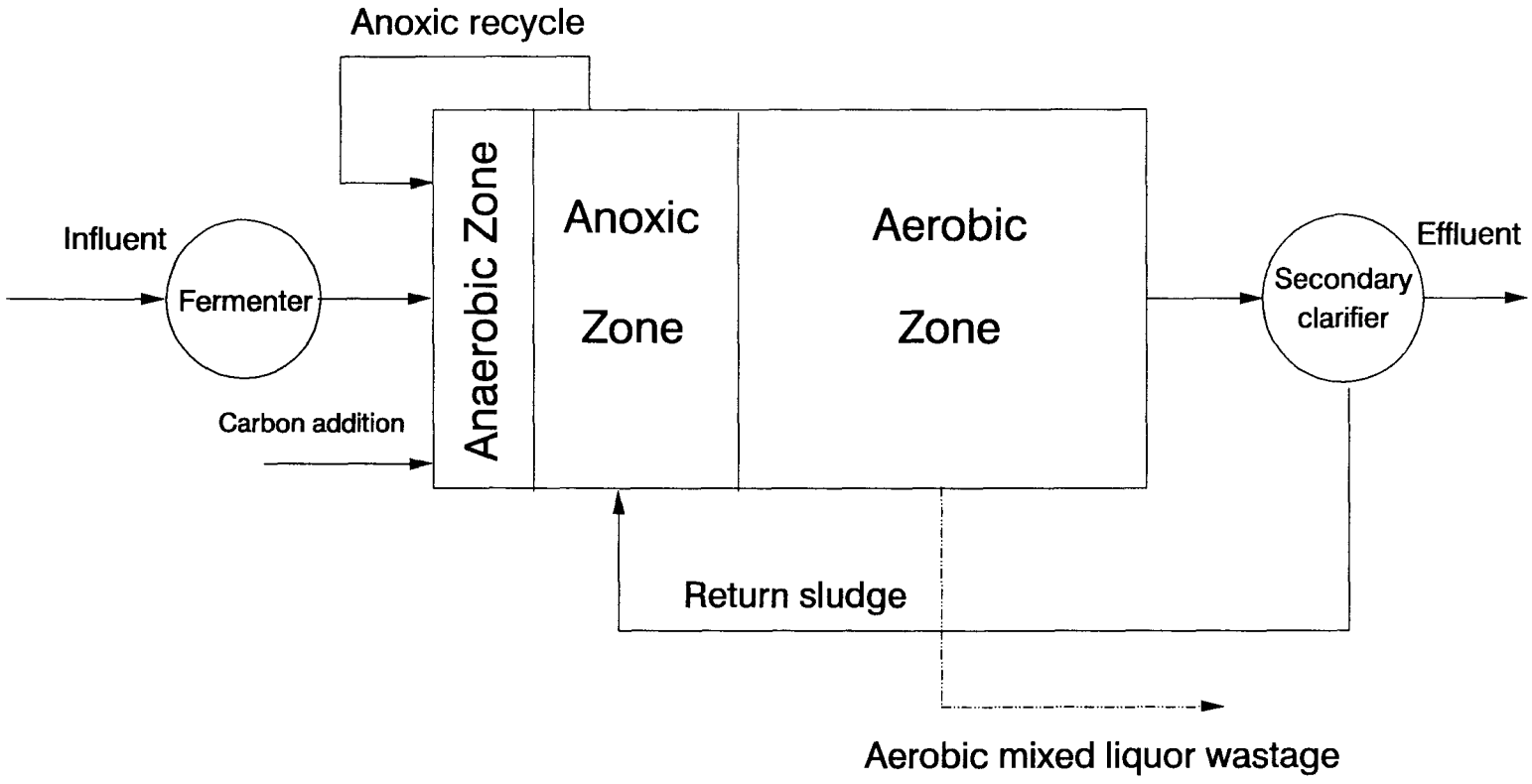


Figure 3.1: UBC bio-nutrient removal process

The strength of the VFA stock solution was 3290 mg/L as acetic acid (HAc). The concentration of HAc added to the influent therefore averaged 9.2 mg/L. There was no mixed liquor recycle from aerobic zone to anoxic zone when the experimental part of this thesis was being performed. The anaerobic and anoxic zones were kept completely mixed with mechanical mixers.

In the aeration zone, coarse bubble aeration through header pipes provides aeration and thorough mixing conditions. The dissolved oxygen (DO) concentration in the aerobic zone was maintained at 2 - 3 mg/L. The mixed liquor from the aerobic zone is wasted at the rate of 110 L per day.

The process ends up in a 500 L secondary clarifier. The sludge is returned from the bottom of the secondary clarifier to the anoxic zone at a flow rate of 2.5 L/min.

3.2.2 Process mechanism

The UBC pilot plant process, as shown in Figure 3.1, did not have the mixed liquor recycle from the aerobic zone to the anoxic zone when this research was conducted. The nitrate concentration was high in the aerobic zone where organic nitrogen and ammonia in the influent were converted into nitrate by nitrification. A mixed liquor recycle from the aerobic zone to the anoxic zone is needed to facilitate the UBC process with efficient nitrate removal. Nitrate can be removed in oxygen-free conditions by denitrification in the anoxic zone.

It is essential to have complete denitrification in the anoxic zone, so as to achieve efficient phosphorus removal in the process when both the aerobic recycle (from the aerobic zone to the anoxic zone) and the anoxic recycle (from the anoxic zone to the anaerobic zone as shown in Figure 3.1) are present. If the residual nitrates in the anoxic zone entered the anaerobic zone by the anoxic recycle line, the denitrifiers would be able to grow in the anaerobic zone by utilizing the easily available volatile fatty acid provided

by the fermenter. The competition between denitrifiers and phosphate accumulators for the available simple carbon substrate would have a negative impact on phosphate accumulators. If nitrates in the anoxic zone continued to enter the anaerobic zone, phosphate accumulating organisms would be reduced in number, and the phosphate removal process would be jeopardized (Oldham, 1988). It is important to have complete denitrification in the anoxic zone to facilitate efficient phosphate removal.

3.3 Experimental Set-up

3.3.1 Data log-in system

Oxidation reduction potentials were collected by the use of a log-in system called REMDACS (Remote Data Acquisition and Control System). The system included a 10 channel connection board, a set of high impedance instrumentation amplifiers, a multi - channel 12 bit analogue to digital converter, and a microcomputer as shown in Figure 3.2. ORP data were collected continuously from as many as 10 channels simultaneously. The resolution was 0.5 mv. Data collected from scanned channels were recorded on disks in formatted blocks in digital form for subsequent evaluation and analysis.

3.3.2 QBASIC program

A QBASIC program was used in the data log-in system. Users could set file names, the channel scan rate, and the experimental run-time. The channel scan rate decided how frequently the ORP was to be collected. For each scan interval, the user could decide whether to record an averaged value or to record an instantaneous value. Users could also record the initiating time of each channel. Data log-in termination could be preset. The data files could be imported into Lotus 1-2-3 for analysis and evaluation.

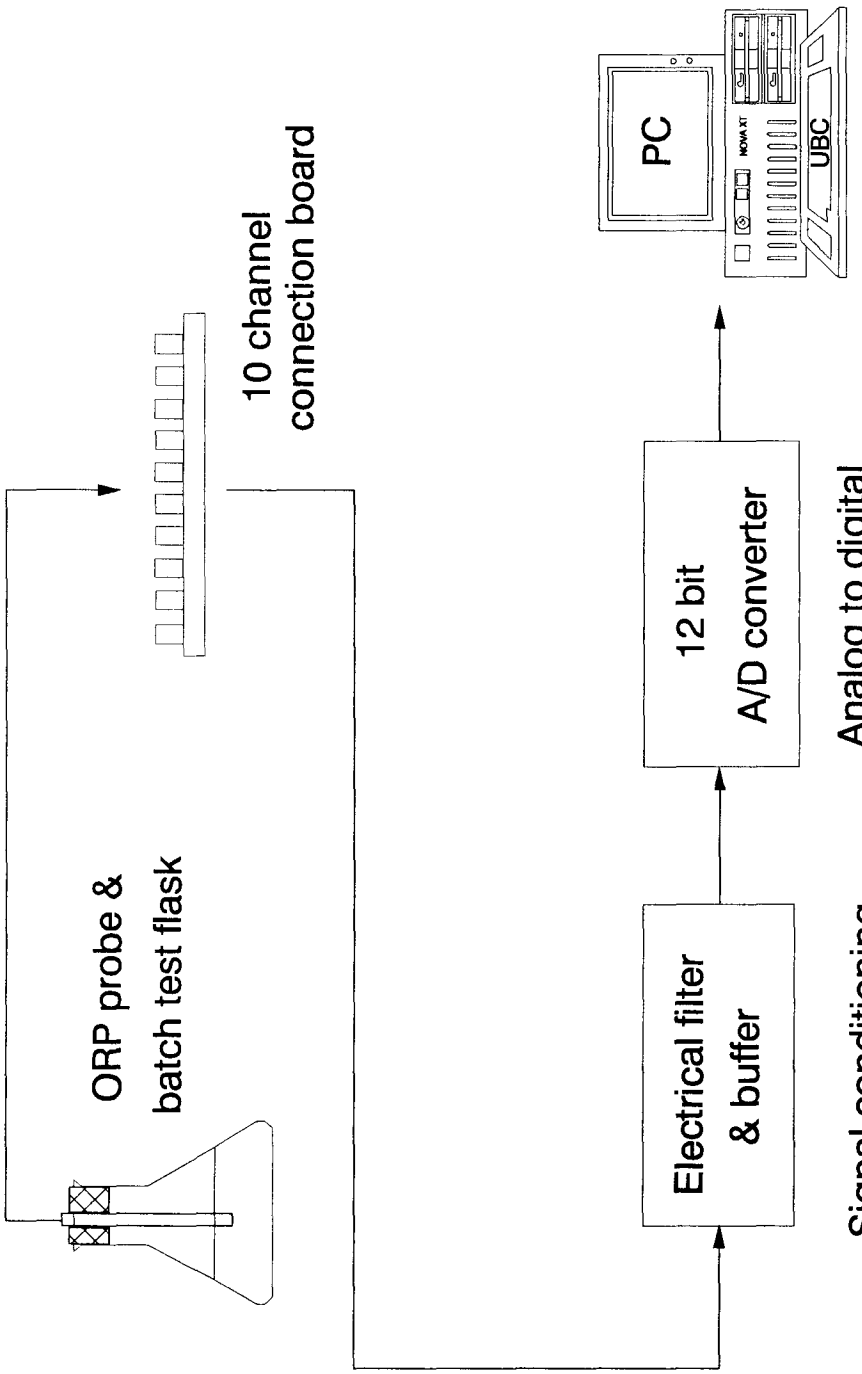


Figure 3.2: Data log-in system scheme

3.3.3 Batch testing apparatus

The testing apparatus used in this research is shown in Figure 3.3. Erlenmeyer flasks of 2.8 L capacity were used in all batch tests. Each flask was sealed with a rubber stopper which was fitted with a rubber septum. Rubber balloons filled with nitrogen were attached to syringe needles which were pierced through the septum. When sampling started, nitrogen was displaced from the the balloon with positive pressure, and pushed the mixed liquor out of the flask through a sampling tube which was inserted through the stopper and went down to the bottom of flask. Nitrogen that replaced any liquid withdrawn from the flask kept an inert atmosphere above the liquid to prevent air leakage into the flask. The septum was also used for the injection of chemicals. Each flask had a magnetic stirrer to insure complete mixing condition during the course of the experiment.

Each flask was fitted with two ORP probes which were attached to plastic tubes and inserted in the stopper. Duplicate measurements provided direct confirmation of ORP values. The collected mixed liquor samples were filtered and refrigerated before analysis. All experiments were conducted at ambient room temperature. No pH adjustment was applied in the experiments, but pH and temperature were monitored.

3.3.4 ORP probes and probe maintenance

The ORP probes used in this research were supplied by the Broadley James Corporation, as shown in Figure 3.4.

The probe has a 1/8 inch platinum ring located near its tip. The noble metal accepted and donated electrons, but did not participate in other oxidation/reduction reactions in the tested system. The reference electrode was a silver metal strip coated with solid AgCl, and the Ag/AgCl electrode was immersed in KCl solution. Based on the solubility product principle as shown in Equation (3.1), the concentration of the cation associated

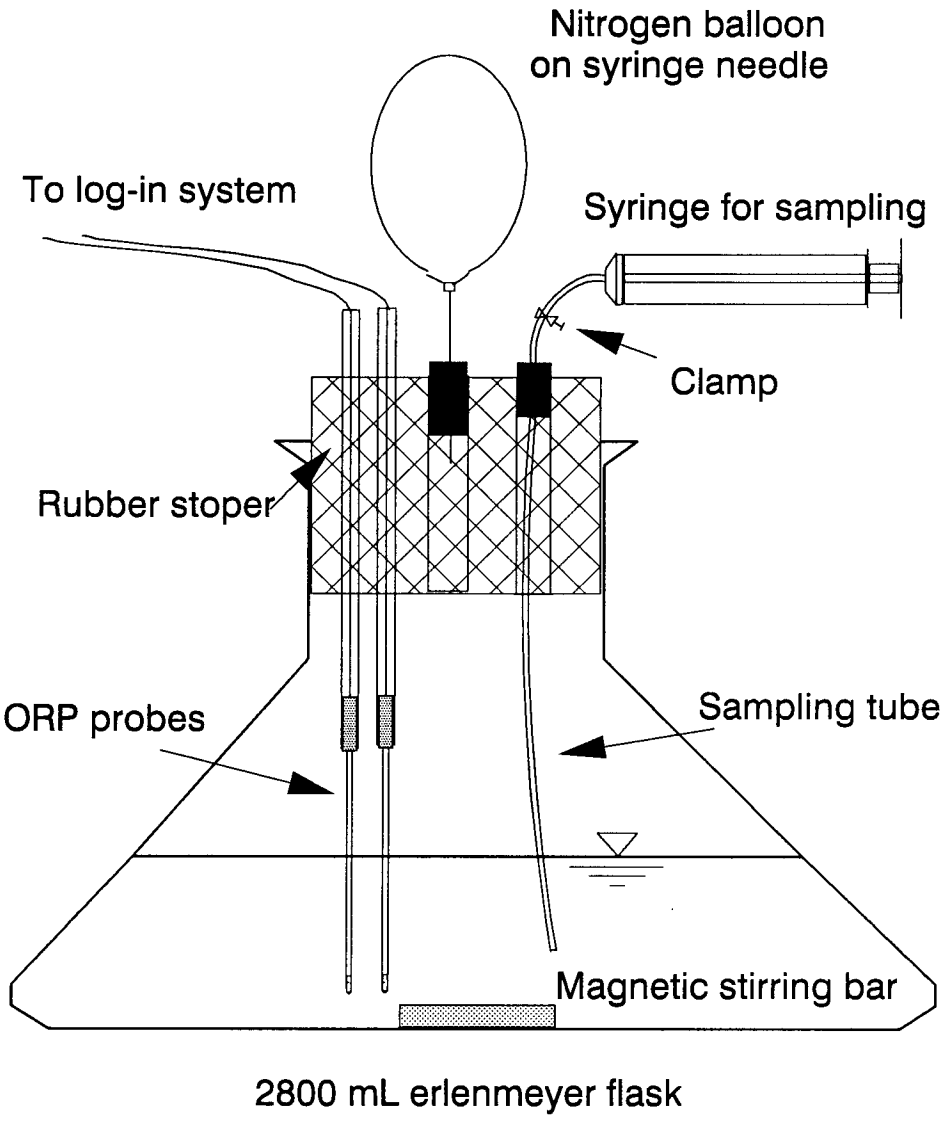


Figure 3.3: Batch test apparatus

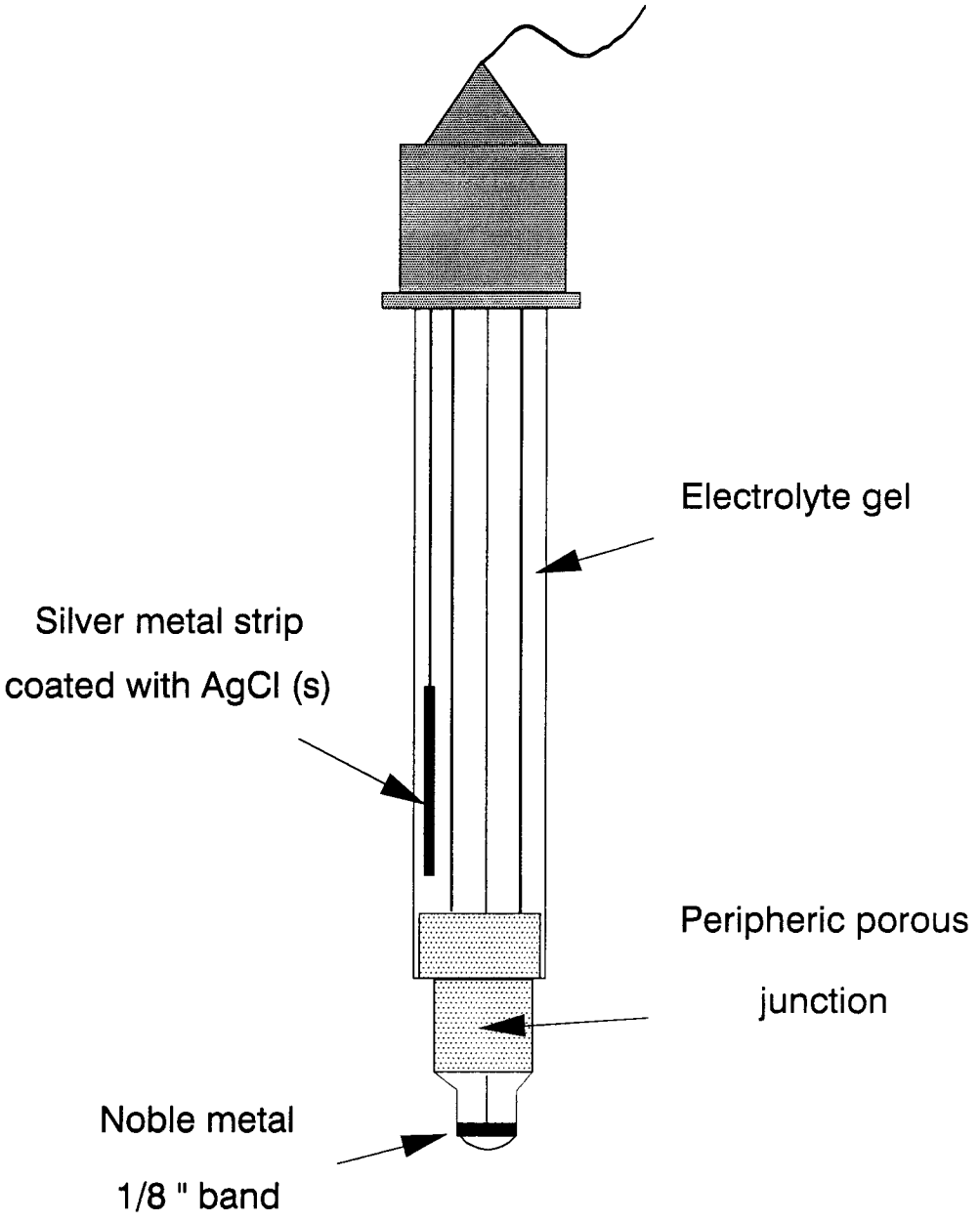


Figure 3.4: ORP probe

with the electrode metal was kept constant, therefore the reference electrode potential had a fixed value (Wareham, 1988).

$$Ag(s) + Cl^- \rightleftharpoons AgCl(s) + e \tag{3.1}$$

The ORP measured by the probe was the electro-motive force (emf) difference between the ORP metallic indicating electrode and the reference electrode. All ORP values shown in this thesis are therefore relative to the Ag/AgCl electrode. Probes were cleaned with a distilled water rinse after each test to remove any chemical and biological impurities. Between experiments, probes were kept in storage boots which were filled with 2M KCl (Broadley, 1990).

3.4 Analytical Parameters and Techniques

3.4.1 NO_x (NO_3^- and NO_2^-)

NO_x is a comprehensive measure of both NO_3^- and NO_2^- in a sample. It is the most important parameter in assessing a biological denitrification process. NO_x monitoring in batch tests can inform researchers about the biological denitrification process in flasks. Samples were filtered through Whatman #4 filter paper, then analyzed by the Lachat Quickhem AE auto-analyzer (automated cadmium reduction method) (Lachat, 1988. APHA, 1989). The detection limit was 0.05 mg/L (as NO_3^--N). The instrumental calibration solutions' concentrations ranged from 0.05 mg/L to 20.0 mg/L.

3.4.2 MLSS and MLVSS

MLSS stands for mixed liquor suspended solid, which is the nonfilterable residue that remained on the filter after evaporation and dried to a constant weight at 104 ^oC. MLVSS (mixed liquor volatile suspended solid) is the volatile residue, and is determined by

igniting MLSS at 550 ^{o}C (APHA, 1989). MLSS is an indicator of sludge concentrations in the system. MLVSS can be used to estimate live bacteria in the system (Metcalf & Eddy, 1979).

3.4.3 pH

The ORP of an aqueous solution is sensitive to pH variation when the oxidation/reduction reaction involves either hydrogen or hydroxyl ions. The ORP generally tends to increase with an increase in H^+ and to decrease with an increase in OH^- during such a reaction (ASTM, 1983). Bacteria are sensitive to pH conditions too. The pH was tested throughout experiments by the use of a Cole-Parmer Digi-sense pH meter.

3.4.4 Temperature

The redox potential is dependant on temperature, and all measurements should include a temperature reference to specify the testing conditions (Petersen, 1966). Temperatures were tested by the use of the same Cole-Parmer Digi-sense pH meter.

3.4.5 Chemical oxygen demand

Chemical oxygen demand (COD) was used as a measurement of the laboratory made carbon stock solution (NaAc). The COD analysis was conducted in accordance with Standard Methods (APHA, 1989).

3.5 Data Analysis Techniques

Lotus 1-2-3 (version 2.2) by Lotus Development Corporation was used for the data analysis. Freelance (version 3.01) by Lotus Development Corporation was used for plotting results.

Chapter 4

RESULTS

Experimental results are presented in three groups. Part one is probe testing results, part two is biological batch tests with varied initial nitrate concentrations, and part three is batch tests with external carbon additions (to create varied denitrification rates).

4.1 Probe Testing Results

4.1.1 Introduction

The purpose of probe testing was to verify the reliability of direct values from probes, to determine if the probe tested yielded the true ORP values of the tested solutions. A group of ten probes was tested in quinhydrone buffer solution at the same time, although only four of them were going to be used in batch tests.

The substance quinhydrone is an equimolar compound of benzoquinone (OC_6H_4O), and hydroquinone (HOC_6H_4OH). Quinhydrone is slightly soluble in water (ASTM, 1983). The benzoquinone and hydroquinone, which are referred to as Q and H_2Q respectively, form a reversible oxidation reduction system with hydrogen ions.

$$H_2Q \rightleftharpoons Q + 2H^+ + 2e \tag{4.1}$$

Buffer solutions saturated with quinhydrone have stable oxidation reduction potentials. Nominal millivolt redox values for these reference solutions at various temperatures

Table 4.1: Nominal ORP values of reference quinhydrone solutions

Buffer solution pH	4			7		
Temperature (^{o}C)	20	25	30	20	25	30
ORP (mv)	268	263	258	92	86	79
Reference electrode: silver/silver chloride						

Table 4.2: Buffer solutions' compositions

pH	6	8	9
$N_aH_2PO_4$ (mL)	8	1	0
$N_{a2}HPO_4$ (mL)	2	9	10

are given in Table 4.1 (ASTM, 1983). Excess quinhydrone was used so that solid crystals were always present in order to have a saturated quinhydrone solution. Quinhydrone was added into buffer solutions immediately before each experiment, since these reference solutions are only stable for about 8 hours (ASTM, 1983).

Six buffer solutions with different pH values ranging from 4 to 10 were used in probe testing. These buffer solutions have different voltage levels so that probe behaviour at different ORP levels can be studied. BDH Chemicals provided the buffer solutions of pH 4, 7, and 10. pH 6, 8, and 9 buffer solutions were made by the combination of 0.1 M sodium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate according to Table 4.2 (Gabb, 1968).

The pH and temperature of the buffer solutions were tested in the experiments. The ten probes were put into the same buffer solution with thorough mixing throughout each test. ORPs collected from each probe were logged into the computer in the rate of one reading every 60 seconds. Each test was conducted for 20 minutes. Experimental results included here were conducted on March 4, 1991, April 4, 1991, and May 7, 1991.

Table 4.3: Experimental conditions for probe test 1

pH	4.03	6.30	7.06	7.78	8.78	9.85
Temperature ($^{\circ}C$)	19.7	20.1	19.5	20.1	20.0	19.4

Table 4.4: Experimental conditions for probe test 2

pH	4.10	6.32	7.11	7.85	8.85	9.94
Temperature ($^{\circ}C$)	20.9	21.1	20.8	19.5	19.4	19.4

4.1.2 Probe test 1 (March 4, 1991)

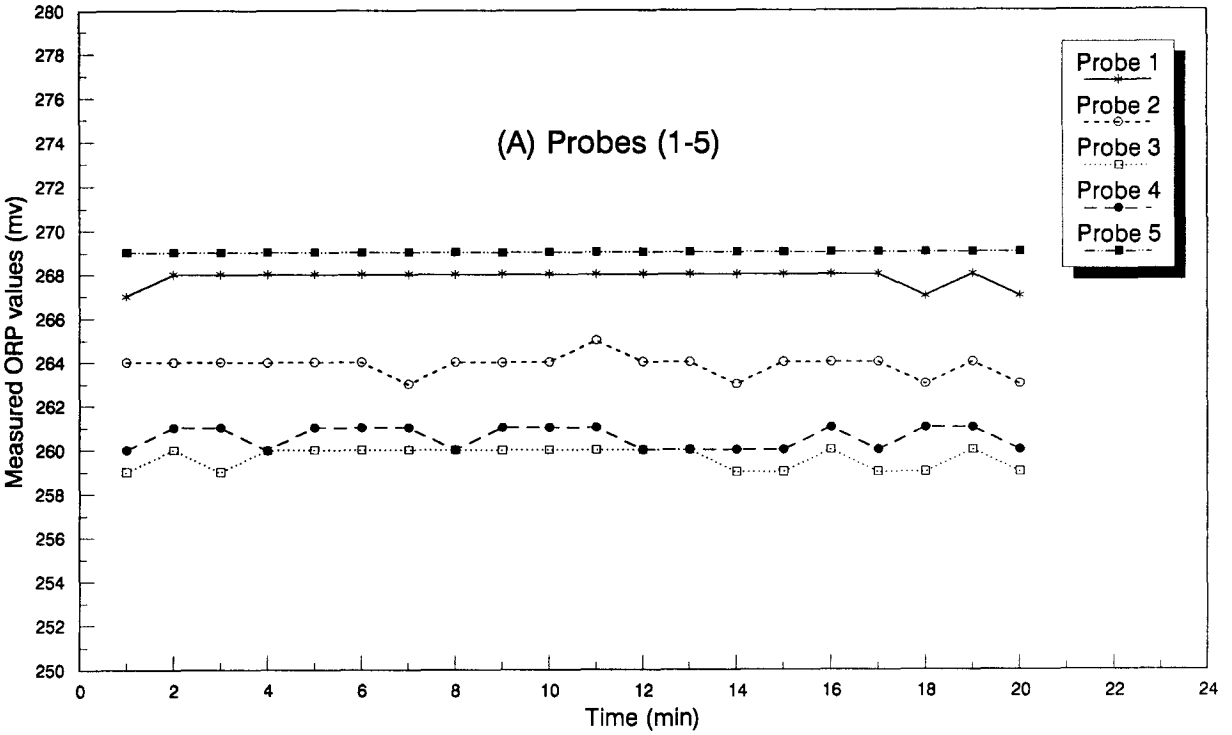
The probe test presented here was done on March 4, 1991. Temperature and pH were monitored during the experiment. It was observed that during the 20 minutes, pH and temperatures of the testing system did not change much, and therefore, are taken as the experimental conditions. The initial test conditions are listed in Table 4.3. The results of probe test 1 are shown in Figures 4.1 to 4.6.

4.1.3 Probe test 2 (April 4, 1991)

Probe test 2 was conducted one month after test 1. The experimental procedures were the same as those which were used in test 1. The repeatability of probe behaviour in buffer solution was tested. Test conditions are listed in Table 4.4. Test results can be found in Appendices A-1 to A-6.

4.1.4 Probe test 3 (May 7, 1991)

Probe test 3 was designed to gather more data for the results analysis. Table 4.5 contains the test conditions of each chemical solution. The test procedures were the same as those in test 2. Test results are listed in Appendices A-7 to A-12.



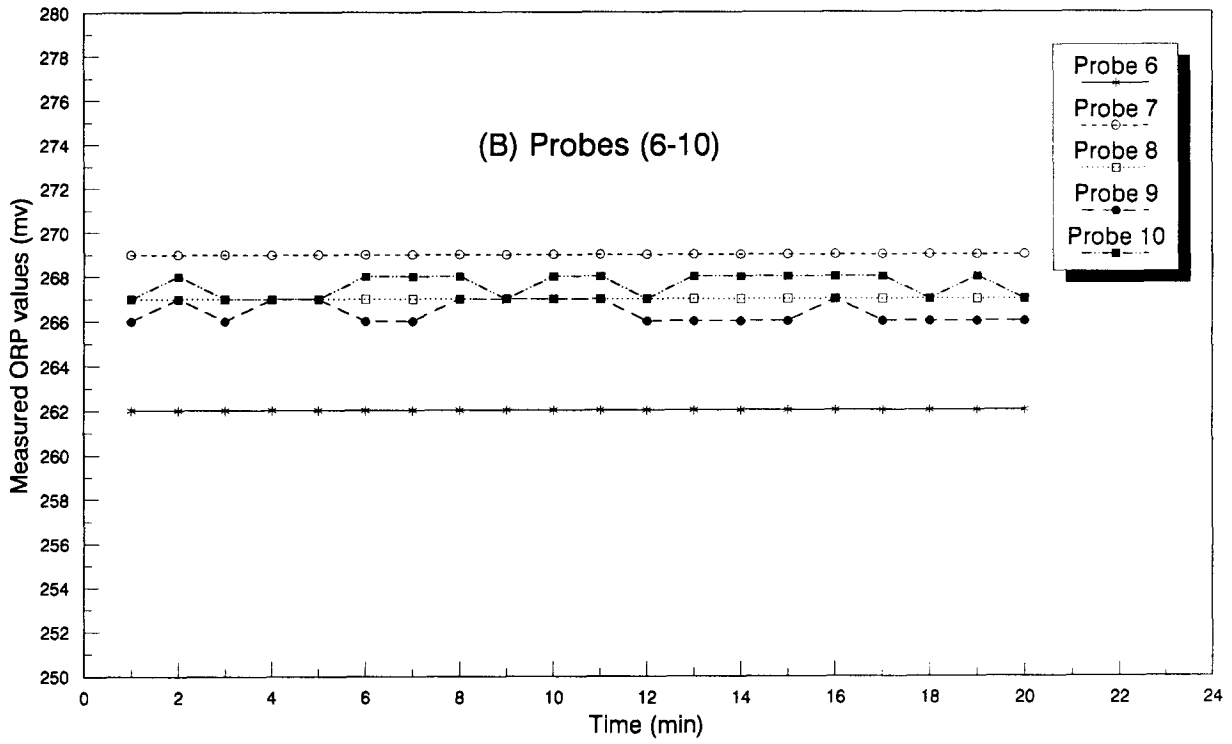
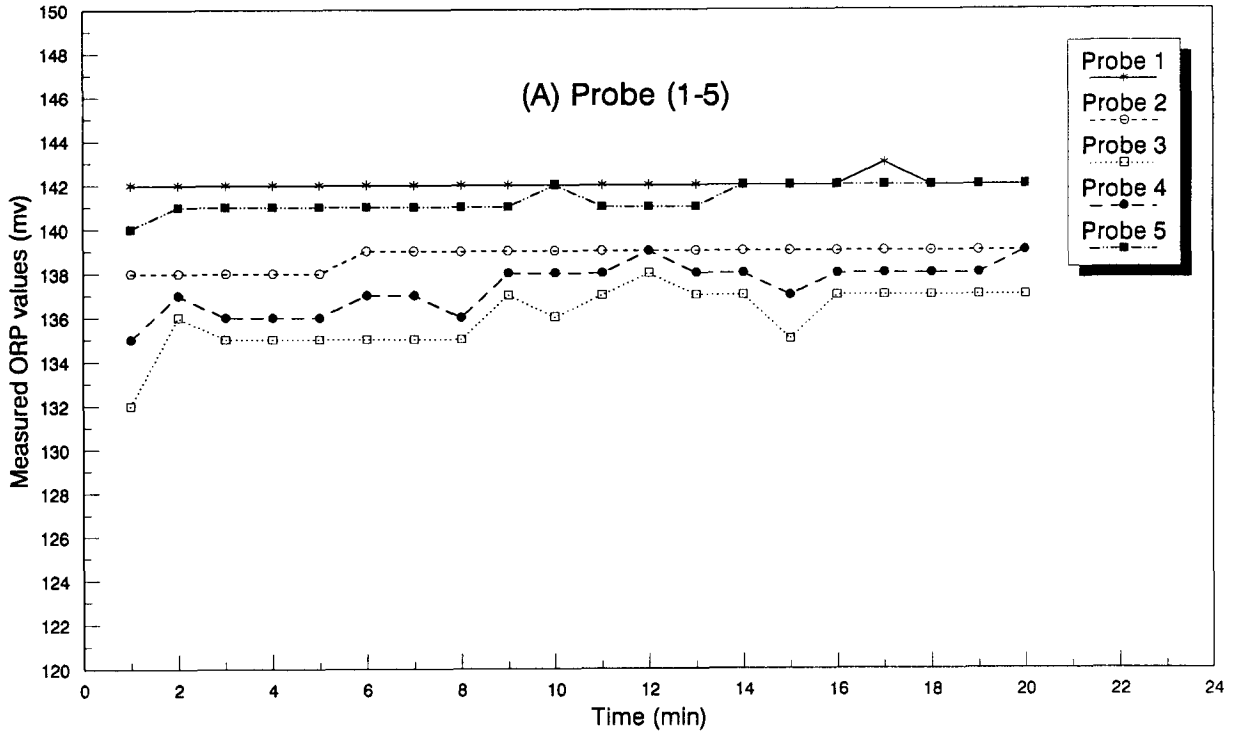


Figure 4.1: Probe test 1.1 (pH 4.03): (A) Probes (1-5). (B) Probes (6-10).



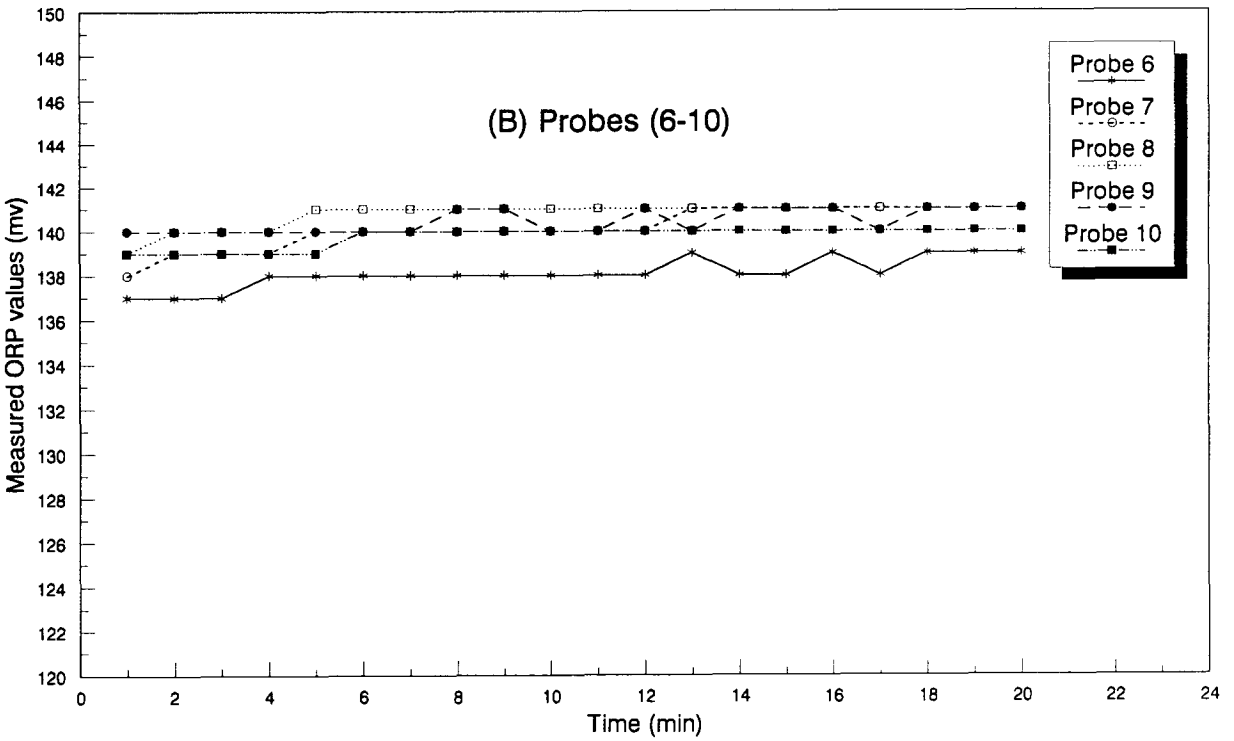


Figure 4.2: Probe test 1.2 (pH 6.30): (A) Probes (1-5). (B) Probes (6-10).

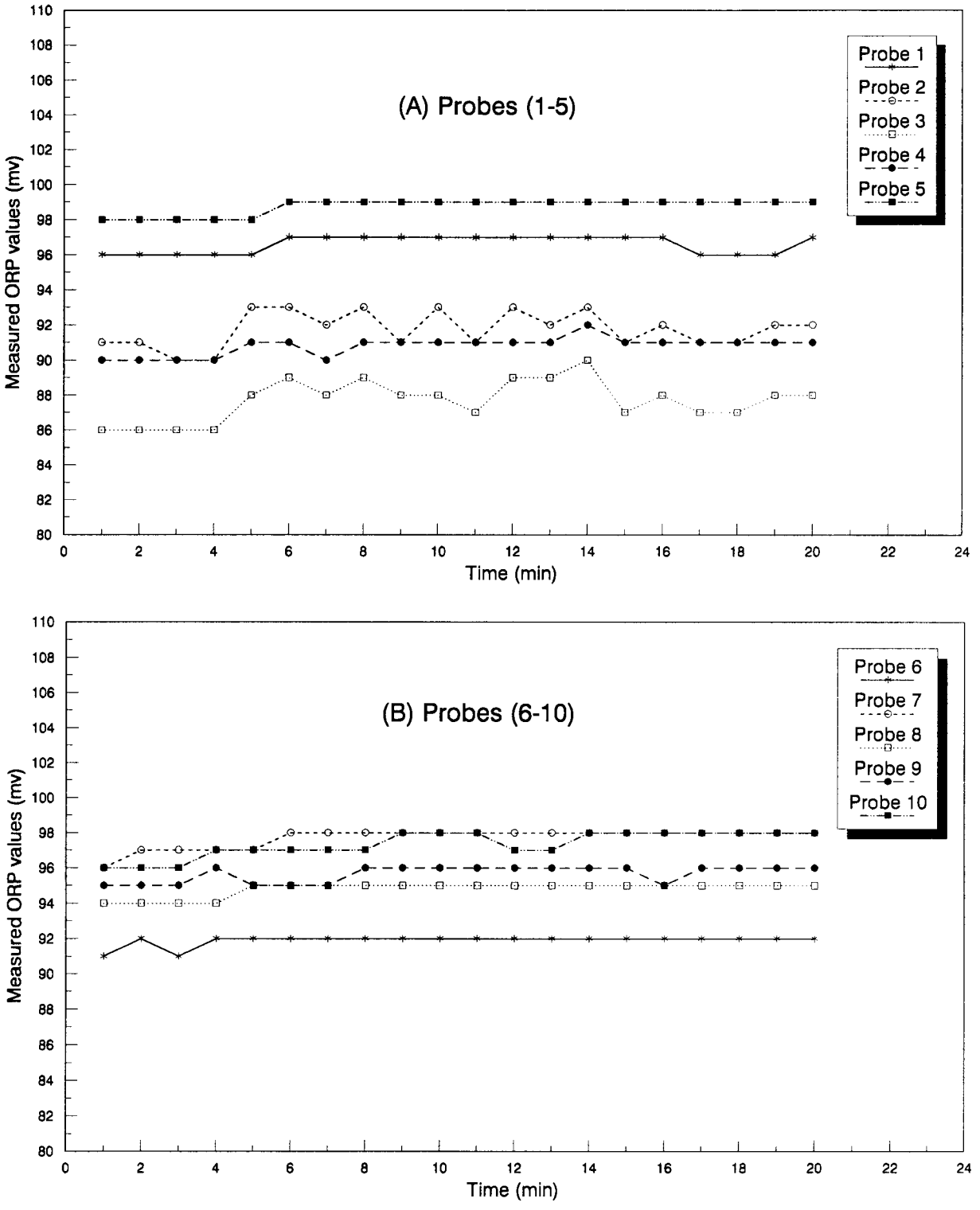


Figure 4.3: Probe test 1.3 (pH 7.06): (A) Probes (1-5). (B) Probes (6-10).

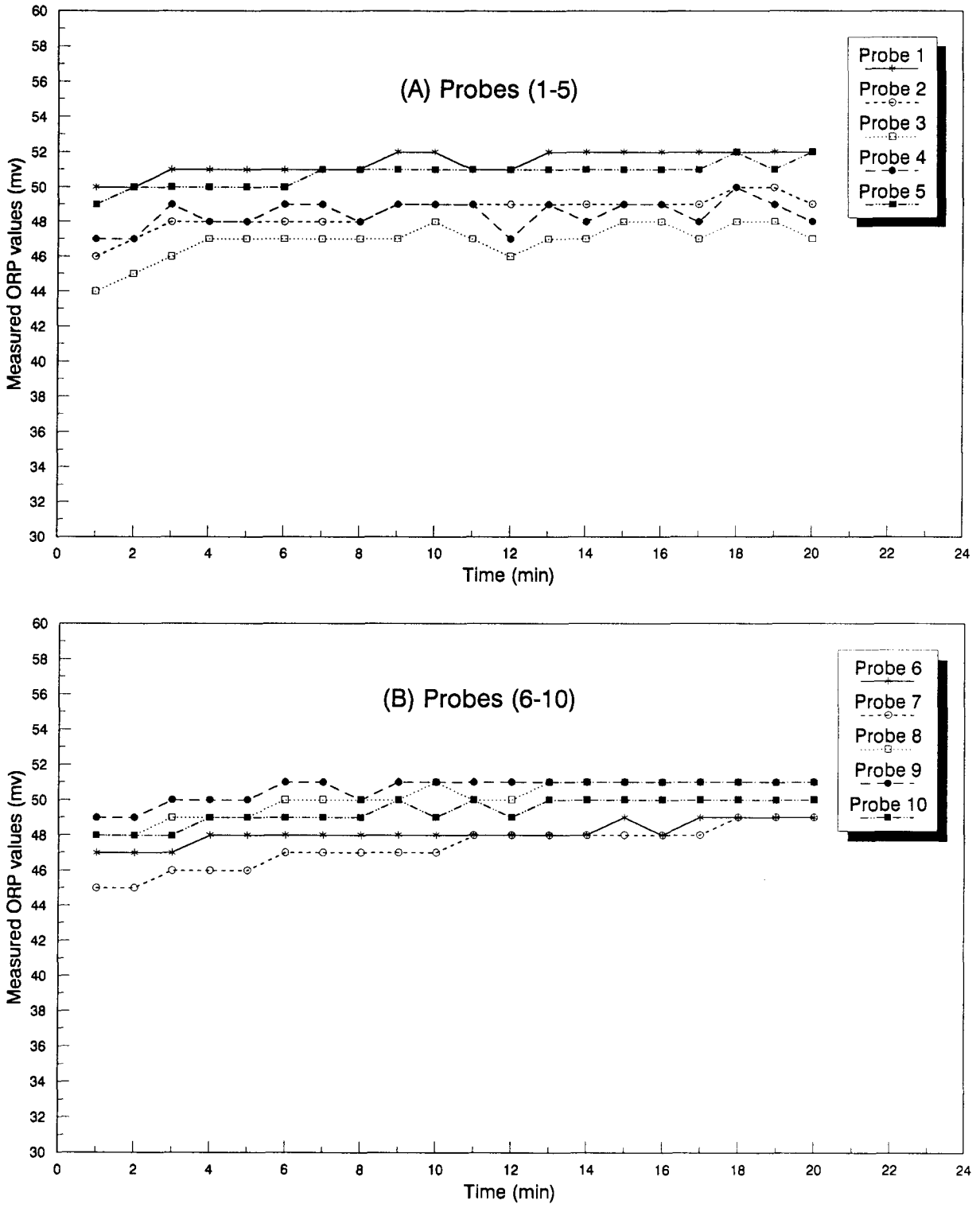


Figure 4.4: Probe test 1.4 (pH 7.78): (A) Probes (1-5). (B) Probes (6-10).

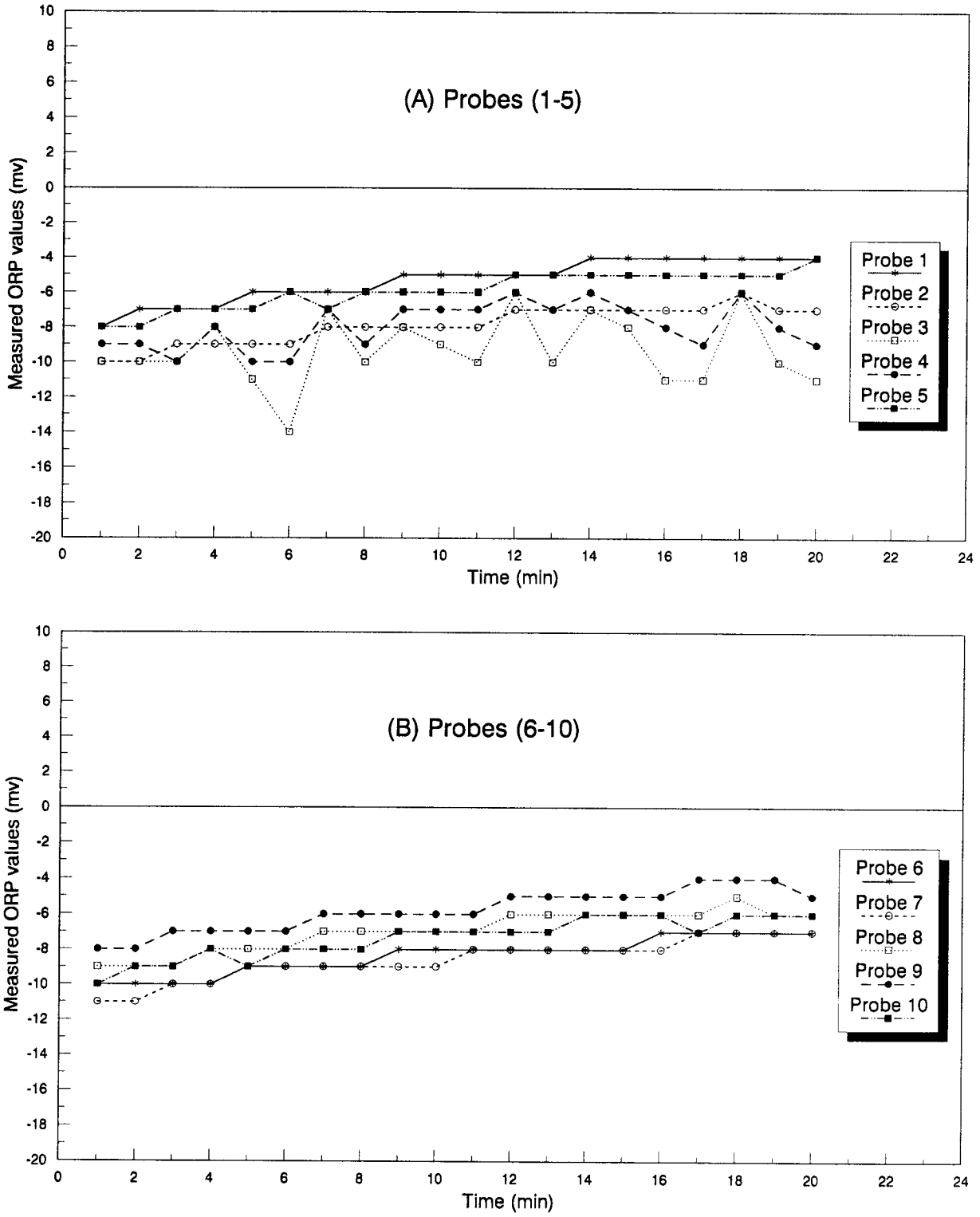


Figure 4.5: Probe test 1.5 (pH 8.78): (A) Probes (1-5). (B) Probes (6-10).

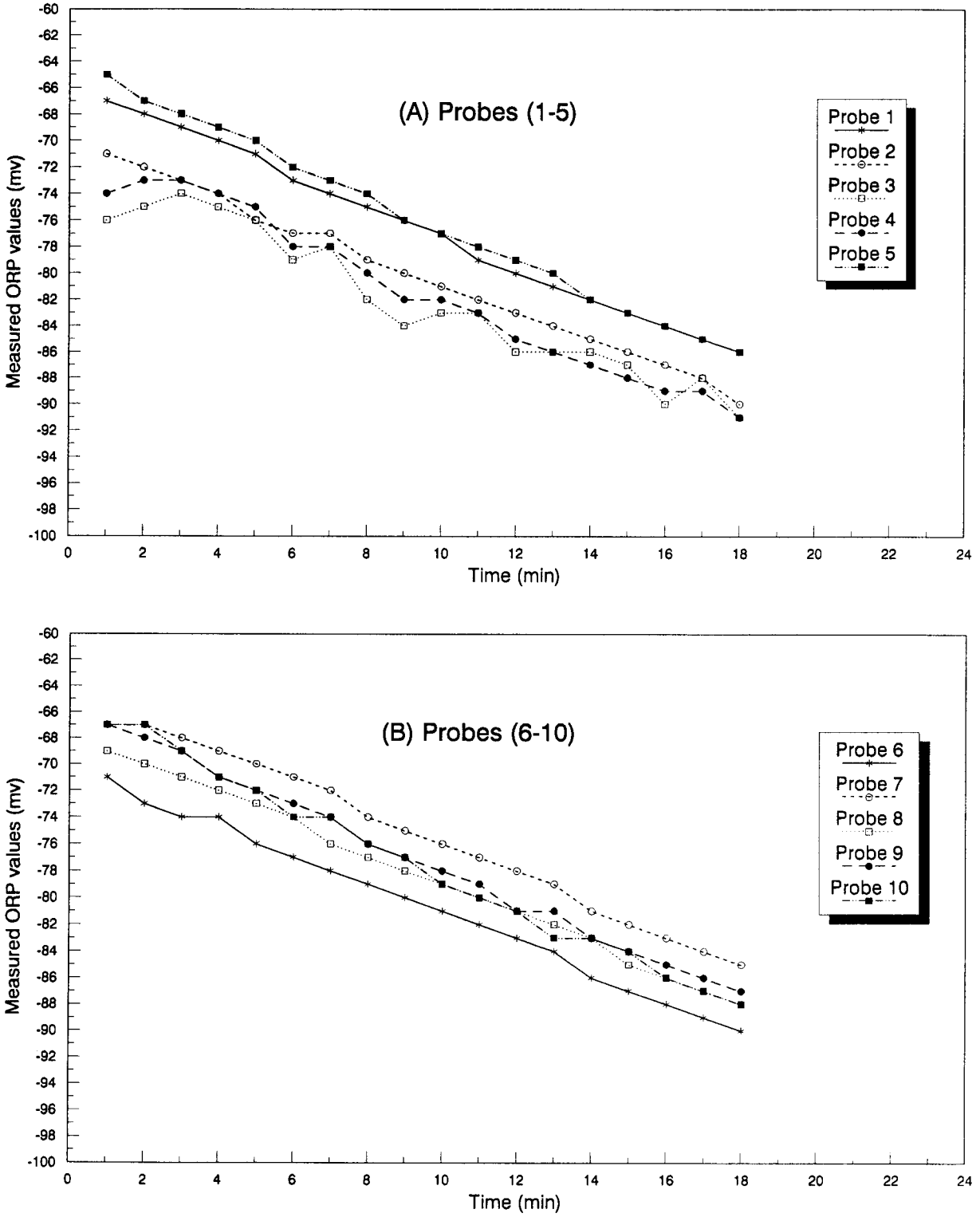


Figure 4.6: Probe test 1.6 (pH 9.85): (A) Probes (1-5). (B) Probes (6-10).

Table 4.5: Experimental conditions for probe test 3

pH	4.06	6.25	7.02	7.75	8.72	9.79
Temperature (^{o}C)	19.1	17.4	18.2	18.8	18.4	18.8

Table 4.6: Mixed liquor combinations

Ratio	Aerobic (mL)	Anaerobic (mL)	Sludge return (mL)
0	0 (0)	1867 (2)	933 (1)
1	700 (1)	1400 (2)	700 (1)
2	1120 (2)	1120 (2)	560 (1)
3	1400 (3)	933 (2)	467 (1)
4	1600 (4)	800 (2)	400 (1)

4.2 Anoxic Batch Tests (Without External Chemical Addition)

4.2.1 Introduction

Anoxic batch tests were designed to exam the impact of initial nitrate concentration on the redox values in complete denitrification conditions. The nitrate levels in the aerobic zone of the UBC process presented in Figure 3.1 was high. The mixed liquor suspensions in the anoxic batch tests were made by combining 2:x:1 volume ratios of mixed liquor contents from the anaerobic zone, the aerobic zone, and the return sludge flow. The variable aerobic mixed liquor ratio (x) was set at values of 4, 3, 2, 1, and 0 respectively in the batch tests to make a total volume of 2800 mL as shown in Table 4.6. In this way, different initial nitrate levels were obtained in flasks.

Temperatures and pH were measured for each sample. It was observed that during the experiments (which usually lasted no longer than 180 minutes), temperatures and pH did not change significantly. The initial pH and temperatures were taken as constant throughout the experiment.

Table 4.7: Process characteristics on March 11, 1991

	NO_x (mg/L)	PO_4^- (mg/L)	MLSS (mg/L)	COD (mg/L)
Influent			49	
Anaerobic zone	0.00	13.92		
Anoxic zone	0.16	8.66		
Aerobic zone	10.27	0.00	2950	
Effluent	10.29	0.05	4	33
30 min settling (mL/L)			910	

The anoxic denitrification experiments presented here were conducted on March 11, 1991, March 21, 1991, and March 28, 1991. No external chemicals were added to the flasks. The biological systems in the flasks were kept oxygen free throughout experiments. Probes 3, 4, 5, and 6 were used in these experiments. Each flask had two probes installed with probes 3 and 4 in one group and probes 5 and 6 in the second group. Sampling frequency was once every 10 minutes. Samples were filtered by Whatman #4 qualitative filter paper and then kept in a freezer until they were analyzed. MLSS and MLVSS were tested for each batch test. Process operation conditions for the experiment days (influent, effluent and process characteristics) were monitored. ORPs were collected at the rate of one sample every 60 seconds. Tests were terminated manually.

4.2.2 Anoxic batch test 1 (March 11, 1991)

Anoxic batch test 1 was conducted on March 11, 1991. Table 4.7 shows the process information for the pilot plant on that day. Experimental conditions for the batch test are listed in Table 4.8. Figures 4.7 to 4.11 are experimental results for ratios 0, 1, 2, 3, and 4 respectively. NO_x analysis results are shown in Figures 4.12.

Table 4.8: Experimental conditions for anoxic batch test 1

Ratio	pH	Temp. (^oC)	MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS (%)
0	7.15	14.3	2563	2190	86
1	7.26	15.2	2690	2280	85
2	7.21	15.2	2510	2150	86
3	7.17	14.4	2583	2145	83
4	7.19	14.1	2460	2067	84

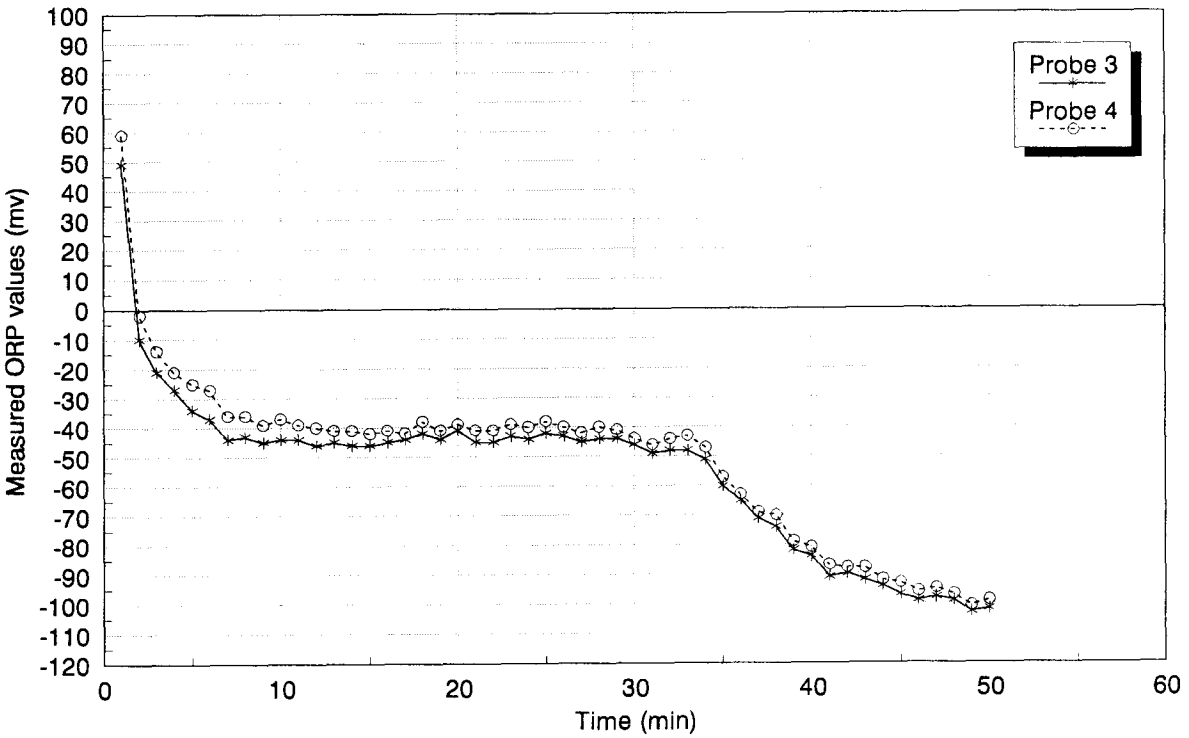


Figure 4.7: Anoxic batch test 1.1 (ratio 0)

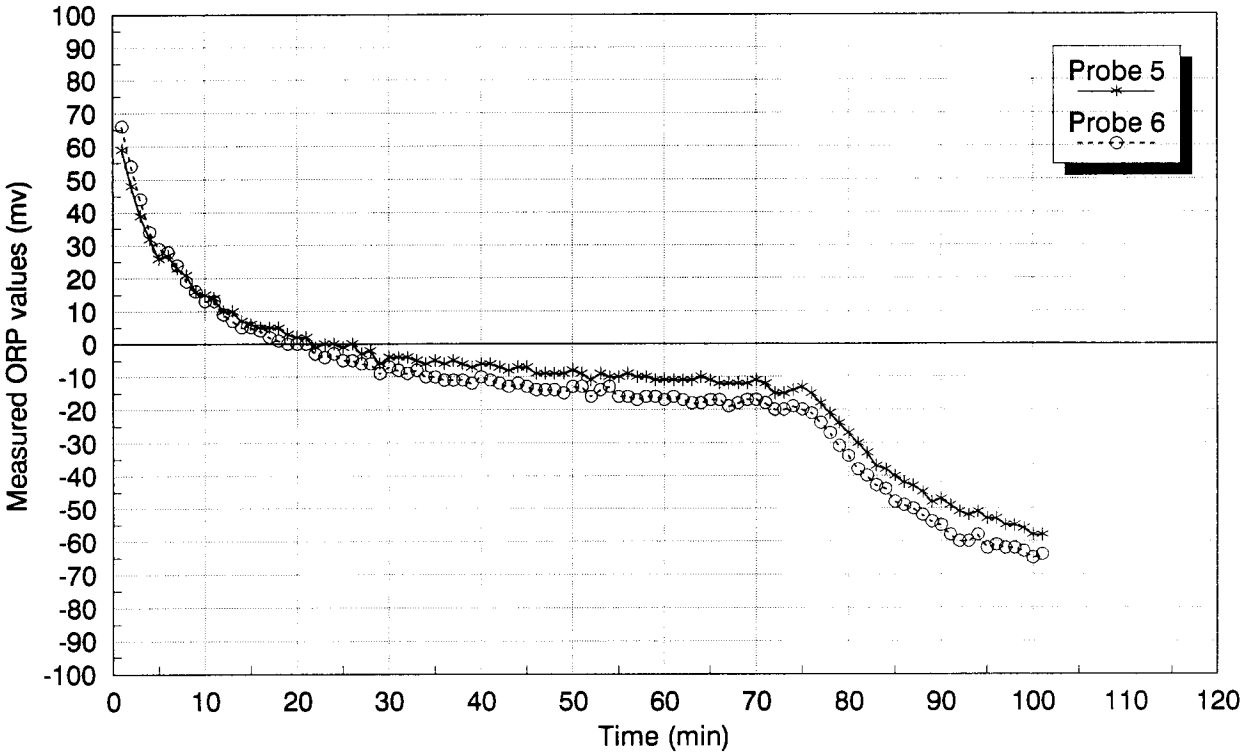


Figure 4.8: Anoxic batch test 1.2 (ratio 1)

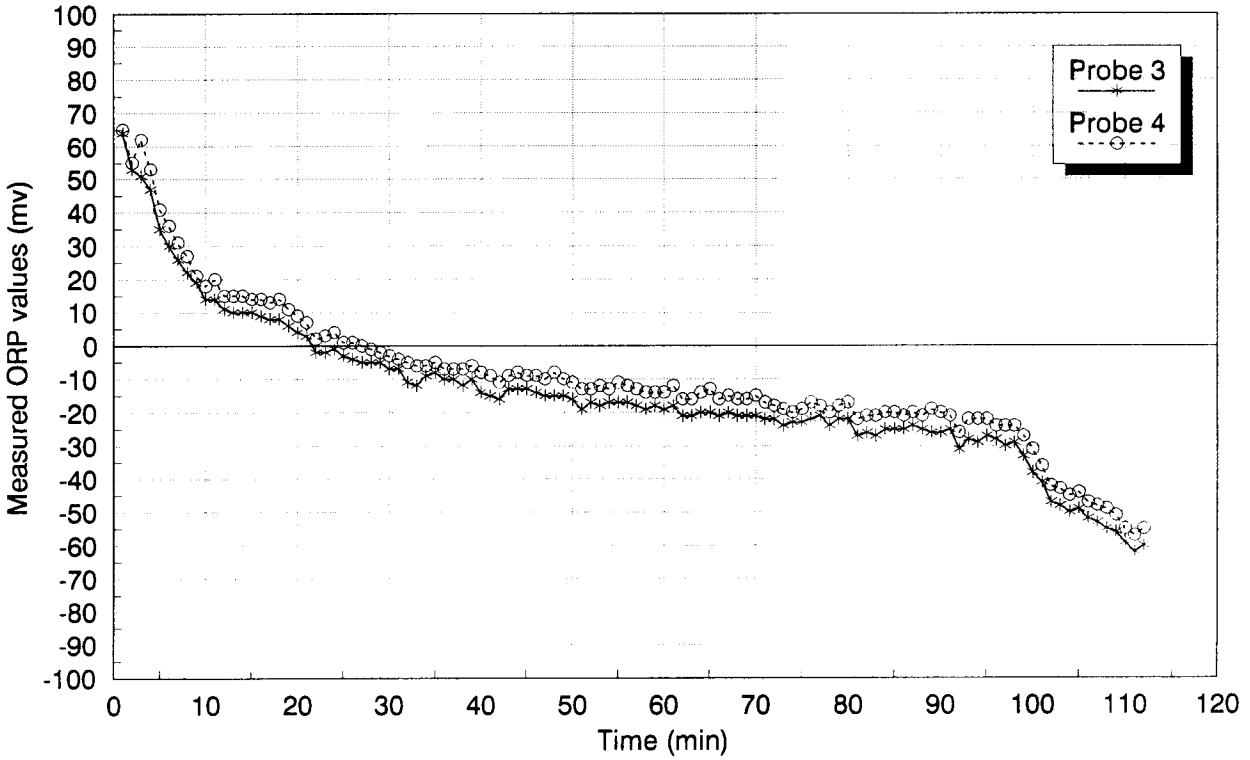


Figure 4.9: Anoxic batch test 1.3 (ratio 2)

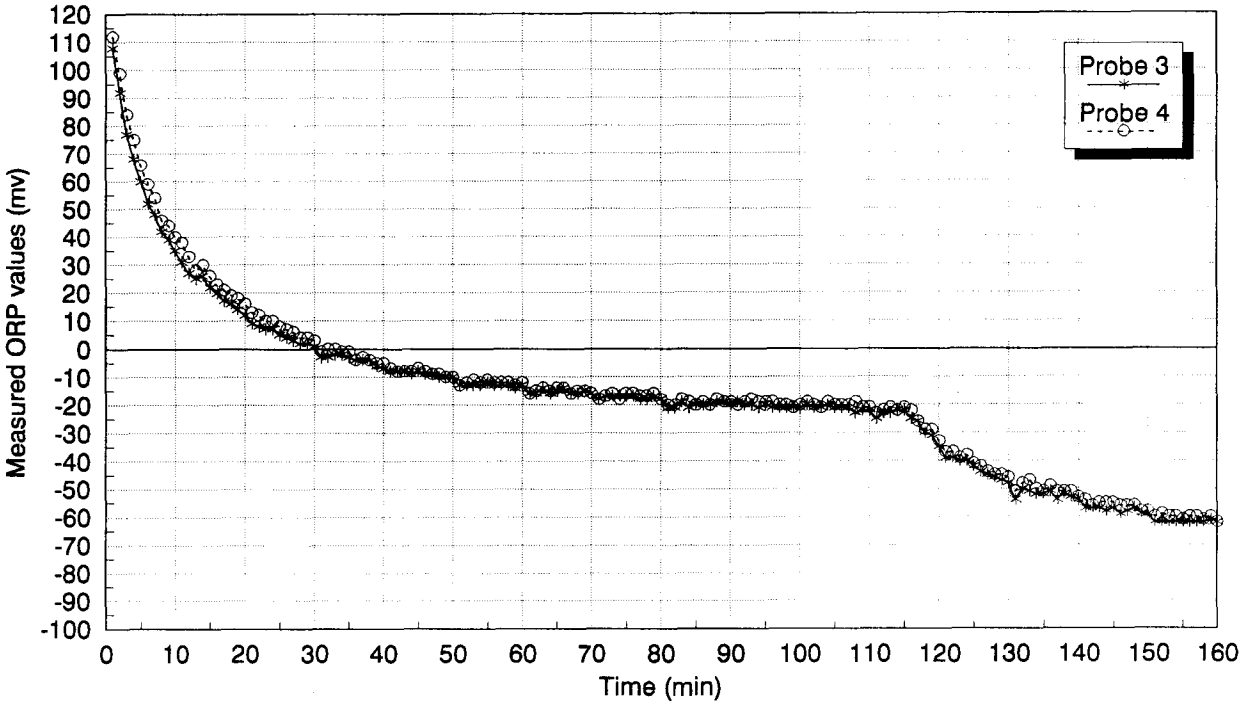


Figure 4.10: Anoxic batch test 1.4 (ratio 3)

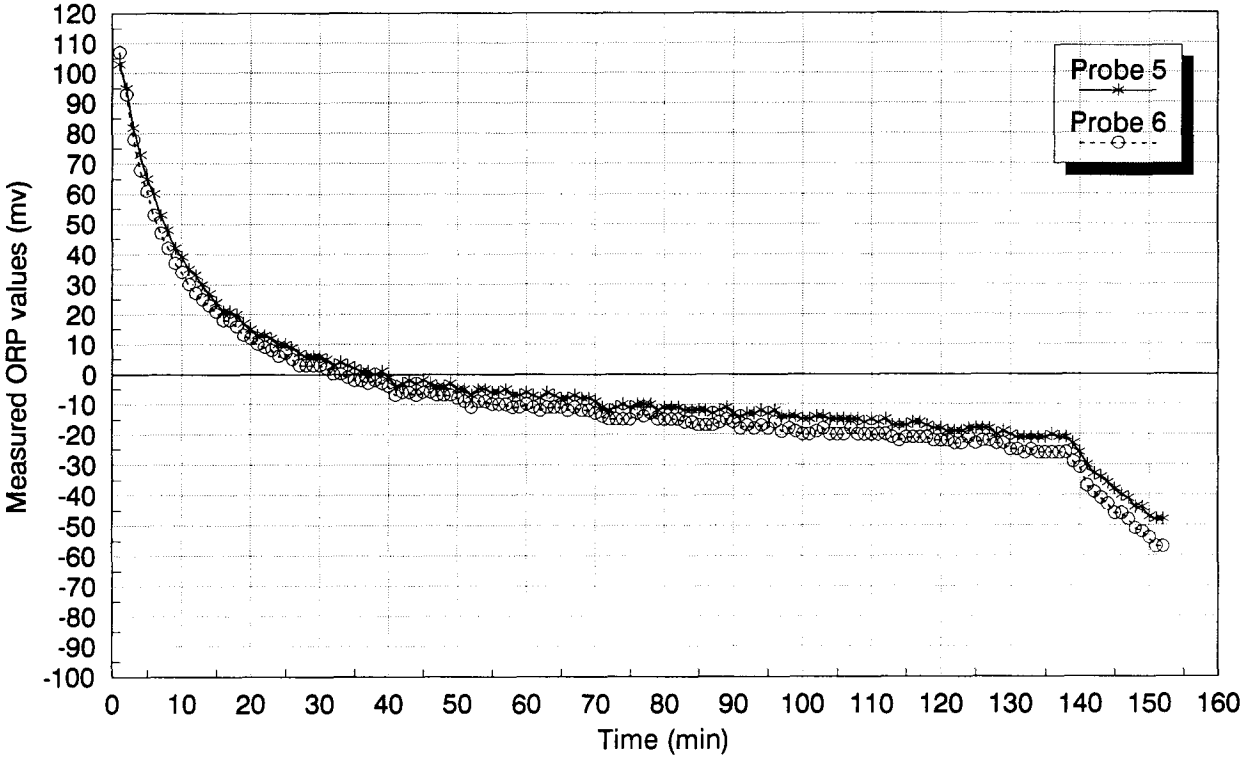


Figure 4.11: Anoxic batch test 1.5 (ratio 4)

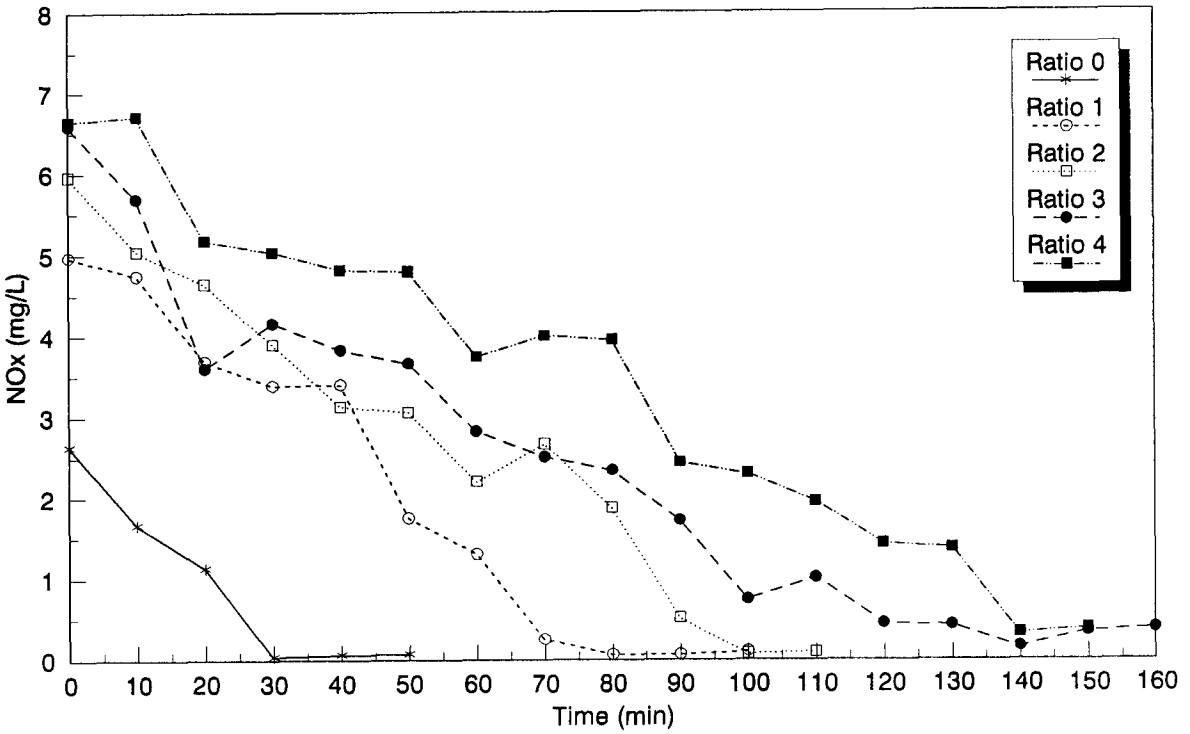


Figure 4.12: NOx test results (anoxic test 1)

4.2.3 Anoxic batch test 2 (March 21, 1991)

Anoxic batch test 2 was a repeat test of anoxic batch test 1. In the test 2, the proportions of mixed liquors were the same as those in the test 1, but it was conducted on a different day, for which the Process characteristics are presented in Table 4.9. Experimental conditions can be found in Table 4.10. ORP and NO_x testing results are included in Appendices B-1 to B-6.

4.2.4 Anoxic batch test 3 (March 28, 1991)

Anoxic batch test 3 was designed to increase the amount of data available for analysis, because the influence of random errors on the conclusion will be diminished when more data are used in the analysis. Table 4.11 includes process characteristics. Table 4.12 shows experimental conditions. ORP and NO_x results can be found in Appendices B-7 to B-12.

Table 4.9: Process characteristics on March 21, 1991

	NO_x (mg/L)	PO_4^- (mg/L)	MLSS (mg/L)	COD (mg/L)
Influent			191	333
Anaerobic zone	0.22	16.69		
Anoxic zone	0.06	10.62		
Aerobic zone	8.40	0.04	2910	
Effluent	8.17	0.04	2	25
30 min settling (mL/L)			910	

Table 4.10: Experimental conditions for anoxic batch test 2

Ratio	pH	Temp. (^oC)	MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS (%)
0	7.06	16.5	3080	2573	84
1	7.15	16.2	3123	2566	82
2	7.14	16.1	2997	2474	83
3	7.08	15.9	2867	2450	85
4	7.10	15.9	3177	2650	83

Table 4.11: Process characteristics on March 28, 1991

	NO_x (mg/L)	PO_4^- (mg/L)	MLSS (mg/L)	COD (mg/L)
Influent			67	319
Anaerobic zone	0.09	14.66		
Anoxic zone	0.06	9.10		
Aerobic zone	7.01	0.02	3310	
Effluent	6.89	0.04	1	27
30 min settling (mL/L)			880	

Table 4.12: Experimental conditions for anoxic batch test 3

Ratio	pH	Temp. ($°C$)	MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS (%)
0	7.13	16.0	3033	2543	84
1	7.19	17.3	3177	2607	82
2	7.20	17.1	3130	2583	83
3	7.25	16.0	3010	2490	83
4	7.18	16.0	3060	2527	83

4.3 Anoxic Batch Tests (With External Carbon Addition)

4.3.1 Introduction

It is known that a biological denitrification process usually requires the addition of an external carbon source to promote the nitrate removal reactions (US EPA, 1975. Metcalf and Eddy, 1979. Narkis *et. al*, 1979. Watanabe *et. al* 1985). The effect of carbon concentration on the rate of denitrification has been modeled in terms of a Monod type of expression. When methanol serves as the carbon source, the expression is (US EPA, 1975):

$$\mu_D = \mu_{D(max)} \frac{M}{K_m + M} \tag{4.2}$$

where:

μ_D = growth rate (day^{-1}).

$\mu_{D(max)}$ = maximum denitrifier growth rate (day^{-1}).

M = methanol concentration (mg/L).

K_m = half saturation constant for methanol (mg/L).

The carbon addition tests were designed to investigate the effect of different denitrification rates on the redox values measured at the end of the denitrification process.

Sodium acetate (NaAc) is one of many commercially available organic compounds that can be used as a readily available carbon source. With the addition of a simple external carbon source, the denitrification rate is increased in the anoxic zone of the process. The NaAc stock solution was prepared at a concentration of 9512 mg/L as COD (testing result).

In experiments, the NaAc stock solution was injected into flasks in the volumes which made up carbon addition of 0, 20, 40, 60 and 80 mg/L as COD. pH and temperatures were measured, and did not show great changes in the experiments. In carbon addition tests, the mixed liquor in each flask was the same combination of 467 mL from the return sludge, 933 mL from the anaerobic zone, and 1400 mL from the aerobic zone. Probes 3, 4, 5 and 6 were used, with probes 3 and 4 as one group and probes 5 and 6 as the other group. The external carbon addition experiments presented here were conducted on February 1, 1991, February 7, 1991, and March 1, 1991.

4.3.2 Carbon addition test 1 (February 1, 1991)

Carbon addition test 1 was conducted on February 1, 1991. Process characteristics on February 1, 1991 are listed in Table 4.13. pH, temperature, MLSS and MLVSS were tested for the initial samples of batch tests and can be found in Table 4.14. The sampling rate was once every 10 minutes. ORP values were automatically averaged and recorded every 180 seconds. The experiment lasted about 120 minutes. The collected ORPs were plotted over time. The graphs are presented in Figures 4.13 to 4.17. NO_x analysis results are presented in Figures 4.18.

4.3.3 Carbon addition test 2 (February 7, 1991)

Carbon addition test 2 was a repeat test of carbon addition test 1. The carbon doses applied in test 2 are the same as those used in test 1, but this test was conducted on

Table 4.13: Process characteristics on February 1, 1991

	NO_x (mg/L)	PO_4^- (mg/L)	MLSS (mg/L)	COD (mg/L)
Influent			45	289
Anaerobic zone	0.43	6.85		
Anoxic zone	0.21	4.67		
Aerobic zone	8.85	0.05	2830	
Effluent	8.64	0.02	5	19
30 min settling (mL/L)			830	

Table 4.14: Experimental conditions for carbon addition test 1

NaAc (mg/L)	pH	Temp. (^oC)	MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS (%)
0	7.05	16.6	3028	2516	83
20	6.94	16.2	3034	2470	81
40	6.97	16.8	3050	2492	82
60	6.79	16.9	3064	2508	82
80	7.17	15.6	3244	2616	81

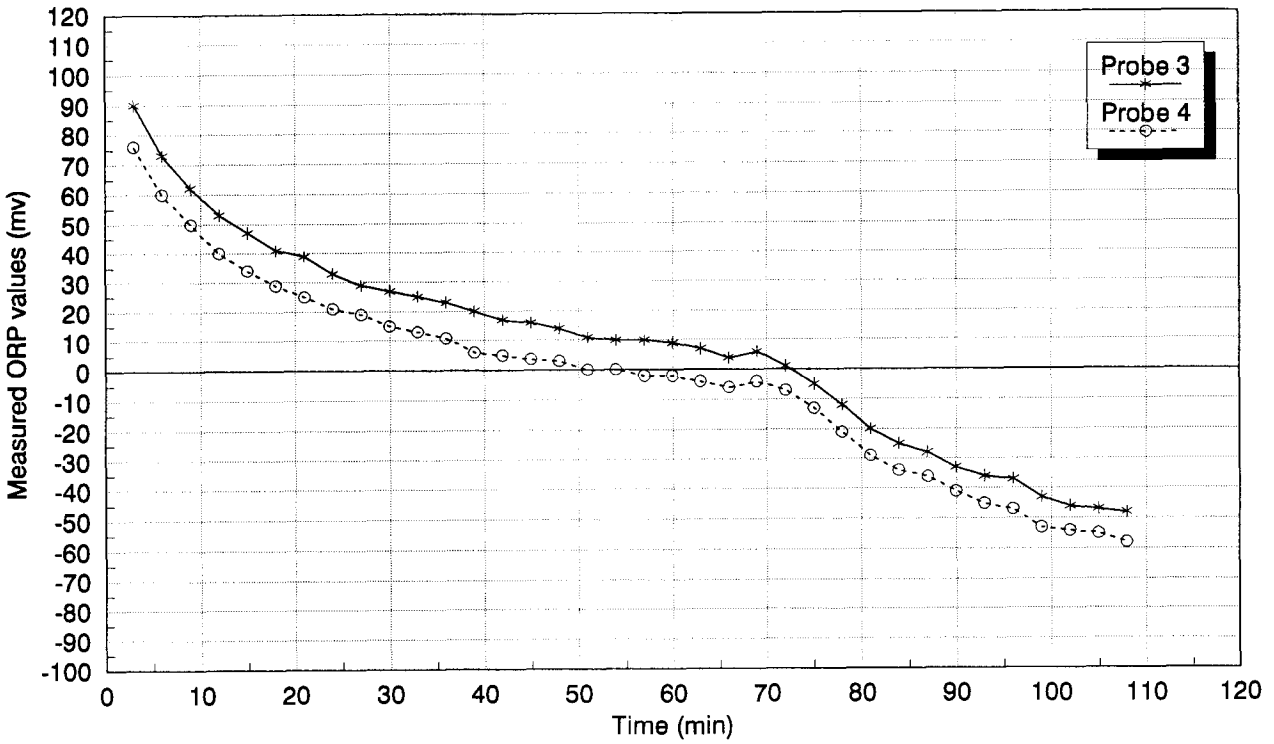


Figure 4.13: Carbon addition test 1.1 (control)

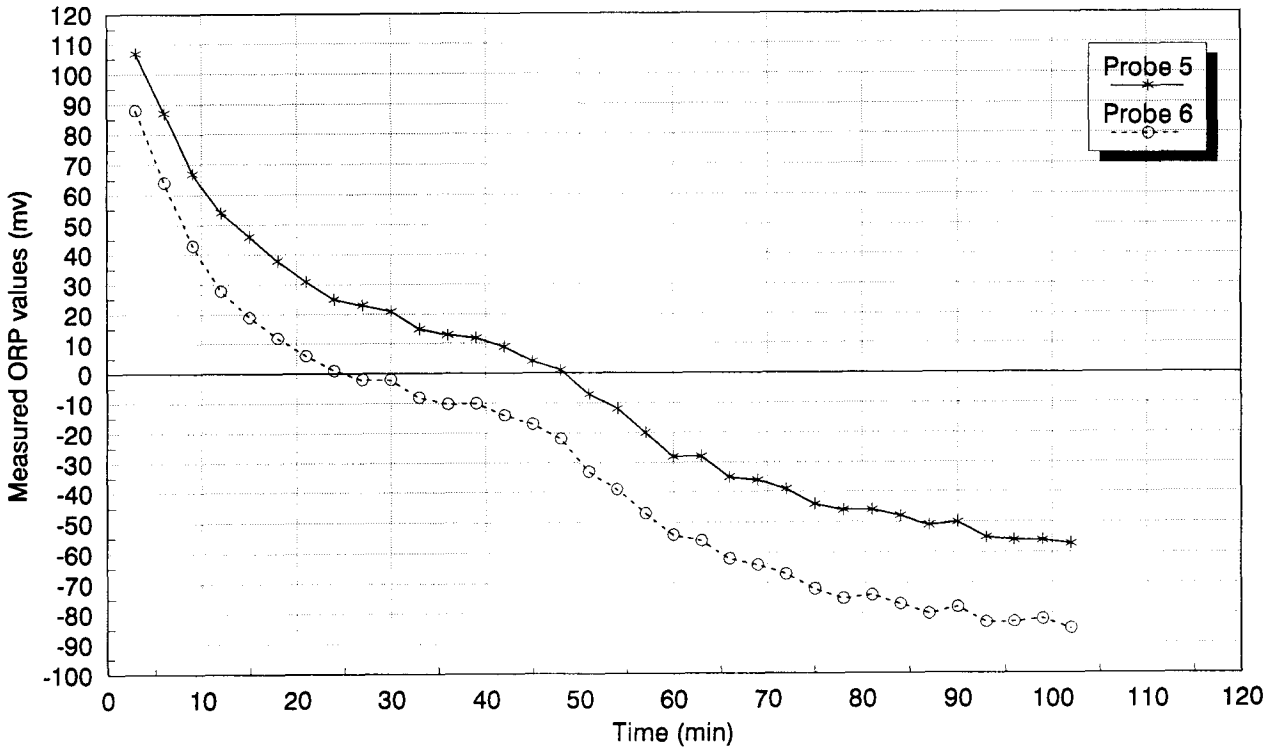


Figure 4.14: Carbon addition test 1.2 (20 mg/L)

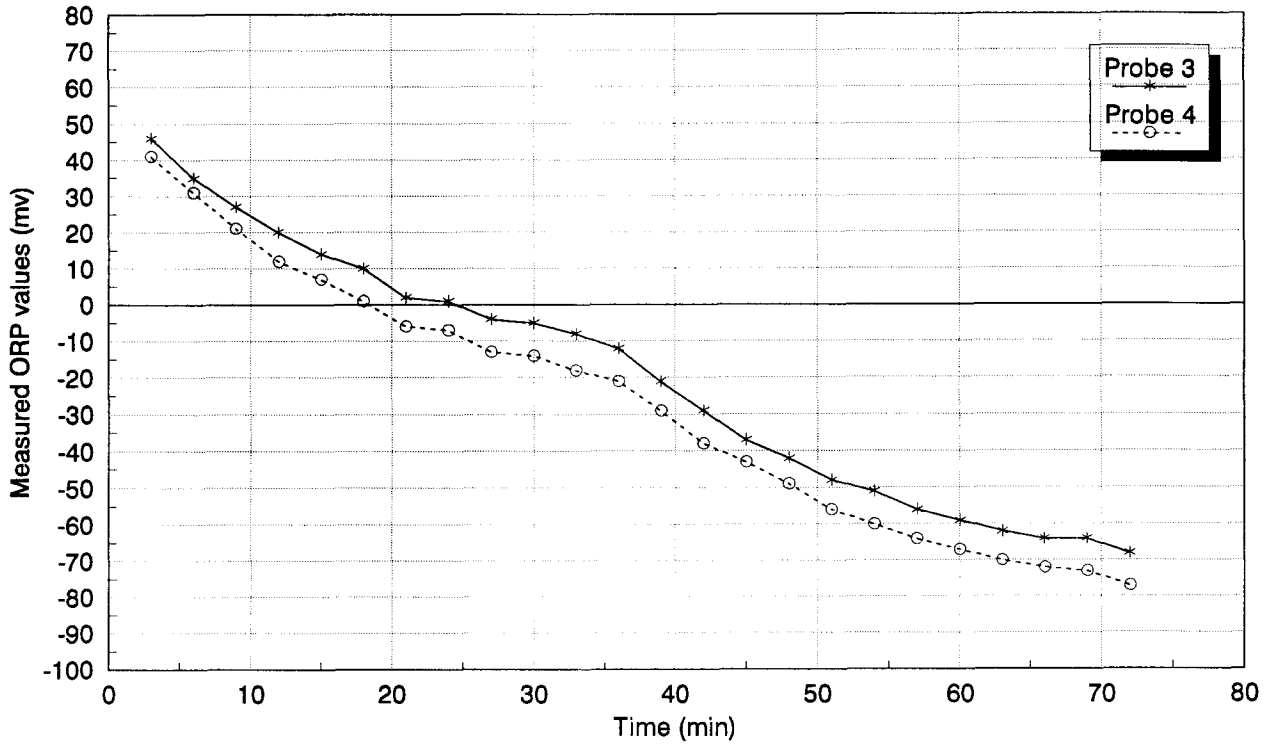


Figure 4.15: Carbon addition test 1.3 (40 mg/L)

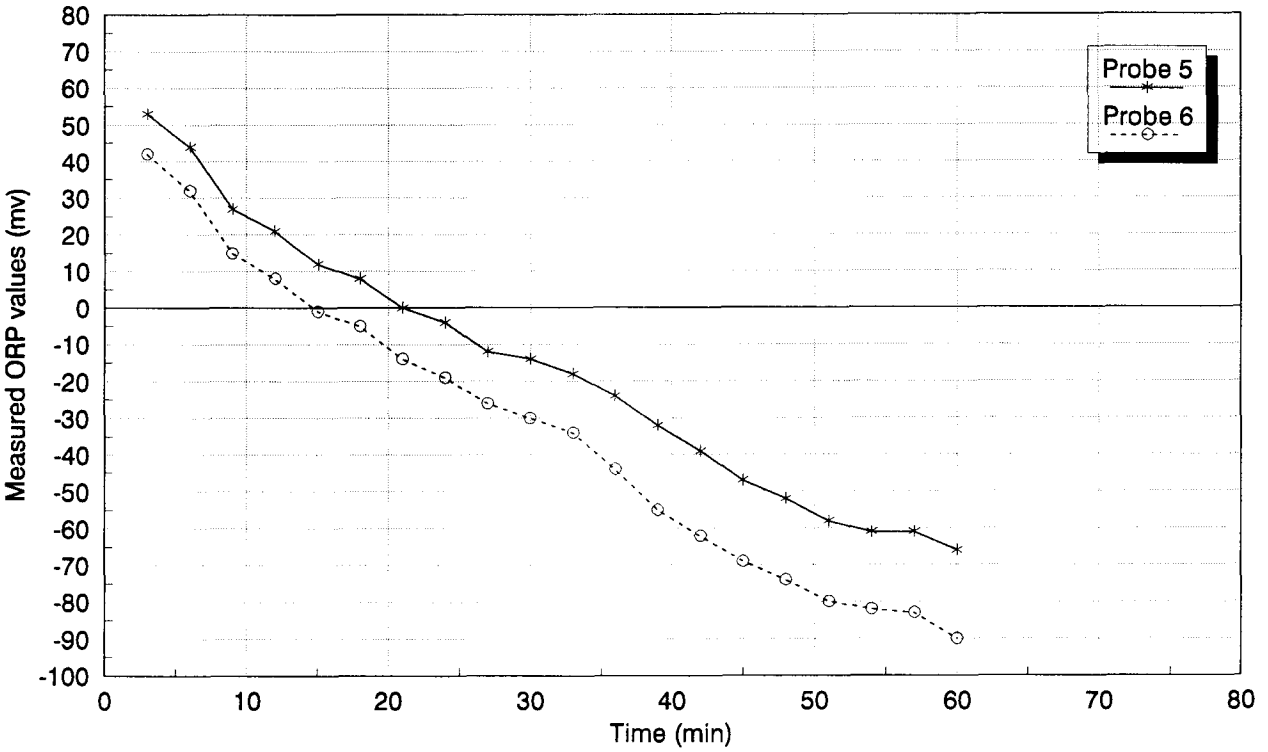


Figure 4.16: Carbon addition test 1.4 (60 mg/L)

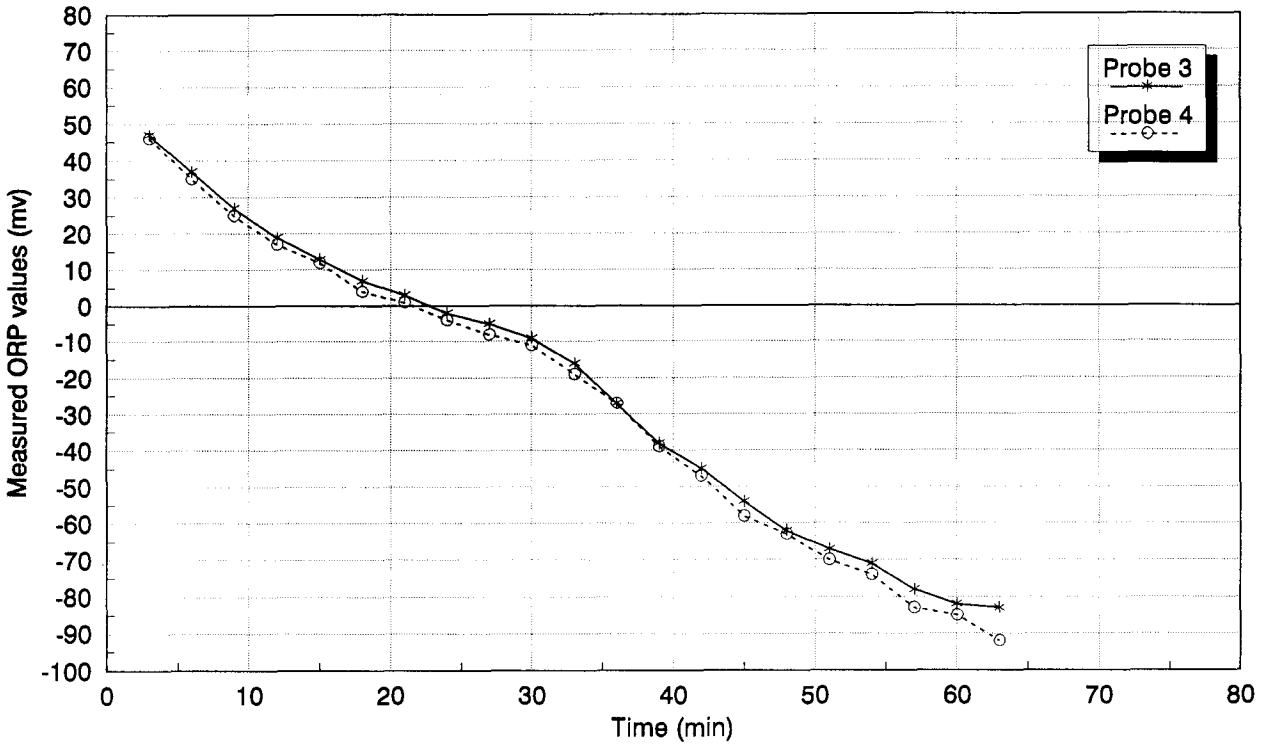


Figure 4.17: Carbon addition test 1.5 (80 mg/L)

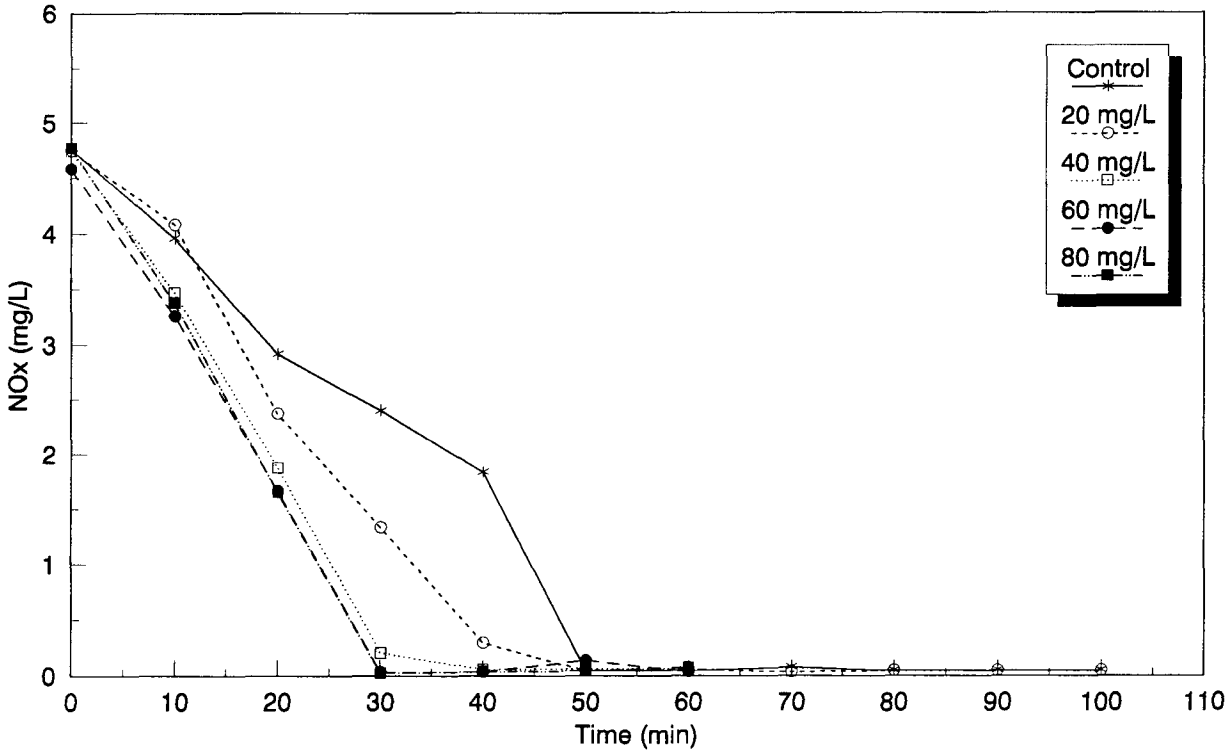


Figure 4.18: NOx test results (carbon addition test 1)

Table 4.15: Process characteristics on February 7, 1991

	NO_x (mg/L)	PO_4^- (mg/L)	MLSS (mg/L)	COD (mg/L)
Influent			42	166
Anaerobic zone	0.17	6.76		
Anoxic zone	0.11	3.32		
Aerobic zone	8.00	0.01	3050	
Effluent	7.87	0.00	1	19
30 min settling (mL/L)			890	

Table 4.16: Experimental conditions for carbon addition test 2

NaAc (mg/L)	pH	Temp. (^oC)	MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS (%)
0	7.13	14.5	3200	2590	81
20	7.03	16.8	3200	2576	80
40	7.16	17.4	3152	2538	81
60	7.04	14.0	3347	2687	80
80	7.10	17.0	3238	2658	82

February 7, 1991. Process characteristics are given in Table 4.15. pH, temperature, MLSS and MLVSS for each test are listed in Table 4.16. The rest of the experimental conditions of test 2 are the same as those in carbon addition test 1. The ORP and NO_x testing results are given in Appendices C-1 to C-6.

4.3.4 Carbon addition test 3 (March 1, 1991)

Carbon addition test 3 was conducted to create more data for final results analysis. Most experimental conditions were the same as those which were used in carbon addition test 2, except that test 3 was conducted on March 1, 1991 and the ORP logging rate was one sample every 60 seconds. Process characteristics are in Table 4.17. pH, temperatures, MLSS and MLVSS are listed in Table 4.18. ORP and NO_x were plotted over time. The

Table 4.17: Process characteristics on March 1, 1991

	NO_x (mg/L)	PO_4^- (mg/L)	MLSS (mg/L)	COD (mg/L)
Influent			56	271
Anaerobic zone	0.52	10.23		
Anoxic zone	0.33	7.90		
Aerobic zone	8.41	0.00		
Effluent	8.11	0.05	3	
30 min settling (mL/L)			735	

Table 4.18: Experimental conditions for carbon addition test 3

NaAc (mg/L)	pH	Temp. (^oC)	MLSS (mg/L)	MLVSS (mg/L)	MLVSS/MLSS (%)
0	7.20	14.2	2210	1813	82
20	7.10	13.7	2403	1960	82
40	7.14	15.0	2527	2177	86
60	7.12	17.0	2413	2056	85
80	7.11	15.4	2543	2180	86

graphs can be found in Appendices C-7 to C-12.

Chapter 5

DISCUSSION

5.1 Introduction

Experimental results of probe tests and biological batch tests are discussed in this chapter. In the discussion of the probe testing results, measured ORP values are compared with the standard ORP values of the tested quinhydrone solutions. The relationship between measured values and standard values is investigated. The necessity of probe testing in order to properly adjust measured ORP values before the application of ORP values is discussed.

Biological batch tests examined the effects of initial NO_x concentrations and denitrification rates on redox values at complete denitrification conditions. The method of defining redox values for complete denitrification conditions is discussed. Redox values in complete denitrification conditions are evaluated to examine the possibility of using them as a biological denitrification control parameter.

5.2 Evaluation of Probe Testing Results

Probe test 1 will be discussed in detail. Experimental results of probe tests 2 and 3 will also be discussed.

5.2.1 The Probe's behaviour in quinhydrone buffer solutions

A group of ten probes was tested in a series of 6 quinhydrone solutions whose pH values ranged from 4 to 9. It was observed that measured ORP values were steady over the testing period shown in Figures 4.1 to 4.5. In Figure 4.6 (probe test 1.6 with a pH value of 9.85), measured ORP values decreased over 20 minutes. Averages (Avg) and standard deviations (Std) are taken on measured ORP values collected in probe tests 1.1 to 1.5 (Figures 4.1 to 4.5). The results are listed Table 5.1.

Petersen (1966) mentioned that quinhydrone buffer solutions have steady ORP values when solutions' pH values are below 9. When the pH is above 9, the high OH^- concentration in the system will make the reaction shown in Equation (4.1) a irreversible one. Therefore, the probe test 1.6 at pH 9.85 does not have a steady ORP value, and is not included in probe testing discussions.

The standard deviations (Std) in Table 5.1 are used to evaluate the reliability of the data log-in system, and to detect any malfunctioning probes. The resolution of the data log-in system in 0.5 mv. In other words, a $\pm$ 0.5 mv difference between the measured value and the true value (in practice, the average is taken as the true value) is acceptable. It is observed that 42% of standard deviations (Std) in Table 5.1 are equal to, or less than 0.5 mv. 72% of the standard deviations are no more than 1.0 mv. These standard deviations indicated that no extraordinary discrepancy was present in the log-in system and from ORP probes.

The relationship between measured redox values (Avg in Table 5.1) and pH values of the corresponding solutions was studied by plotting measured redox values against pH values for each probe. This was done to correlate measured redox values with pH values, and furthermore, to correlate measured redox values with standard values. Figure 5.1 presents the relationship between measured redox values and pH values. It was observed

Table 5.1: ORP values: Avg, Std and SD (probe test 1) (mv)

pH	4.03		6.30		7.06		7.78		8.78	
Probe	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
1	268	0.4	142	0.4	97	0.5	51	0.7	-5	1.2
2	264	0.5	139	0.4	92	1.0	49	0.9	-8	1.1
3	260	0.5	136	1.3	88	1.1	47	1.0	-9	1.9
4	261	0.5	137	1.1	91	0.5	48	0.8	-8	1.3
5	269	0.0	141	0.6	99	0.4	51	0.7	-6	1.1
6	262	0.0	138	0.6	92	0.3	48	0.6	-8	1.1
7	269	0.0	140	0.9	98	0.6	47	1.2	-9	1.2
8	267	0.0	141	0.5	95	0.4	48	1.0	-7	1.2
9	266	0.5	140	0.5	96	0.5	51	0.7	-6	1.2
10	266	0.5	140	0.4	97	0.7	49	0.7	-7	1.2
SD	266		133		88		46		-12	

that measured redox values were linearly related to pH values in the quinhydrone buffer solution. (Quinhydrone solutions have lower redox values when pH values are higher). Since the standard redox values (SD) of quinhydrone solution at pH 4.0 and 7.0 are given in Table 4.1, by using the linear relationship between redox values and pH values, the standard redox values at pH 4.03, 6.30, 7.06, 7.78 and 8.78 (used in probe test 1) were extrapolated (temperature $20^{o}C$), and are listed in Table 5.1. It is observed that measured values from each probe are not necessary the same as the extrapolated standard redox values of that quinhydrone solution. For each probe, at different pH levels, the difference between measured values and standard values are not constant. For each pH value, different probes could have different ORP values on the same quinhydrone solution.

5.2.2 Redox value adjustment

The relationship between measured redox values and standard values was established based on the data listed in Table 5.1, and is presented in Figure 5.2. It was observed

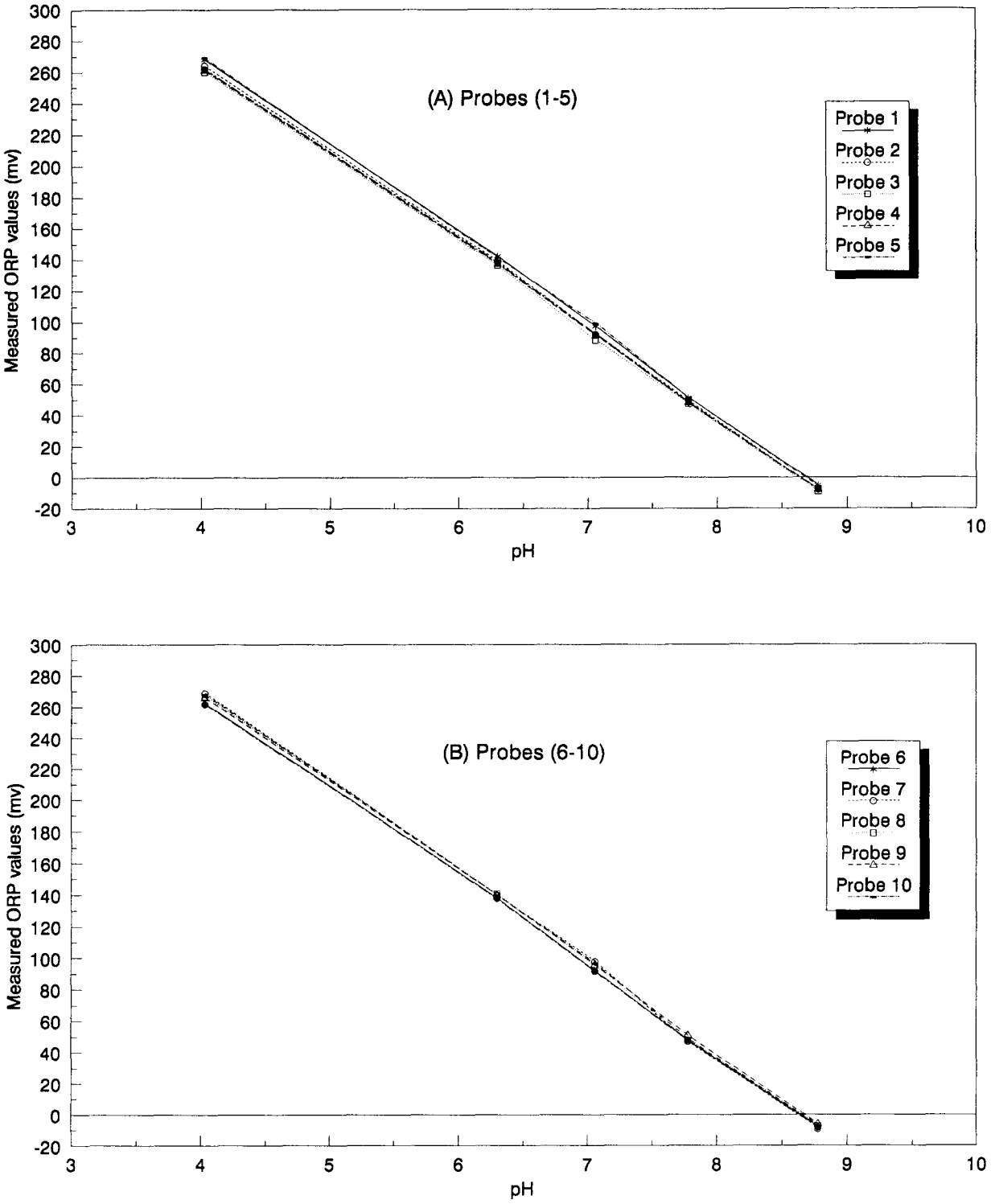


Figure 5.1: Measured ORP values vs pH (probe test 1)

Table 5.2: Adjustment ratios (probe tests 1 to 3)

Y = bX + a						
	Probe test 1		Probe test 2		Probe test 3	
Probes	b	a (mv)	b	a (mv)	b	a (mv)
1	0.98	8	0.98	11	0.99	3
2	0.98	5	0.97	8	0.99	0
3	0.97	3	0.97	5	0.98	-1
4	0.97	5	0.98	6	0.99	1
5	0.99	8	0.99	8	0.99	2
6	0.97	5	0.97	7	0.99	1
7	1.00	5	0.99	11	1.00	7
8	0.99	6	0.98	8	1.00	1
9	0.98	7	0.98	8	0.99	2
10	0.98	6	0.98	7	1.00	1

that a linear relationship exists between measured redox values and standard values in the pH ranges from 4 to 9.

An equation was developed to relate measured redox values to standard values:

$$Y = bX + a \tag{5.1}$$

Y - measured redox values (mv)

X - standard redox values (mv)

b, a - ratios

The values of b and a can be found in Table 5.2.

Probe tests 2 and 3 have similar results to probe test 1. The measured redox values are also linearly related to the corresponding standard redox values. The ratios are listed in Table 5.2.

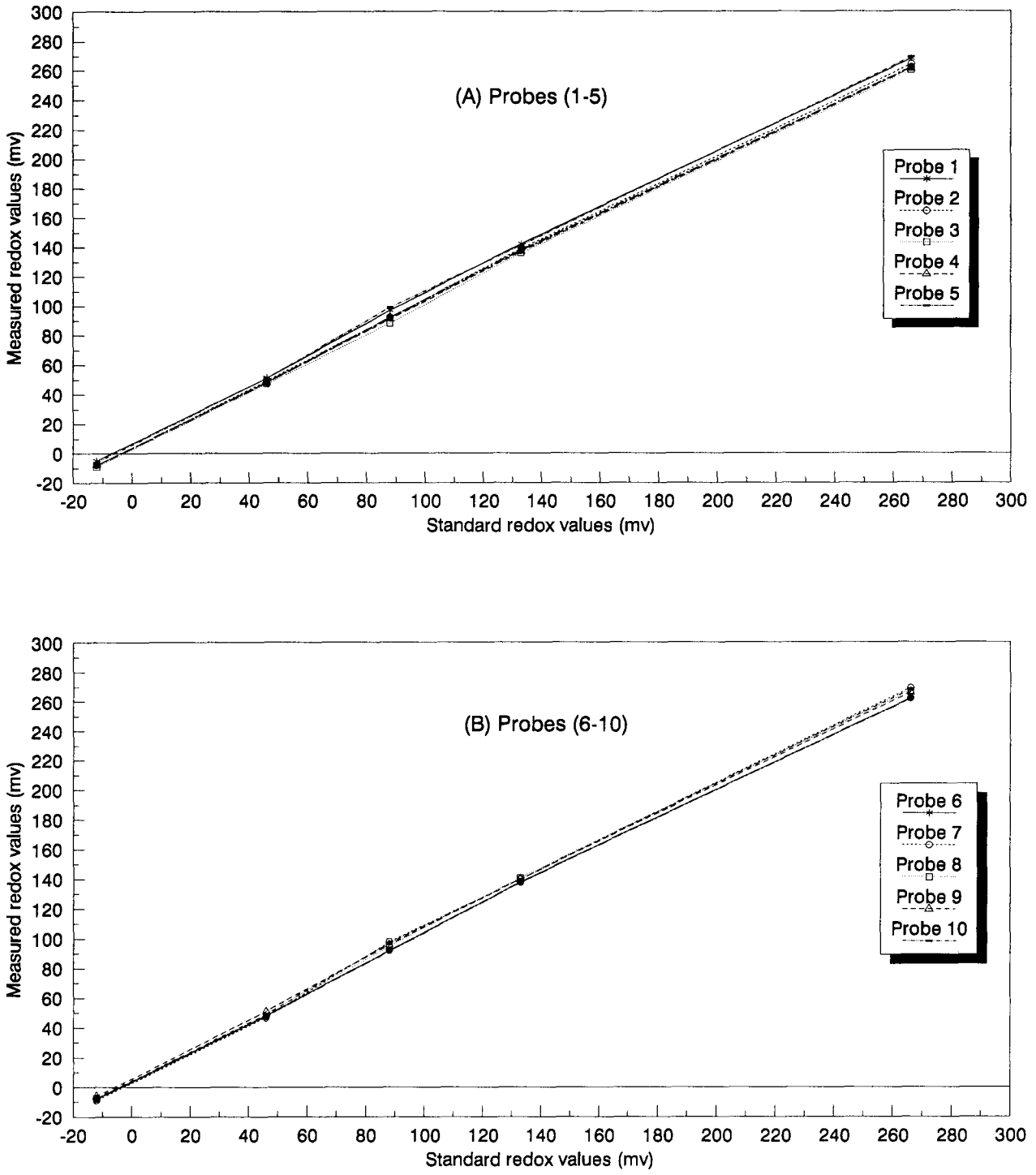


Figure 5.2: Measured ORP values vs standard ORP values (probe test 1)

5.2.3 Evaluation of probe testing results

Probe testing results are discussed based on the data listed in Table 5.2. Ratio b in Table 5.2 varied from 0.97 to 1.00. Every 100 mv change of the solutions' standard values will result in a minimum 97 mv change in measured ORP values.

Ratio a is a major contribution to the difference between the measured redox value and the standard redox value of the tested solution, and to the difference among different probes. It was observed that, for each probe test, the difference between ratio a for different probes was in the 0 - 10 mv range.

The necessity of adjusting measured ORP values before their application will be discussed based on the redox values of the biological batch tests. Although measured values for individual probes may not be the same as the solution's true value, this kind of difference may, or may not have a critical influence on conclusions of a experiment. The necessity of adjusting measured ORP values has to be examined for the individual experiment.

5.3 Redox Values for Complete Denitrification Conditions

5.3.1 Defining ORP values for complete denitrification conditions

The results of anoxic batch test 1 and carbon addition test 1 are presented in Figures 4.7 to 4.11, and Figures 4.13 to 4.17 respectively. It was observed that in each redox value vs time curve, there is a redox value plateau following the initial rapid ORP decrease. At the end of the plateau, redox values were observed to decrease in a faster rate. The slope change point, when the ORP started to decrease at an increasing rate after the plateau, is defined as the knee.

The knee phenomenon is the major interest of this research. The internal relationship between redox values and denitrification process in the tested biological system was

investigated by examining the ORP values at the knees and the NO_x levels at the corresponding time. If redox values at the knees are related to the NO_x disappearance in biological systems, then these redox values can be assessed on the possibility of being used in a denitrification control system.

Since the knee in redox monitoring curves is consistent with the point which has the minimum derivative, then taking the derivative of the redox vs time curve is used as the method to obtain redox values to be used in the discussion of the results. Eye estimation is used to decide the knee position as a confirmation approach of the derivative method, since it is simple and straightforward. The disadvantage of eye estimation method is that not every redox curve has a very sharp knee, in which case it is not easy to define the knee's position.

The derivative method and the eye estimation method work well for the batch test system. They cannot be used however, in a flow through system where measured ORP values are indicative of a steady state condition which may or may not represent the point of complete denitrification. However, the conclusions from a batch test can be used in a flow through process based on the assumption that the biological condition for complete denitrification has the same measured ORP for a batch system and a steady state condition of a flow through process, when they have the same biological materials and operational conditions.

5.3.2 Measured ORP values at the knees

On the basis of eye estimation on Figure 4.7, the knee appeared between the 30th and 40th minute. The derivative method was used to identify the exact time when the knee appeared. The first derivative was taken on the redox curve (shown in Figure 4.7 as an example). Because of the sensitivity of ORP probes and the complexity of a biological system, the plotted data points did not provide a completely smooth curve

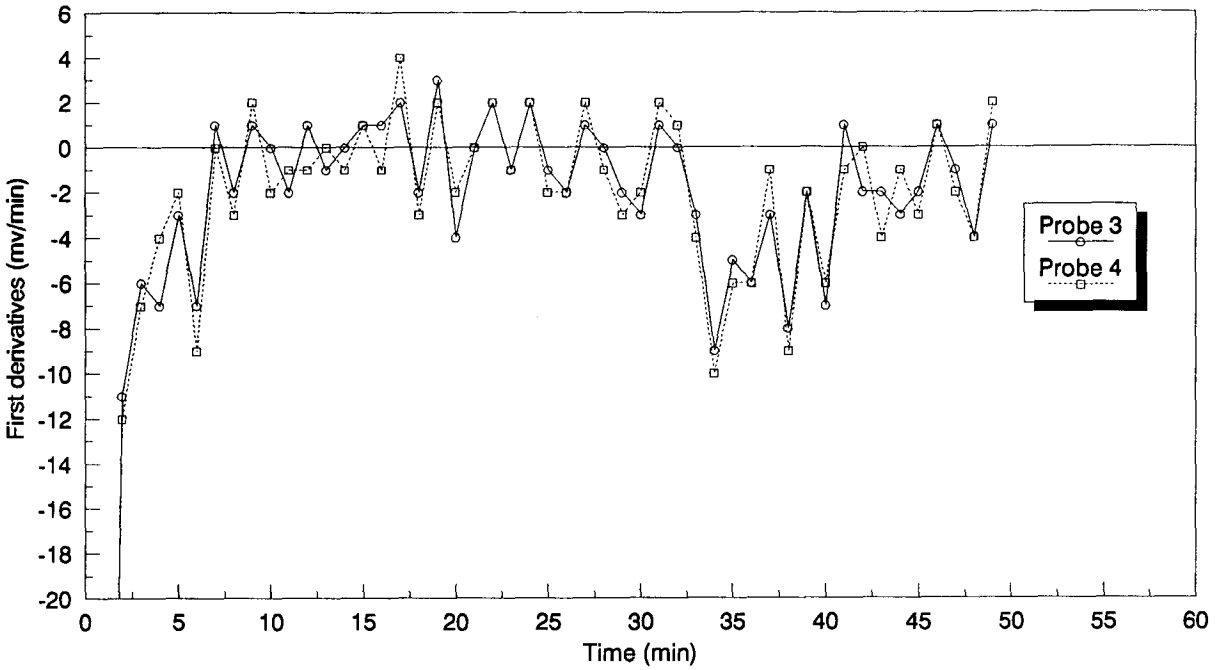


Figure 5.3: Anoxic test 1.1: first derivatives vs time

where the point of inflection was obvious. The effect of these data point irregularities was compounded when a first derivative vs time curve was constructed (see Figure 5.3). The irregularities in Figure 5.3 does not represent the characteristics of the curve in Figure 4.7. For example, ORP values are still in the plateau area between the 15th and 20th minute, however, the several consecutive derivatives in Figure 5.3 are +4, -3, +2, to -2 (mv/minute) for probe 4, which exaggerate the irregularities of the curve. Averaging every five points consecutively was done on Figure 5.3 to get Figure 5.4. The irregularities in Figure 5.3 were smoothed, and the minimum derivative, when the knee appeared, was distinguished, and is shown to occur at the 34th minute.

Figure 5.5 is the result of averaging every ten points consecutively. It was observed that in the time period of the 28th minute to the 35th minute, 7 consecutive points have the same derivative. In this curve, the minimum derivative can not be identified. Ten point averaging will therefore not be used in deciding the position of the knee.

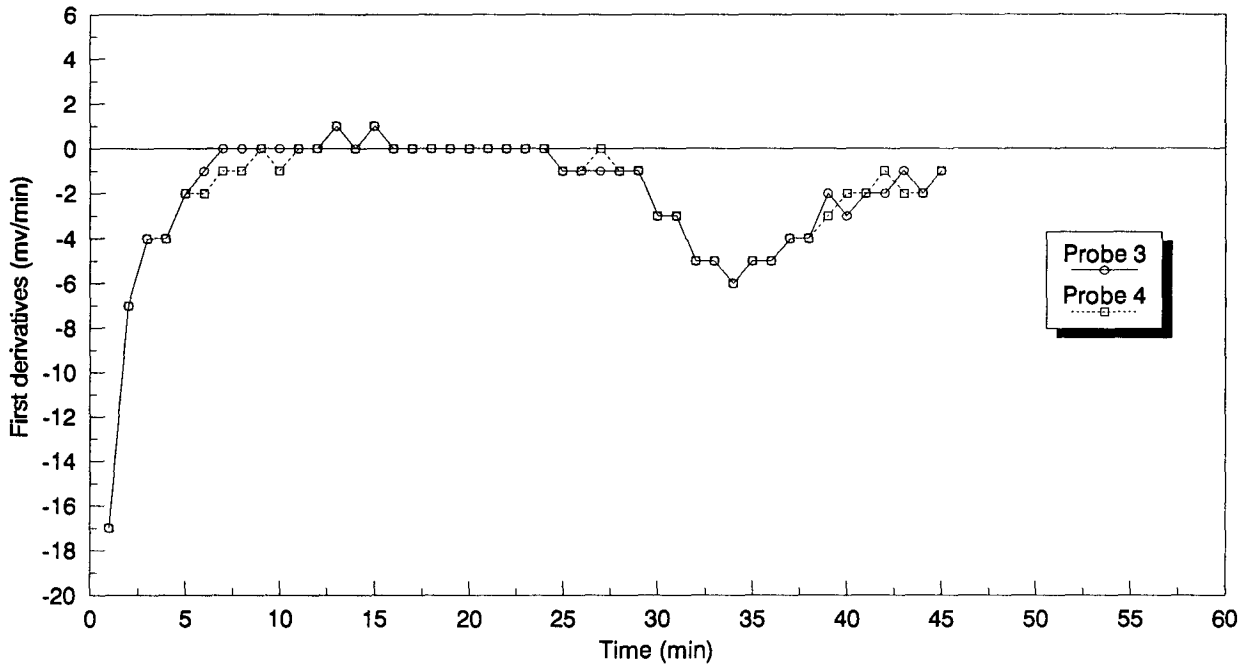


Figure 5.4: Anoxic test 1.1: first derivatives vs time (Avg 5)

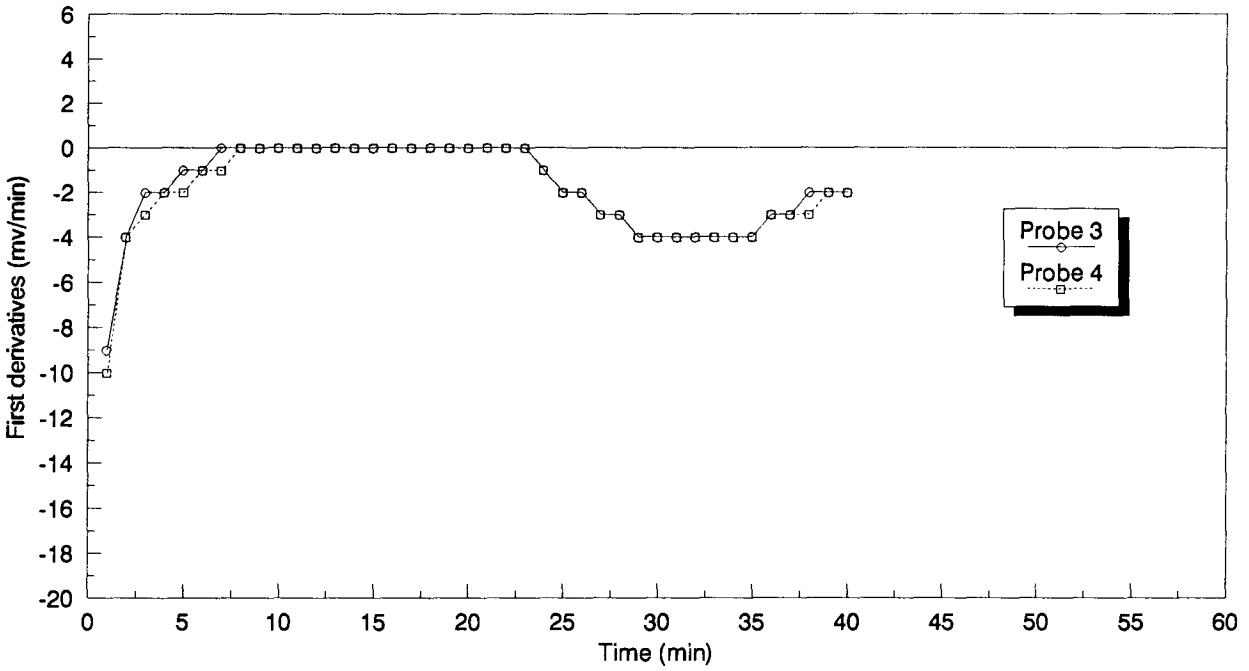


Figure 5.5: Anoxic test 1.1: first derivatives vs time (Avg 10)

Table 5.3: Measured ORP values at the knees (DM, AT1) (mv)

Ratio	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	34	-51	-47		
1	75			-13	-20
2	98	-29	-24		
3	116	-22	-22		
4	138			-21	-26

Table 5.4: Measured ORP values at the knees (DM, AT2) (mv)

Ratio	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	18	-49	-48		
1	46			-9	-22
2	62	-31	-25		
3	69	-18	-21		
4	88			-14	-24

Although the derivative method cannot be used in a flow through process, the conclusions that are drawn from batch testing data will build a solid background for the ORP's application in a flow through process.

It is recommended that five point averaging be used to smooth the first derivative curve. The corresponding redox values defined in this way are listed in Table 5.4. Derivatives of other redox curves have similar results to the one shown in Figure 5.3, and the redox values obtained from the derivative method are listed in Tables 5.4 to 5.8.

In Tables 5.3 to 5.8, DM stands for the derivative method, AT stands for an anoxic test, CA stands for a carbon addition test. The listed redox values are measured ORP values at the knees as determined by the derivative method. Each batch test used two probes (probes 3 and 4, probes 5 and 6). The times listed in Tables 5.3 to 5.8 are used to decide NO_x levels in biological testing systems.

Table 5.5: Measured ORP values at the knees (DM, AT3) (mv)

Ratio	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	20	-55	-54		
1	43			-20	-32
2	59	-36	-30		
3	86	-31	-24		
4	105			-16	-28

Table 5.6: Measured ORP values at the knees (DM, CA1) (mv)

NaAc (mg/L)	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	75	-5	-13		
20	52			-12	-22
40	36	-12	-21		
60	35			-24	-34
80	33	-45	-36		

Table 5.7: Measured ORP values at the knees (DM, CA2) (mv)

NaAc (mg/L)	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	87	-19	-11		
20	54			-13	-25
40	36	-22	-16		
60	36			-17	-31
80	36	-45	-36		

Table 5.8: Measured ORP values at the knees (DM, CA3) (mv)

NaAc (mg/L)	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	115	-25	-20		
20	65			-2	-21
40	44	-26	-15		
60	44			-23	-24
80	43	-26	-17		

Table 5.9: Measured NO_x at the knee position (AT 1-3)

	Anoxic test 1		Anoxic test 2		Anoxic test 3	
Ratio	Time (min)	NO_x (mg/L)	Time (min)	NO_x (mg/L)	Time (min)	NO_x (mg/L)
0	34	0.05	18	0.42	20	0.38
1	75	0.16	46	0.34	43	0.26
2	98	0.16	62	0.24	59	0.13
3	116	0.67	69	0.44	86	0.31
4	138	0.53	88	0.35	105	0.10

Table 5.10: Measured NO_x at the knee position (CA 1-3)

	Carbon test 1		Carbon test 2		Carbon test 3	
NaAc (mg/L)	Time (min)	NO_x (mg/L)	Time (min)	NO_x (mg/L)	Time (min)	NO_x (mg/L)
0	75	0.07	87	0.10	115	0.63
20	52	0.05	54	0.10	65	0.28
40	36	0.12	36	0.15	44	0.31
60	35	0.04	36	0.07	44	0.36
80	33	0.03	36	0.08	43	0.44

5.3.3 NO_x levels at the knees

The NO_x levels at the knees are used to exam the relationship between redox values at the knees and the completeness of the denitrification process in a biological system. NO_x levels at the time of the minimum derivative are presented in Tables 5.9 to 5.10. Initial NO_x levels and NO_x removal efficiencies are listed in Tables 5.11 and 5.12.

It was observed that among measured NO_x levels in Tables 5.9 and 5.10, 43% of them are lower than 0.15 mg/L, and 90% of them are no more than 0.50 mg/L. The NO_x detection limit is 0.05 mg/L. The NO_x removal efficiencies are averaged to be 92.6% in anoxic tests 1-3, and to be 96.2% in the carbon addition tests 1-3. The NO_x testing results

Table 5.11: Initial NO_x levels and removal efficiencies (anoxic tests 1-3)

	Anoxic test 1		Anoxic test 2		Anoxic test 3	
Ratio	NO_x @ t=0 (mg/L)	% removal @ knee	NO_x @ t=0 (mg/L)	% removal @ knee	NO_x @ t=0 (mg/L)	% removal @ knee
0	2.64	98.1	2.21	81.0	2.10	81.9
1	4.97	96.8	4.28	92.1	3.29	92.1
2	5.96	97.3	5.24	95.4	4.04	96.8
3	6.59	89.8	5.29	91.7	4.58	93.2
4	6.65	92.0	5.17	93.2	5.21	98.1

Table 5.12: Initial NO_x levels and removal efficiencies (carbon tests 1-3)

	Carbon test 1		Carbon test 2		Carbon test 3	
NaAc (mg/L)	NO_x @ t=0 (mg/L)	% removal @ knee	NO_x @ t=0 (mg/L)	% removal @ knee	NO_x @ t=0 (mg/L)	% removal @ knee
0	4.76	98.5	4.83	97.9	4.85	87.0
20	4.75	98.9	4.86	97.9	4.98	94.4
40	4.74	97.5	4.66	96.8	5.10	93.9
60	4.58	99.1	4.57	98.5	5.09	92.9
80	4.77	99.4	4.79	98.3	5.32	91.7

Table 5.13: Adjusted ORP values at the knees (DM, AT1) (mv)

Ratio	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	34	-56	-53		
1	75			-21	-26
2	98	-33	-30		
3	116	-26	-28		
4	138			-29	-32

indicate that denitrification processes in biological systems are essentially complete at the time the knees are present. The knee phenomenon also strongly indicates the internal relationship between redox values and the denitrification process in a batch test system, because of the relationship between the slope change in redox vs time curves and the NO_x disappearance in the system.

5.3.4 The possibility of using ORP as a control parameter

It was observed in Section 5.2 that the measured ORP values of different probes are different from standard values for the tested solution, and there are differences among ORP probes. Before evaluation of ORP as a denitrification control parameter, measured ORP values listed in Tables 5.3 to 5.8 were adjusted based on the relationship presented in Equation (5.1), so that these redox values are made to be comparable. Adjustment factors used the results of probe test 1 in Table 5.2, since all biological batch tests were conducted before the end of March, 1992. The adjusted redox values are listed in Tables 5.13 to 5.18.

In the evaluation of anoxic tests 1-3, the batch test from ratio 0 was not included. A flow through nitrate removal process normally has the aerobic mixed liquors recycled back to the anoxic zone for denitrification. The ratio 0 batch test system did not have any biological material from the aerobic zone (see Table 4.6), and therefore was not used

Table 5.14: Adjusted ORP values at the knees (DM, AT2) (mv)

Ratio	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	18	-54	-54		
1	46			-17	-28
2	62	-35	-31		
3	69	-22	-27		
4	88			-22	-30

Table 5.15: Adjusted ORP values at the knees (DM, AT3) (mv)

Ratio	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	20	-60	-61		
1	43			-28	-38
2	59	-40	-36		
3	86	-35	-30		
4	105			-24	-34

Table 5.16: Adjusted ORP values at the knees (DM, CA1) (mv)

NaAc (mg/L)	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	75	-9	-18		
20	52			-20	-28
40	36	-16	-27		
60	35			-32	-40
80	33	-50	-42		

Table 5.17: Adjusted ORP values at the knees (DM, CA2) (mv)

NaAc (mg/L)	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	87	-23	-16		
20	54			-21	-31
40	36	-26	-21		
60	36			-25	-37
80	36	-50	-42		

Table 5.18: Adjusted ORP values at the knees (DM, CA3) (mv)

NaAc (mg/L)	Time (min)	Probe 3	Probe 4	Probe 5	Probe 6
0	115	-29	-25		
20	65			-10	-27
40	44	-30	-20		
60	44			-31	-30
80	43	-30	-22		

Table 5.19: Avg and Std at the redox knees (AT 1-3 and CA 1-3)

	Anoxic tests			Carbon addition tests		
	Range (mv)	Averages (mv)	Std (mv)	Range (mv)	Averages (mv)	Std (mv)
Test 1	-33 to -21	-28	4	-50 to -9	-28	13
Test 2	-35 to -17	-27	6	-50 to -16	-29	11
Test 3	-40 to -24	-33	5	-31 to -10	-25	7
All tests	-40 to -17	-29	6	-50 to -9	-25	10
Avg = -28 mv Std = 8 mv						

in the evaluation of redox values at the knees. The ratio 0 batch test was designed to simulate the anoxic zone of the process for which no aerobic recycling is done (shown in Figure 3.1). It could be interpreted as a "control" system.

Averages and standard deviations (Std) were taken for adjusted redox values in Tables 5.13 to 5.18. The averages and standard deviations of redox values at the knees from anoxic batch tests 1-3 (ratio 1 to 4), and carbon addition tests 1-3 are listed in Table 5.19.

When the average was taken on all 54 data sets (24 from anoxic tests, 30 from carbon addition tests), the average is -28 mv, and the standard deviation is 8 mv. Statistically, the 68% confidence interval is one standard deviation ($\pm$ 8mv), and the 95% confidence interval is two standard deviation ($\pm$ 16 mv). Therefore any adjusted redox values at the

Table 5.20: NO_x (adjusted ORP value is -12 mv, AT1)

Ratio	Time (min)		NO_x (mg/L)	
1	29 (P5)	29 (P6)	3.42 (P5)	3.42 (P6)
2	32 (P3)	36 (P4)	3.75 (P3)	3.44 (P4)
3	44 (P3)	41 (P4)	3.76 (P3)	3.81 (P4)
4	47 (P5)	47 (P6)	4.80 (P5)	4.80 (P6)

knee has a 95% possibility to fall into a range of (-28±16) mv, or -12 to -44 mv.

In deciding which redox value (the upper limit of -12 mv, the average of -28 mv, or the lower limit of -44 mv) should be used as a control guideline of the biological denitrification process, Figures 4.7 to 4.11, and Figures 4.13 to 4.17 were examined. Redox values decreased over the time of the biological denitrification process in all batch tests. Because of the plateau, the time when the adjusted redox values is -12 mv will occur much more quickly than when the knee occurs. The NO_x in the system is far from being removed completely. Table 5.20 lists the time when the adjusted ORP value is -12 mv (measured ORP values were calculated by using the Equation (5.1) and the ratios from probe test 1 listed in Table 5.2). P3, P4, P5, and P6 stand for probe 3, probe 4, probe 5, and probe 6. Because the ratios a and b are different for different probes, the time when the same adjusted ORP value of -12 mv occurs are different in Table 5.20. NO_x levels were decided from Figures 4.12 and 4.18 by using the time listed in Table 5.20.

When the redox value of -28 mv (adjusted) is used, biological systems may or may not be NO_x low, since the -28 mv is an averaged value. In Table 5.21, one batch test (ratio 2) in the anoxic test 3 has a NO_x of 1.80 mg/L, which does not indicate complete denitrification.

The lower limit of -44 mv is the most promising redox value that can be used in

Table 5.21: NO_x (adjusted ORP value is -28 mv, AT3)

Ratio	Time (min)		NO_x (mg/L)	
1	43 (P5)	17 (P6)	0.34 (P5)	1.67 (P6)
2	29 (P3)	42 (P4)	1.80 (P3)	1.23 (P4)
3	69 (P3)	84 (P4)	1.19 (P3)	0.31 (P4)
4	106 (P5)	96 (P6)	0.09 (P5)	0.45 (P6)

Table 5.22: NO_x (adjusted ORP value is -44 mv, AT1)

Ratio	Time / intervals (min)		NO_x (mg/L)	
1	83 (P5) / 8	81 (P6) / 6	0.06 (P5)	0.06 (P6)
2	101 (P3) / 3	102 (P4) / 4	0.07 (P3)	0.07 (P4)
3	123 (P3) / 7	123 (P4) / 7	0.44 (P3)	0.44 (P4)
4	144 (P5) / 6	142 (P6) / 4	0.34 (P5)	0.33 (P6)

denitrification process control. First, redox values at the knees statistically have 95% possibility to be higher than -44 mv in this research, no matter what initial NO_x levels, or what denitrification rates the batch test systems have. Second, after the knee, redox values decreased in an increasing rate, thus, the time when redox value is -44 mv is not too much longer than the time when the knee occurs. The time and the corresponding NO_x levels when the redox value (adjusted) is - 44 mv are listed in Tables 5.22 to 5.27.

Tables 5.22 to 5.24 include anoxic tests 1 to 3. Tables 5.25 to 5.27 present carbon

Table 5.23: NO_x (adjusted ORP value is -44 mv, AT2)

Ratio	Time / intervals (min)		NO_x (mg/L)	
1	53 (P5) / 7	50 (P6) / 4	0.46 (P5)	0.51 (P6)
2	63 (P3) / 1	65 (P4) / 3	0.23 (P3)	0.24 (P4)
3	73 (P3) / 4	73 (P4) / 4	0.34 (P3)	0.34 (P4)
4	93 (P5) / 5	90 (P6) / 2	0.23 (P5)	0.31 (P6)

Table 5.24: NO_x (adjusted ORP value is -44 mv, AT3)

Ratio	Time / intervals (min)		NO_x (mg/L)	
1	47 (P5) / 3	45 (P6) / 2	0.15 (P5)	0.21 (P6)
2	61 (P3) / 2	61 (P4) / 2	0.07 (P3)	0.07 (P4)
3	89 (P3) / 3	90 (P4) / 4	0.31 (P3)	0.31 (P4)
4	110 (P5) / 5	107 (P6) / 2	0.06 (P5)	0.08 (P6)

Table 5.25: NO_x (adjusted ORP value is -44 mv, CA1)

mg/L	Time / intervals (min)		NO_x (mg/L)	
0	99 (P3) / 24	90 (P4) / 15	0.05 (P3)	0.05 (P4)
20	69 (P5) / 17	54 (P6) / 2	0.04 (P5)	0.05 (P6)
40	48 (P3) / 12	42 (P4) / 6	0.07 (P3)	0.06 (P4)
60	42 (P5) / 7	36 (P6) / 1	0.06 (P5)	0.04 (P6)
80	42 (P3) / 9	39 (P4) / 6	0.04 (P3)	0.04 (P4)

Table 5.26: NO_x (adjusted ORP value is -44 mv, CA2)

mg/L	Time / intervals (min)		NO_x (mg/L)	
0	99 (P3) / 12	99 (P4) / 12	0.05 (P3)	0.05 (P4)
20	72 (P5) / 18	63 (P6) / 9	0.06 (P5)	0.14 (P6)
40	45 (P3) / 9	48 (P4) / 12	0.05 (P3)	0.05 (P4)
60	45 (P5) / 9	39 (P6) / 3	0.08 (P5)	0.08 (P6)
80	36 (P3) / 10	39 (P4) / 3	0.08 (P3)	0.07 (P4)

Table 5.27: NO_x (adjusted ORP value is -44 mv, CA3)

mg/L	Time / intervals (min)		NO_x (mg/L)	
0	119 (P3) / 4	121 (P4) / 6	0.08 (P3)	0.05 (P4)
20	81 (P5) / 16	70 (P6) / 5	0.07 (P5)	0.36 (P6)
40	49 (P3) / 5	52 (P4) / 8	0.13 (P3)	0.14 (P4)
60	49 (P5) / 5	48 (P6) / 4	0.23 (P5)	0.26 (P6)
80	46 (P3) / 3	48 (P4) / 5	0.40 (P3)	0.37 (P4)

addition tests 1 to 3. The intervals in Tables 5.22 to 5.27 are the time between the position of the knee and the position of - 44 mv (adjusted value). Among the NO_x levels in Tables 5.22 to 5.27, 63% of them are not higher than 0.15 mg/L, and 98% of them are lower than 0.50 mg/L. Therefore, -44 mv is a good redox value for indicating the completeness of the denitrification in the tested systems of this research. When redox values of a biological system reach - 44 mv (adjusted value), the denitrification in the system can be assumed to be complete.

The intervals listed in Tables 5.22 to 5.24 (anoxic tests 1 to 3) have an average of 4 minutes with a range of 1 to 8 minutes. In Tables 5.25 to 5.27, the intervals average is 8 minutes, the range is 0 to 24 minutes. Although the maximum interval in Tables 5.25 to 5.27 is 24 minutes, 83% of intervals are not longer than 12 minutes. Therefore, when -44 mv is used as a control redox value, and if the knees are taken as the NO_x disappearance positions, the biological system will not have been transformed into the anaerobic condition, from the anoxic condition, for a very long period of time. The phosphorus removal will not be affected in such a denitrification system.

5.4 The Necessity of Adjusting Measured ORP Values

As discussed in Section 5.2, the measured ORP values are different from the standard values. Different probes may have different values for the redox value of the same solution. In Section 5.3, the possibility of using ORP values as a control parameter in assessing the completeness of a denitrification process was discussed on adjusted redox values with the consideration that adjusted redox values are closest to the true values of the tested solutions.

The necessity of adjusting measured redox values is examined by investigating the 54 data points listed in Tables 5.3 to 5.8 (excluding ratio 0 in anoxic tests 1 to 3). The

Table 5.28: NO_x (measured ORP value is -42 mv, AT1)

Ratio	Time / Interval (min)		NO_x (mg/L)	
1	86 (P5) / 11	83 (P6) / 8	0.06 (P5)	0.06 (P6)
2	102 (P3) / 4	102 (P4) / 4	0.07 (P3)	0.07 (P4)
3	125 (P3) / 9	126 (P4) / 10	0.43 (P3)	0.43 (P4)
4	148 (P5) / 10	144 (P6) / 6	0.37 (P5)	0.34 (P6)

Table 5.29: NO_x (measured ORP value is -42 mv, AT2)

Ratio	Time / Interval (min)		NO_x (mg/L)	
1	56 (P5) / 10	51 (P6) / 5	0.41 (P5)	0.49 (P6)
2	64 (P3) / 2	65 (P4) / 3	0.24 (P3)	0.24 (P4)
3	73 (P3) / 4	73 (P4) / 4	0.34 (P3)	0.34 (P4)
4	94 (P5) / 6	91 (P6) / 3	0.28 (P5)	0.28 (P6)

average is -22 mv, and the standard deviation is 10 mv. Therefore, the lower limit of the 95% confidence interval is (-22-20) mv = -42 mv. The time when the redox vs time curves of all batch tests reach -42 mv are listed in Tables 5.28 to 5.33. NO_x levels at corresponding time and time intervals between the knees and -42 mv positions are listed in Tables 5.28 to 5.33 as well.

When the redox value of -42 mv (measured value) is used as a control guideline, among the NO_x data listed in Tables 5.28 to 5.33, 59% of them are lower than 0.15 mg/L, and

Table 5.30: NO_x (measured ORP value is -42 mv, AT3)

Ratio	Time / Interval (min)		NO_x (mg/L)	
1	48 (P5) / 5	46 (P6) / 3	0.12 (P5)	0.18 (P6)
2	61 (P3) / 2	61 (P4) / 2	0.07 (P3)	0.07 (P4)
3	89 (P3) / 3	91 (P4) / 5	0.31 (P3)	0.32 (P4)
4	112 (P5) / 7	108 (P6) / 3	0.13 (P5)	0.08 (P6)

Table 5.31: NO_x (measured ORP value is -42 mv, CA1)

mg/L	Time / Interval(min)		NO_x (mg/L)	
0	99 (P3) / 24	93 (P4) / 18	0.05 (P3)	0.05 (P4)
20	75 (P5) / 23	57 (P6) / 2	0.05 (P5)	0.06 (P6)
40	48 (P3) / 12	45 (P4) / 9	0.07 (P3)	0.07 (P4)
60	45 (P5) / 10	36 (P6) / 11	0.09 (P5)	0.04 (P6)
80	42 (P3) / 9	42 (P4) / 9	0.04 (P3)	0.04 (P4)

Table 5.32: NO_x (measured ORP value is -42 mv, CA2)

mg/L	Time / Interval (min)		NO_x (mg/L)	
0	99 (P3) / 22	99 (P4) / 22	0.05 (P3)	0.05 (P4)
20	81 (P5) / 27	66 (P6) / 12	0.06 (P5)	0.11 (P6)
40	45 (P3) / 9	48 (P4) / 12	0.05 (P3)	0.05 (P4)
60	45 (P5) / 9	42 (P6) / 6	0.08 (P5)	0.08 (P6)
80	36 (P3) / 0	39 (P4) / 3	0.08 (P3)	0.07 (P4)

Table 5.33: NO_x (measured ORP value is -42 mv, CA3)

mg/L	Time / Interval (min)		NO_x (mg/L)	
0	120 (P3) / 5	122 (P4) / 7	0.05 (P3)	0.05 (P4)
20	85 (P5) / 20	73 (P6) / 8	0.19 (P5)	0.26 (P6)
40	49 (P3) / 5	54 (P4) / 10	0.13 (P3)	0.19 (P4)
60	50 (P5) / 6	49 (P6) / 5	0.21 (P5)	0.23 (P6)
80	47 (P3) / 4	49 (P4) / 6	0.38 (P3)	0.35 (P4)

100% of them are lower than 0.50 mg/L. Therefor, -42 mv can be used to indicate the NO_x disappearance.

The intervals between the knee and the -42 mv (measured value) position are averaged to be 5 minutes for anoxic tests 1 to 3, and to be 11 minutes for carbon addition tests 1 to 3. The maximum interval is 11 minutes for anoxic tests 1 to 3, and 24 minutes for carbon addition tests 1 to 3. In carbon addition tests 1 to 3, 77% of the intervals are not longer than 12 minutes. The standard deviation of the 54 data points listed in Tables 5.3 to 5.8 (excluding ratio 0) is 10 mv, which is 2 mv higher than the 8 mv standard deviation determined from the 54 adjusted data in Tables 5.13 to 5.18. It is realized that, without adjusting measured ORP values in Tables 5.3 to 5.8, the lower limit of the 95% confidence interval is still a good indicator of the completeness of a denitrification process. In this research, the redox value is -42 mv, that is, when measured ORP values drops to -42 mv, the NO_x removal in the system can be assumed to be complete, and the biological system is still a good environment for phosphorus removal because it has not been in the anaerobic condition for long.

It has to be pointed out that although adjusting measured ORP values is not necessary in this research, probe testing is still recommended before their application in any process control. One reason is that probe testing can identify any malfuntioning probes. The second reason is that different processes may have different requirements on the accuracy and precision of measured ORP values. Without probe testing, it is not easy to project whether the difference between measured ORP values and true values is critical or not in evaluating the use of redox values in a process control system.

Chapter 6

CONCLUSIONS and RECOMMENDATIONS

6.1 Conclusions

Based on results of probe testing experiments, biological batch tests (anoxic batch tests, and carbon addition tests), this research has led to the following conclusions:

6.1.1 Probe testing experiments

1. The designed probe testing system was reliable and flexible for conducting oxidation reduction potential experiments.

2. ORP probes tested in quinhydrone buffer solutions, whose pH values are in the range of 4 to 9, have steady ORP values over the testing time. Standard deviations of measured ORP values from each probe test were less than 2 mv. 43% of them were no more than 0.5 mv, and 72% of them were no more than 1.0 mv.

3. Measured ORP values from probes may not be equal to the standard value of the tested quinhydrone solution. When the same probe was tested in quinhydrone solutions whose pH values were different, the differences between measured values and standard values were not, in general, constant (the differences varied between 2 mv to 9 mv for probe 1). When the same quinhydrone solution was used, different probes had different measured ORP values (the differences varied between -6 mv to 3 mv for pH 4.03). A linear relationship was developed between measured ORP values and standard ORP values of the tested quinhydrone solutions.

4. Adjustment factors for measured ORP values were developed. The necessity of adjusting measured ORP value is discussed in Section 6.1.3.

6.1.2 The accuracy and precision of ORP monitoring

1. The knee phenomenon was observed from the ORP monitoring curves in anoxic and carbon addition batch tests. The knee position is defined as the position on the curve which exhibits the minimum derivative in a plot of millivolts vs time.

2. The knee could be used as an indication of the complete denitrification condition in the tested biological system. At the time corresponding to the occurrence of the knee, 43% of the tested NO_x levels were lower than 0.15 mg/L, and 90% of the tested NO_x were lower than 0.5 mg/L. The average NO_x removal efficiencies were 92.6% in anoxic tests, and 96.2% in the carbon addition tests.

3. When the average of the 54 adjusted redox values (24 from anoxic tests excluding ratio 0 batch tests, 30 from carbon addition tests) is evaluated, it was found to be - 28 mv, and the standard deviation was 8 mv. Any adjusted redox values at the knees have a 95% possibility to be above -44 mv (adjusted value).

4. At -44 mv (adjusted value), 63% of NO_x levels in the system are not higher than 0.15 mg/L. 98% of the NO_x levels are lower than 0.50 mg/L. The denitrification can be assumed to be complete when redox values reach -44 mv (adjusted value).

5. The intervals between knees and the position of -44 mv (adjusted value) are 4 minutes on average for anoxic tests 1 - 3, and 8 minutes on average for carbon addition tests 1 - 3. The biological system is still in a favourable state for phosphorus removal in the process.

6. Anoxic batch tests were designed to have different initial NO_x concentrations. Carbon addition tests were designed to have different denitrification rates. Redox values collected from these different batch tests generated a guideline of -44 mv (adjusted value) which can be used as an indicator of complete denitrification in biological systems used in this research (other biological systems may not have the same ORP value at the complete denitrification condition). The knee phenomenon revealed the internal relationship between redox testing and the NO_x disappearance. Therefore, there is a good possibility that ORP testing can be used as a control tool in a denitrification process.

6.1.3 The necessity of adjusting measured ORP values

1. When adjustment was not applied to the 54 redox values, the average was -22 mv, and the standard deviation was 10 mv. Comparing this with the standard deviation of 8 mv from the adjusted values, it is seen, that, without adjustment, the standard deviation is only 2 mv higher.

2. When the -42 mv (measured value, the lower limit of the 95% confidence interval) is used as a control guideline, 59% of the NO_x data are lower than 0.15 mg/L, and 100% of NO_x data are lower than 0.5 mg/L. Thus, -42 mv (measured value) can be used as a redox value indicating NO_x disappearance in the system.

3. The time intervals between the knee and the -42 mv (measured value) position have an average of 5 minutes for anoxic tests 1 to 3, and 11 minutes for carbon addition tests 1 to 3. The system with -42 mv (measured value) redox value is still a good environment for phosphorus removal in the process.

4. On the basis of the results of this research, it is not necessary to adjust measured ORP values to arrive at conclusion 6 in Section 6.1.2 for this specific application. However, probe testing is still recommended before using the ORP probe as a control tool. The testing procedures are presented in Section 6.2.

6.2 Recommendations

As a result of this work, the following probe testing procedures are recommended:

1. Read the output from the probes in two quinhydrone buffer solutions with two different pH values.

2. Determine the standard redox values of the buffer solutions.

3. Assume a linear relation between the measured redox values and the standard redox values for each tested probe by using the following equation:

$$Y_{measured} = constant(X_{standard}) + constant \tag{6.1}$$

4. Adjust the measured values (Y) to get the standard value (X), and apply the standard value in the process control system.

5. Recheck the probe compliance with the equation on approximately a monthly basis.

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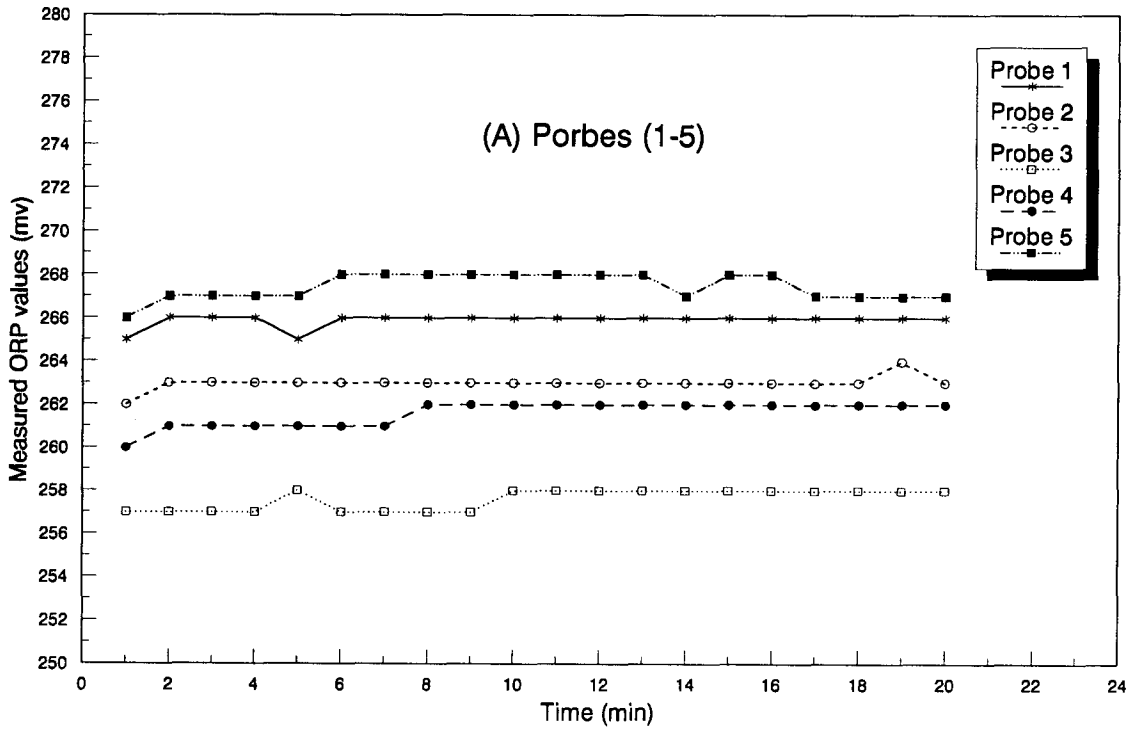
Appendix A

Results of Probe Test 2 and Probe Test 3



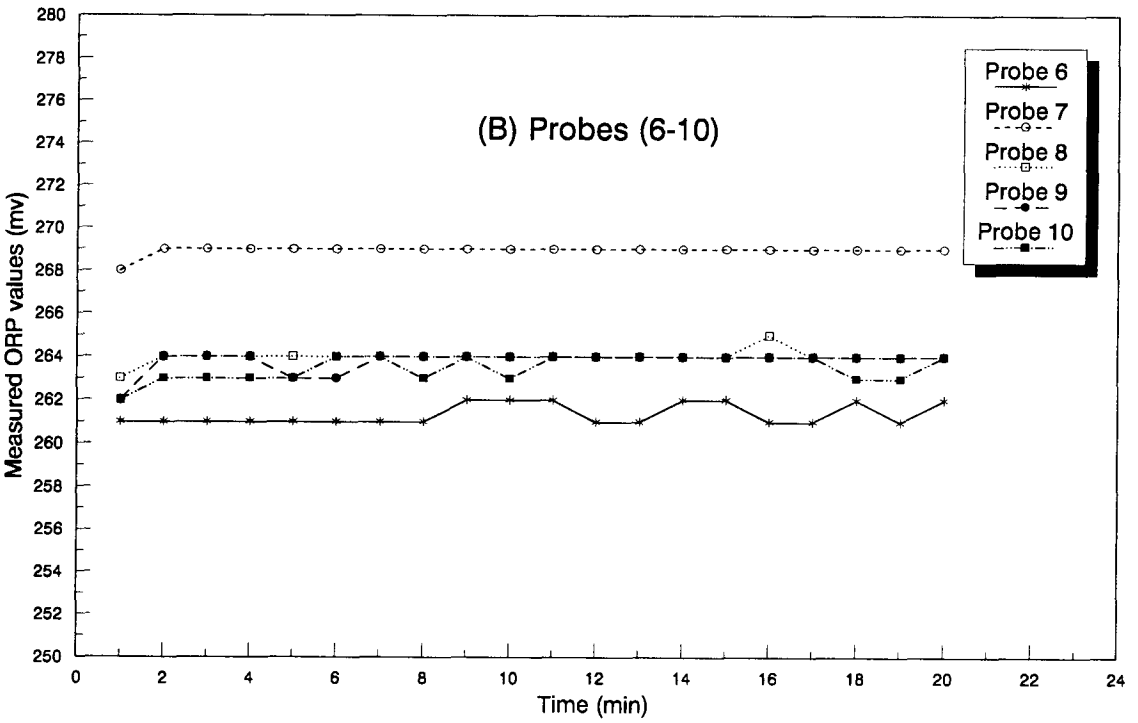


Figure A-1: Probe test 2.1 (pH 4.10)

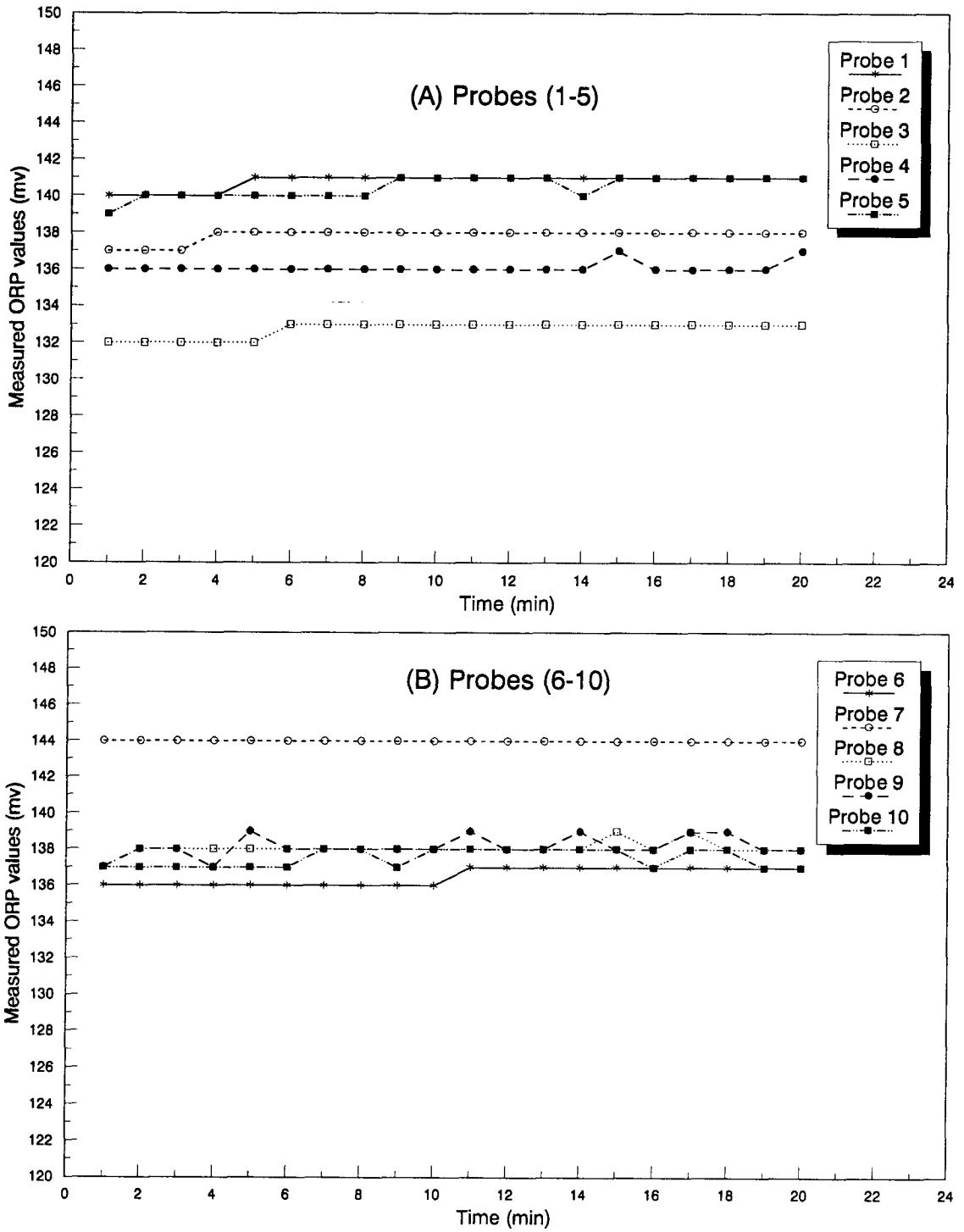


Figure A-2: Probe test 2.2 (pH 6.32)

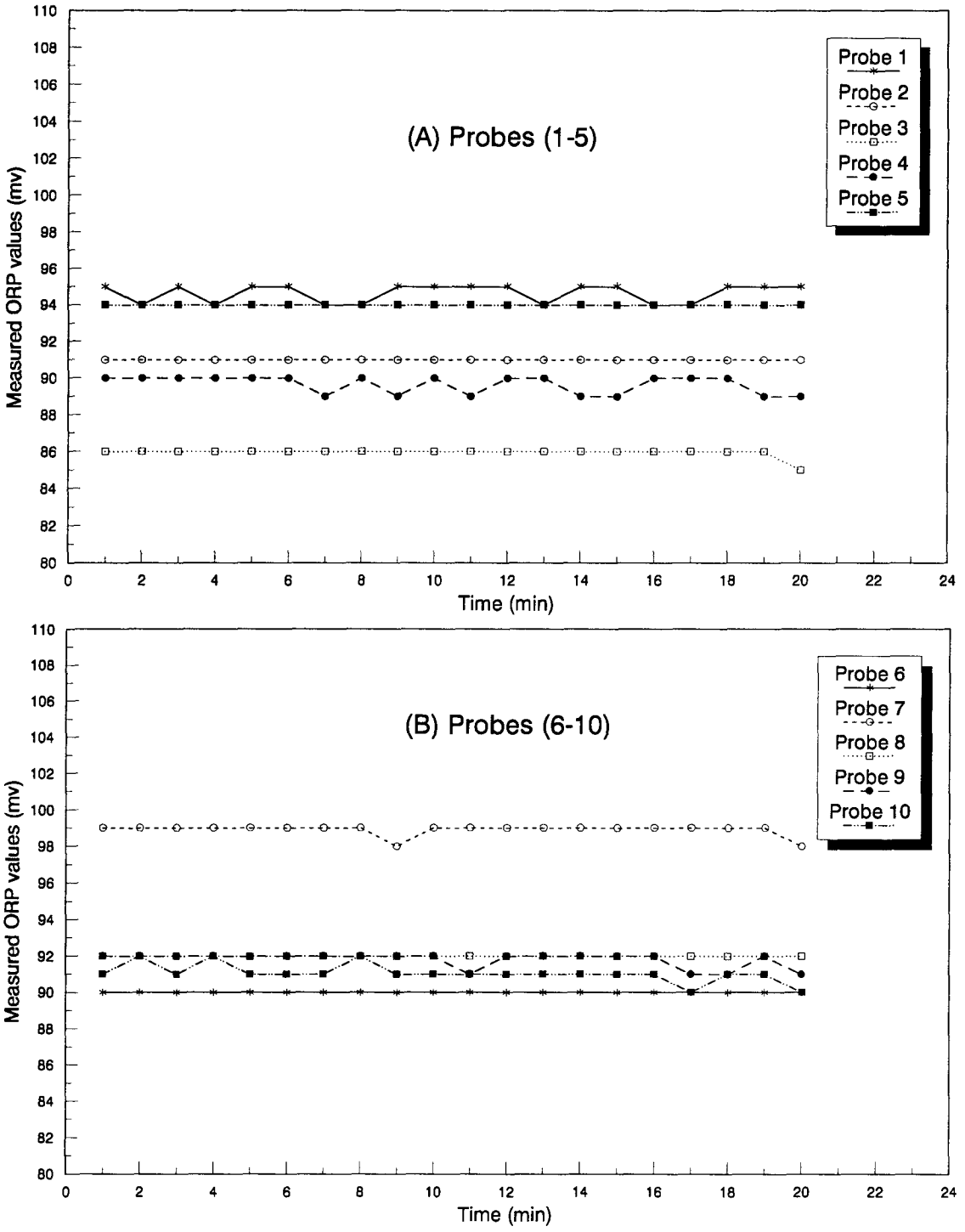


Figure A-3: Probe test 2.3 (pH 7.11)

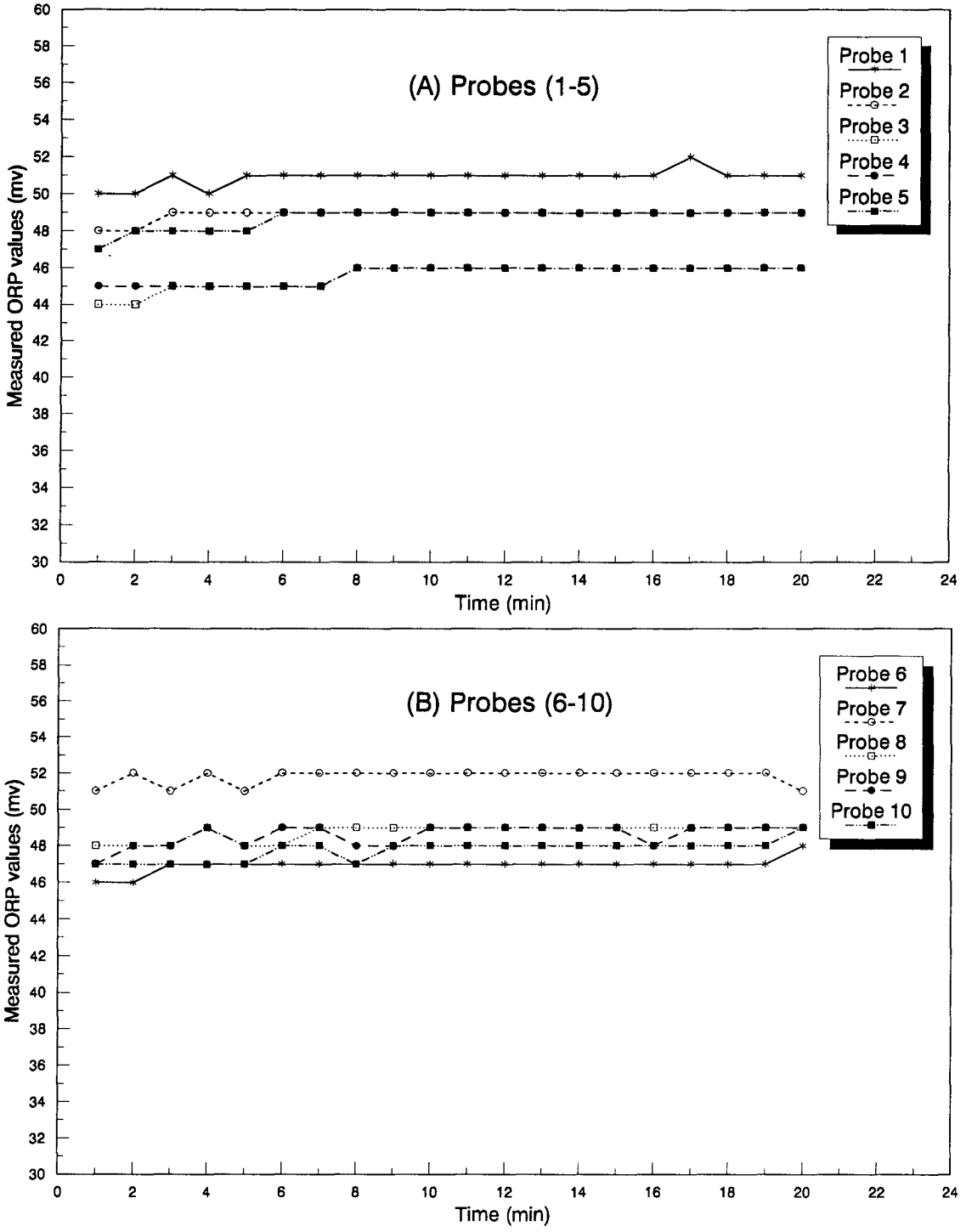


Figure A-4: Probe test 2.4 (pH 7.85)

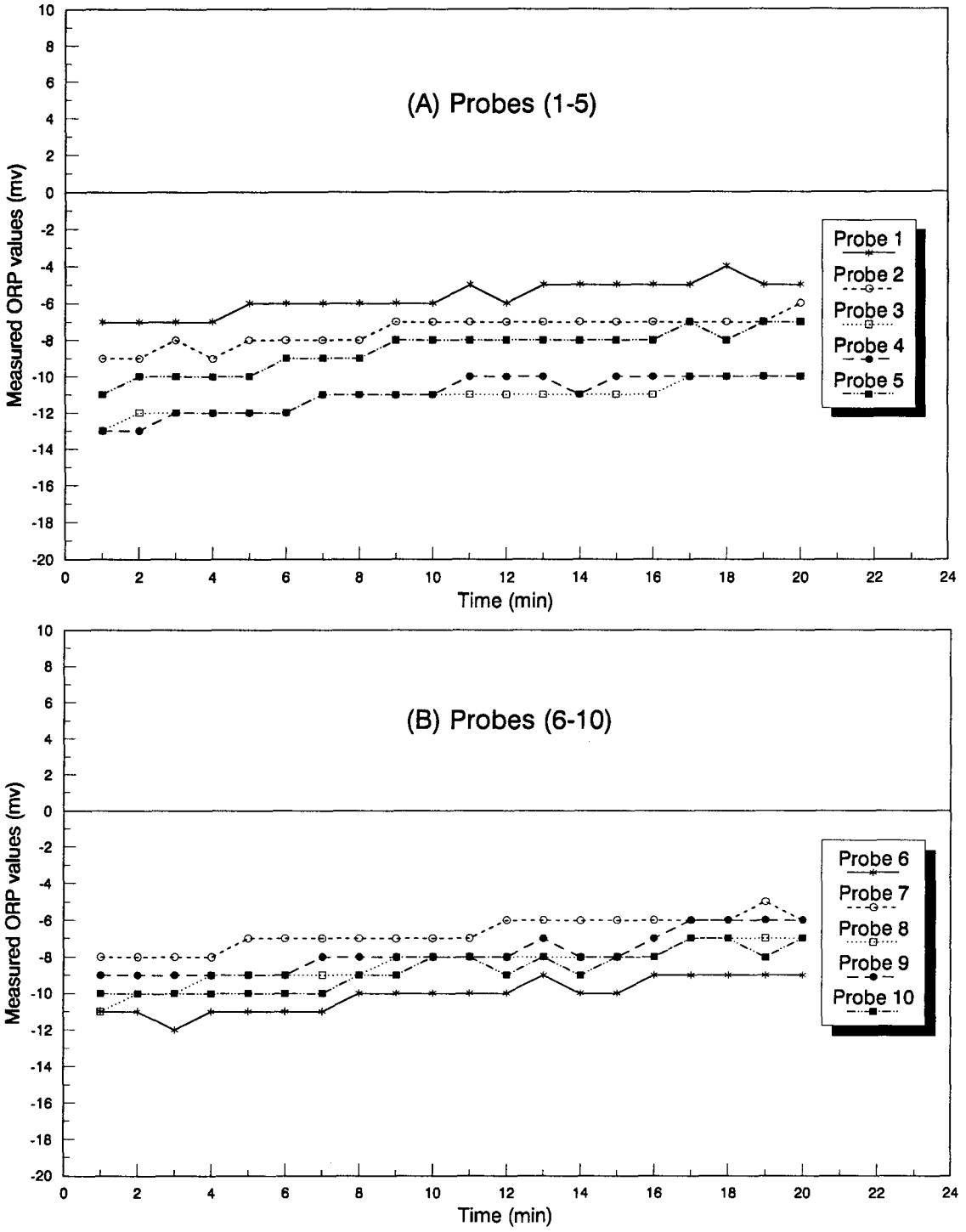


Figure A-5: Probe test 2.5 (pH 8.85)

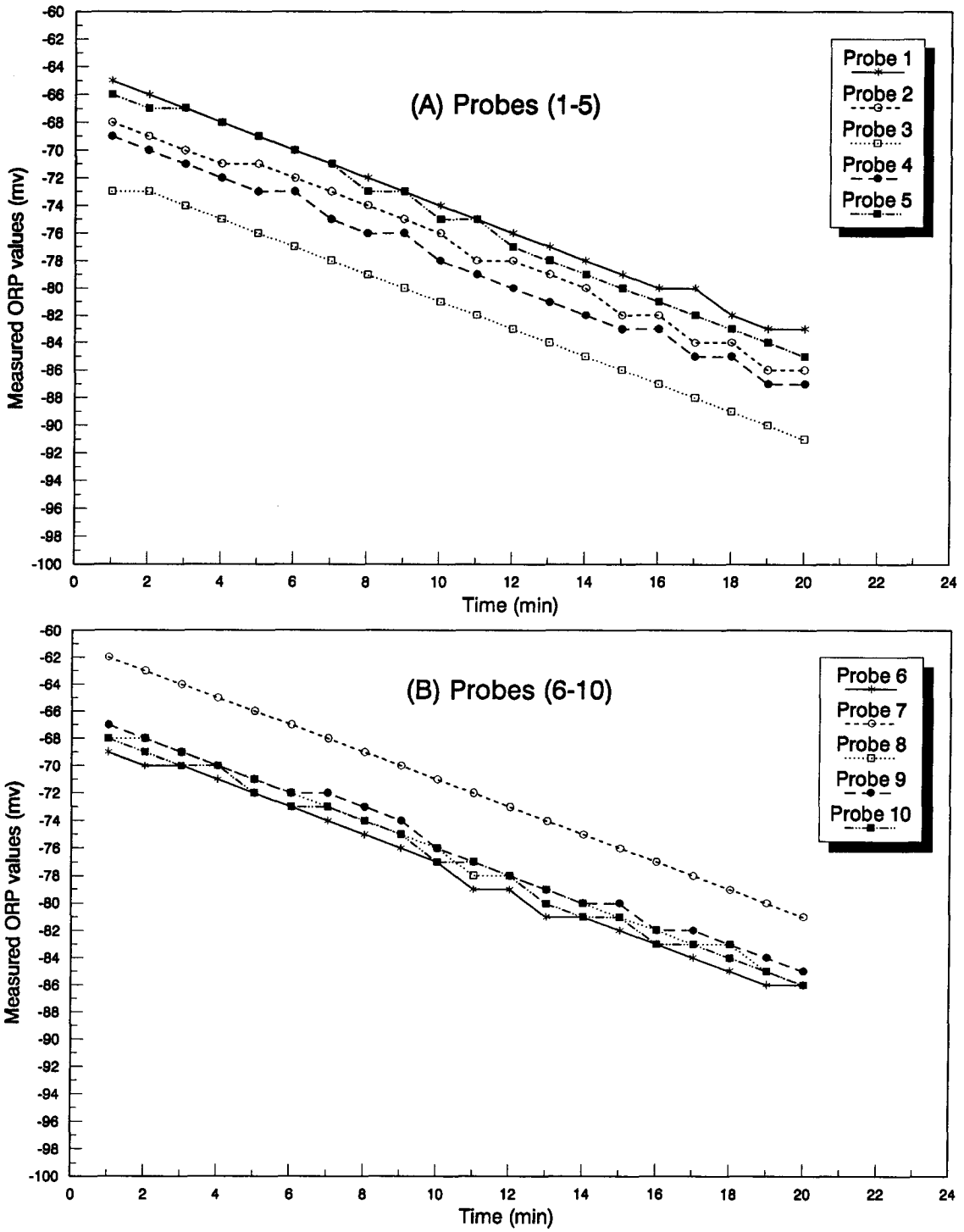


Figure A-6: Probe test 2.6 (pH 9.94)

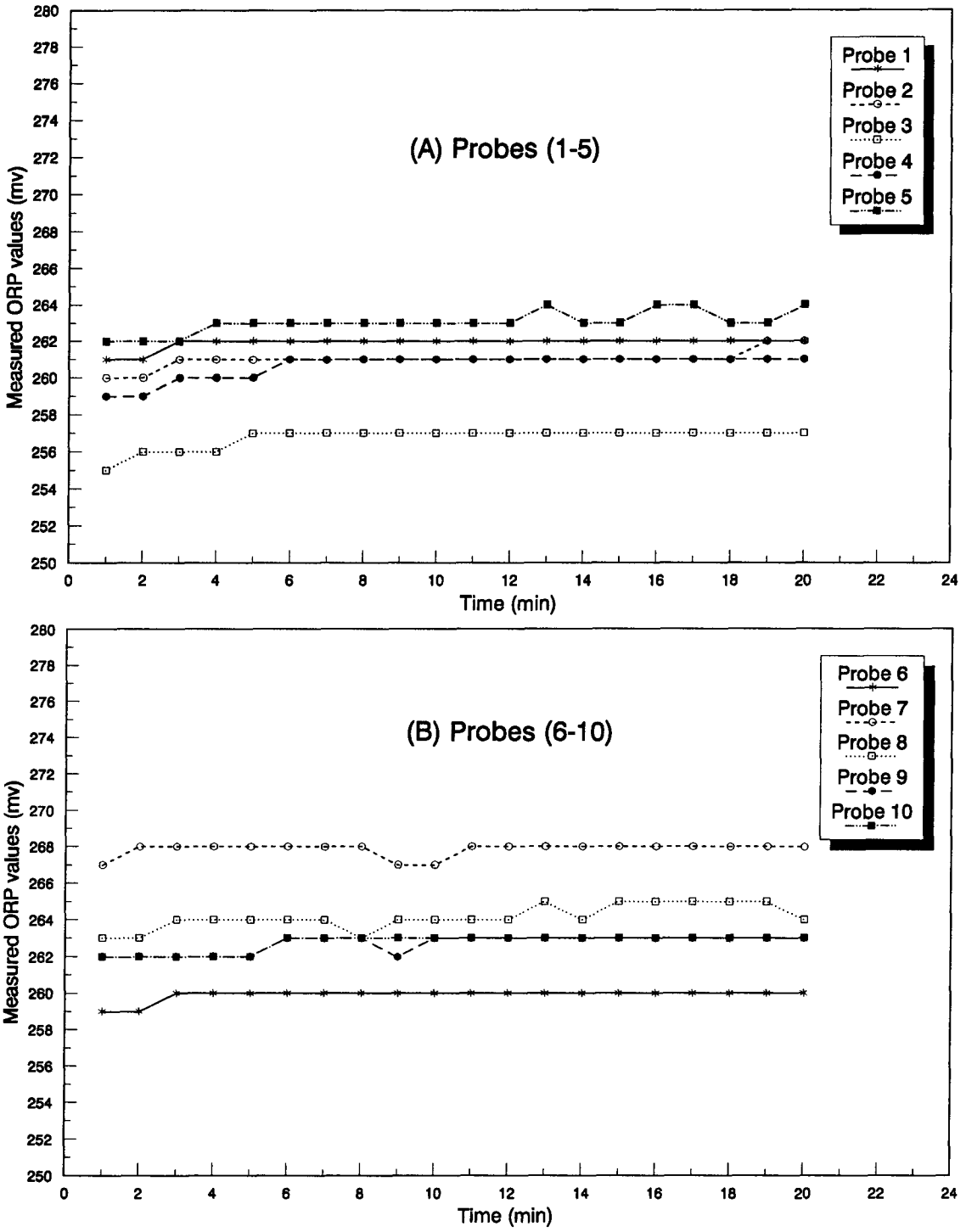


Figure A-7: Probe test 3.1 (pH 4.06)

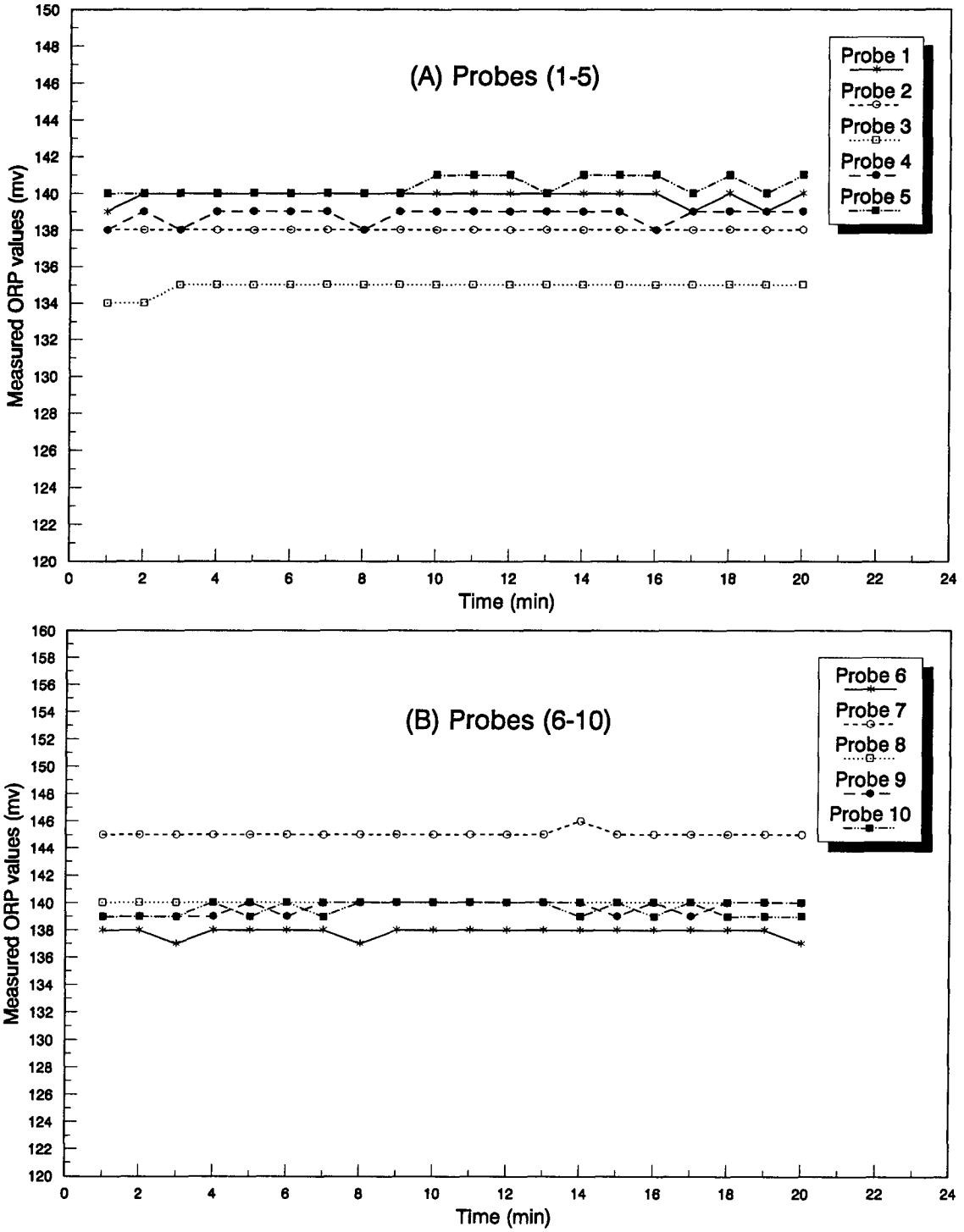


Figure A-8: Probe test 3.2 (pH 6.25)

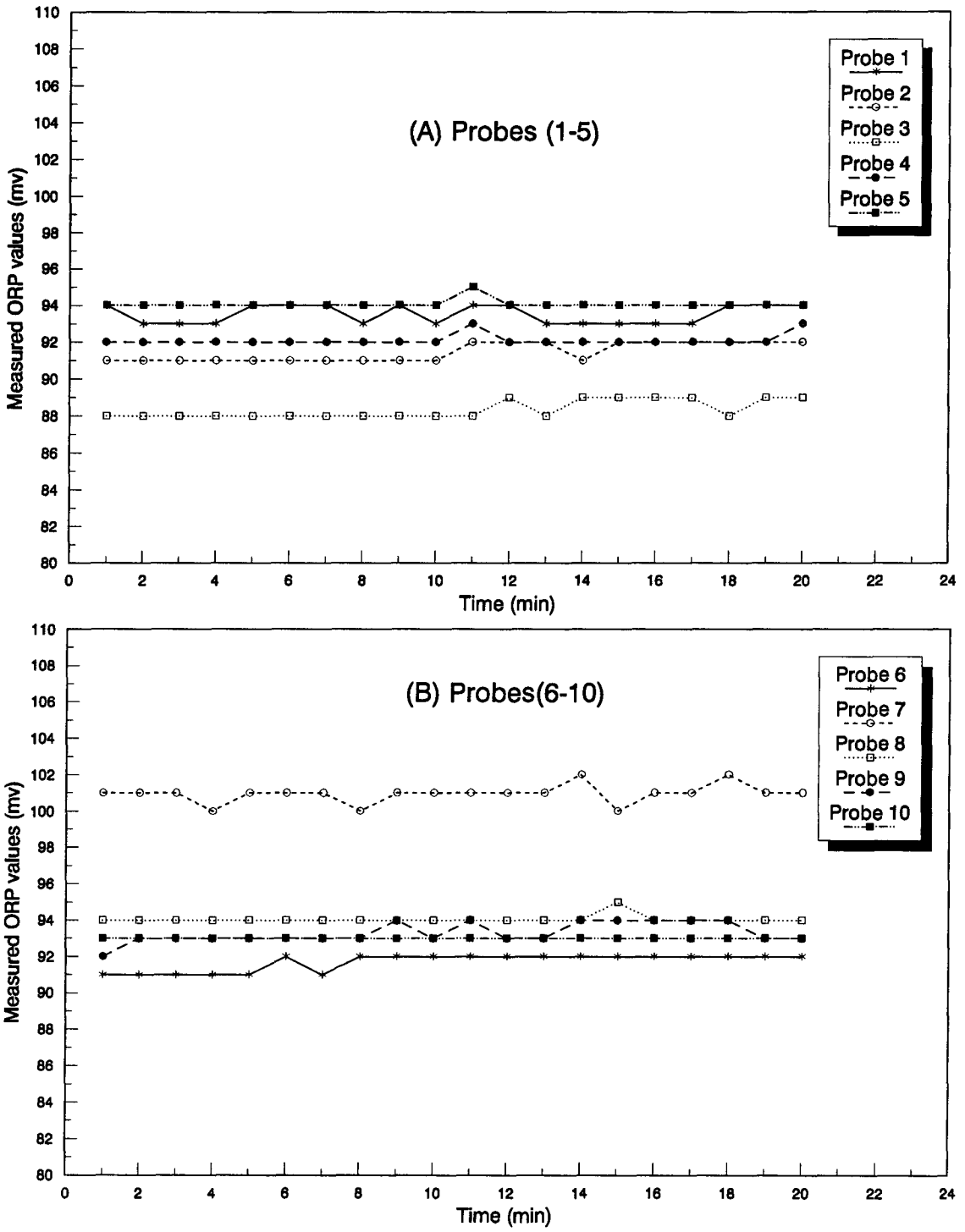


Figure A-9: Probe test 3.3 (pH 7.02)

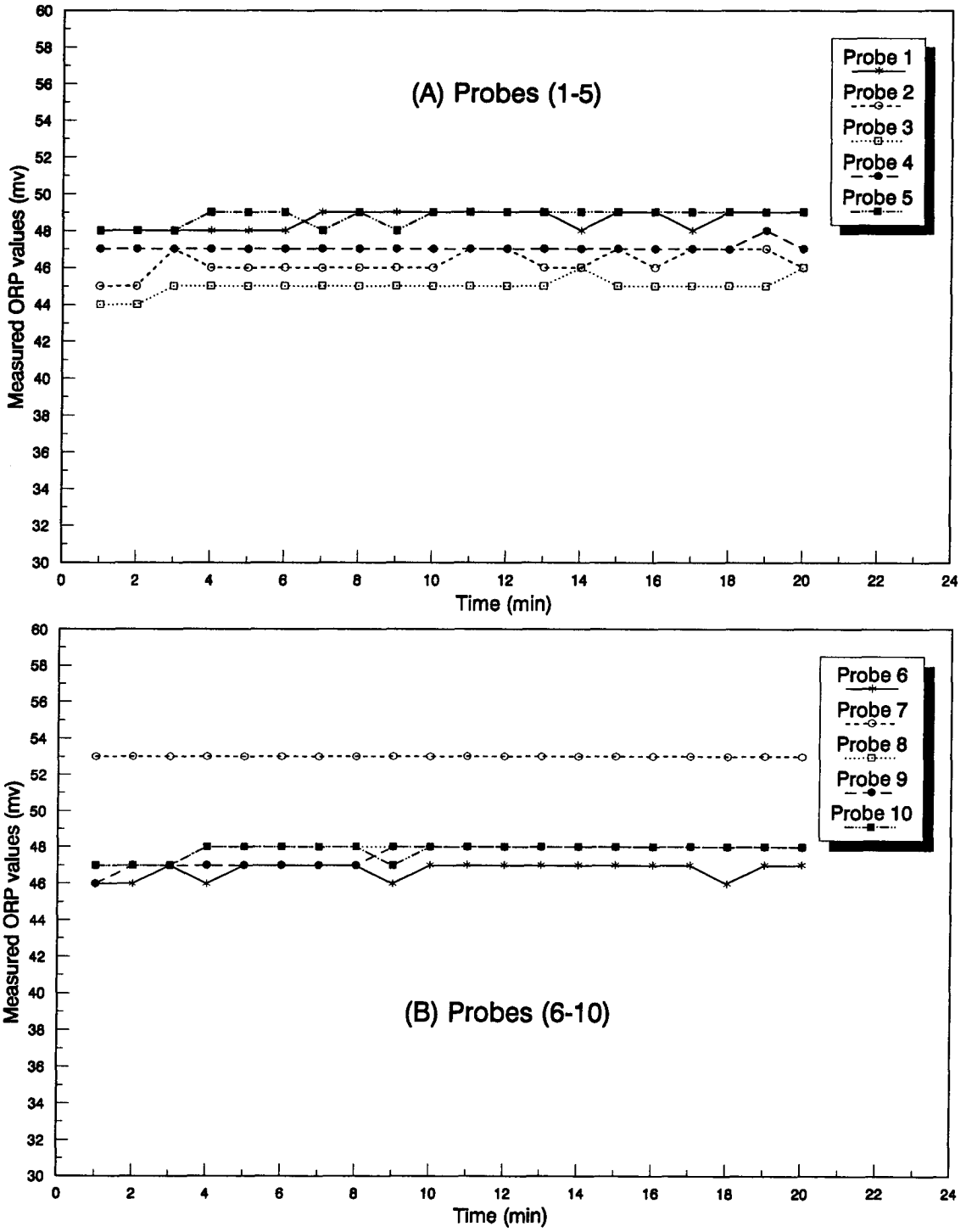


Figure A-10: Probe test 3.4 (pH 7.75)

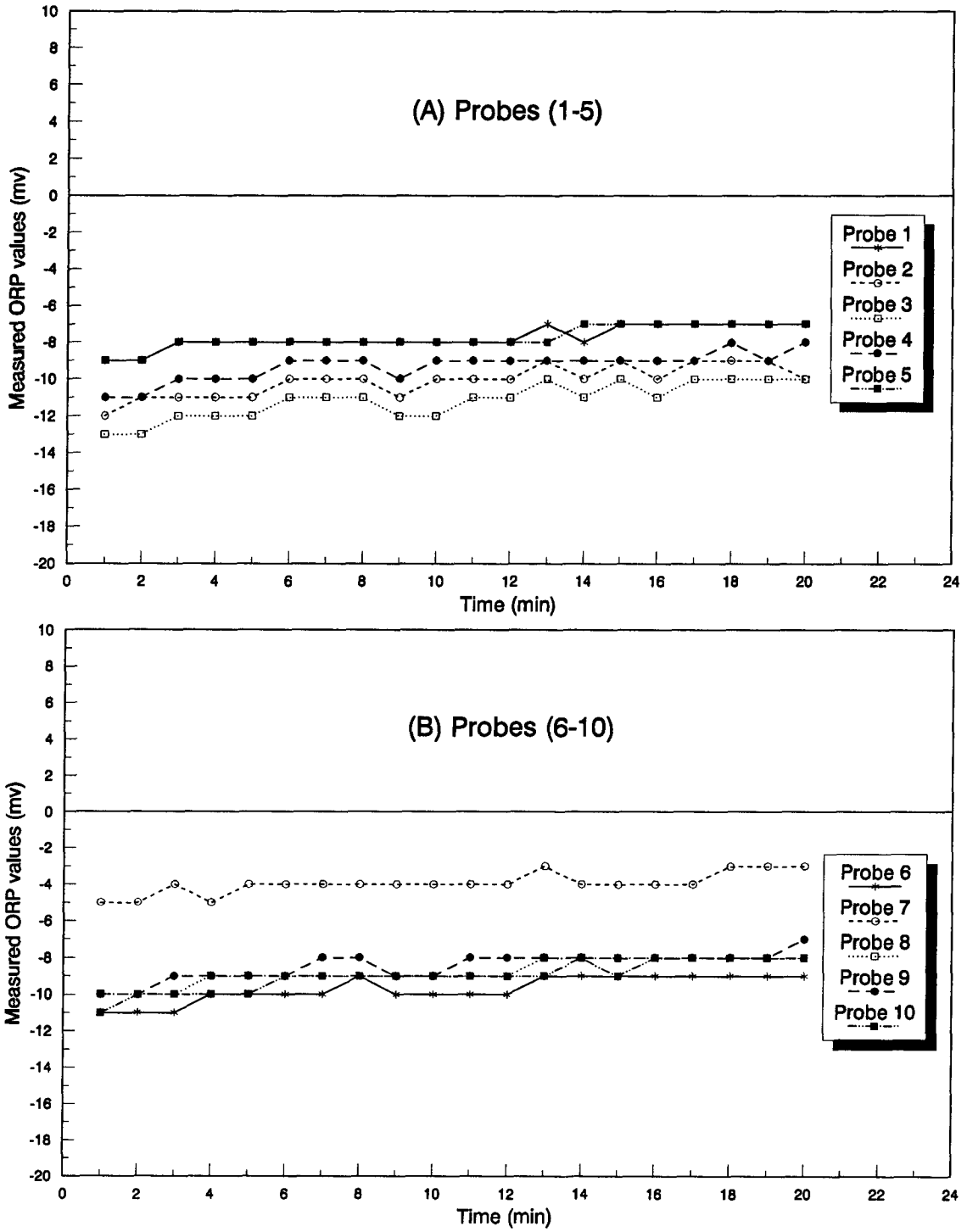


Figure A-11: Probe test 3.5 (pH 8.72)

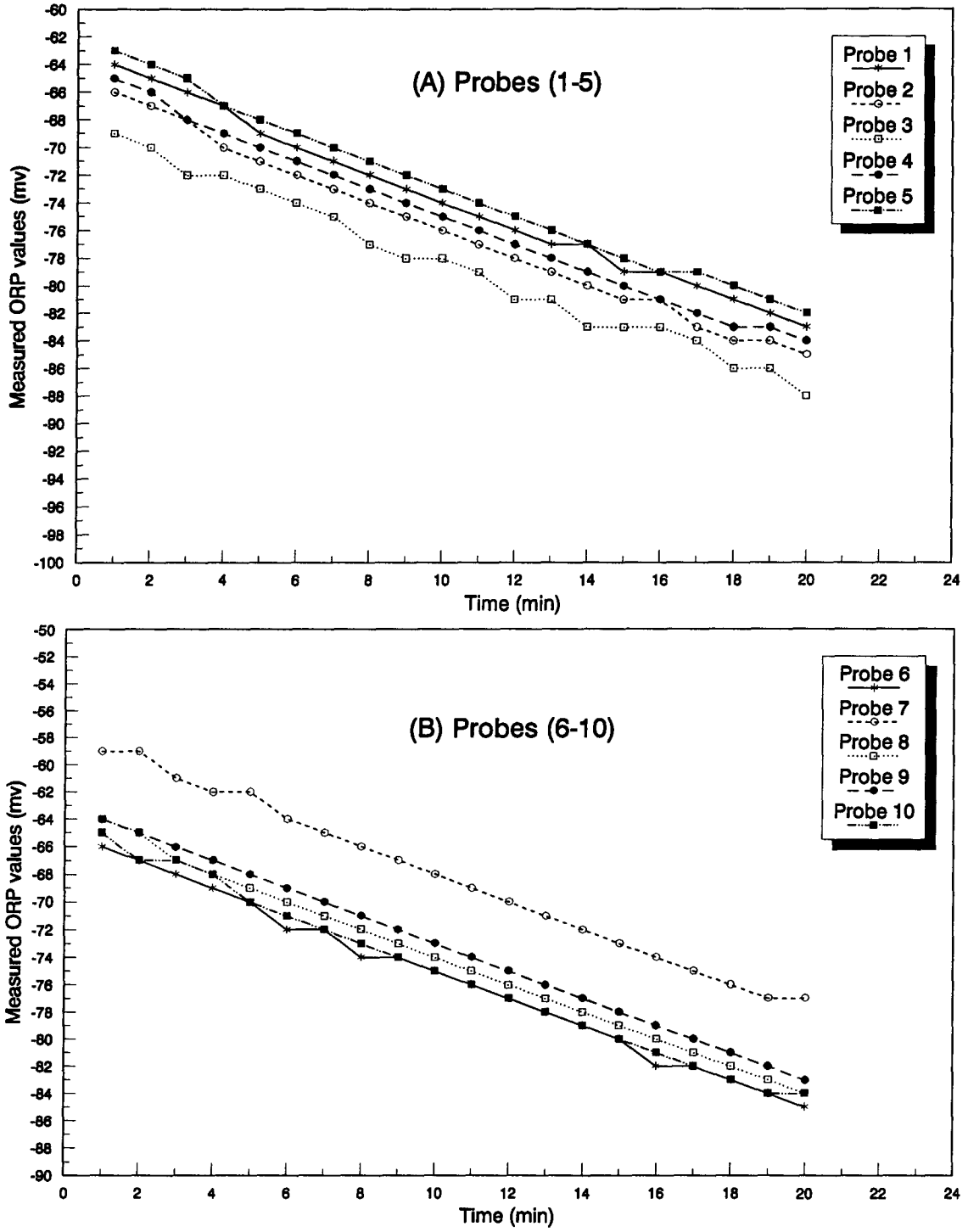


Figure A-12: Probe test 3.6 (pH 9.79)

Appendix B

Results of Anoxic Batch Test 2 and Anoxic Batch Test 3

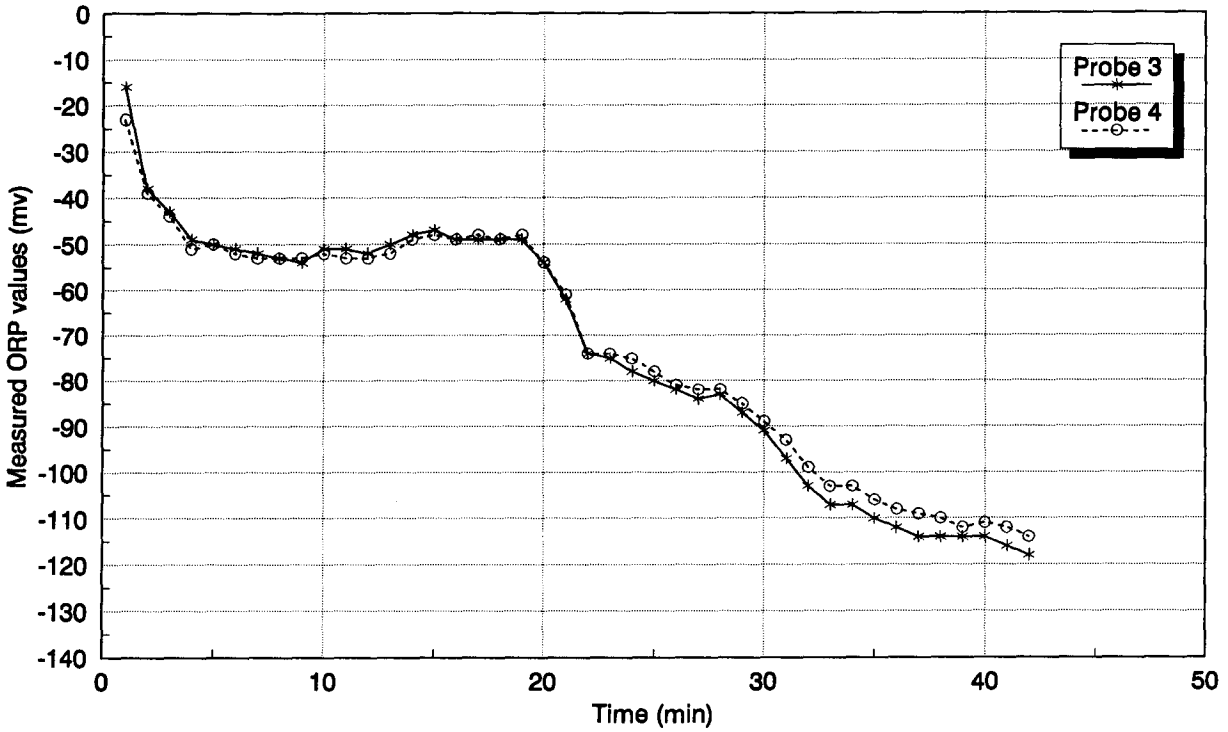


Figure B-1: Anoxic batch test 2.1 (ratio 0)

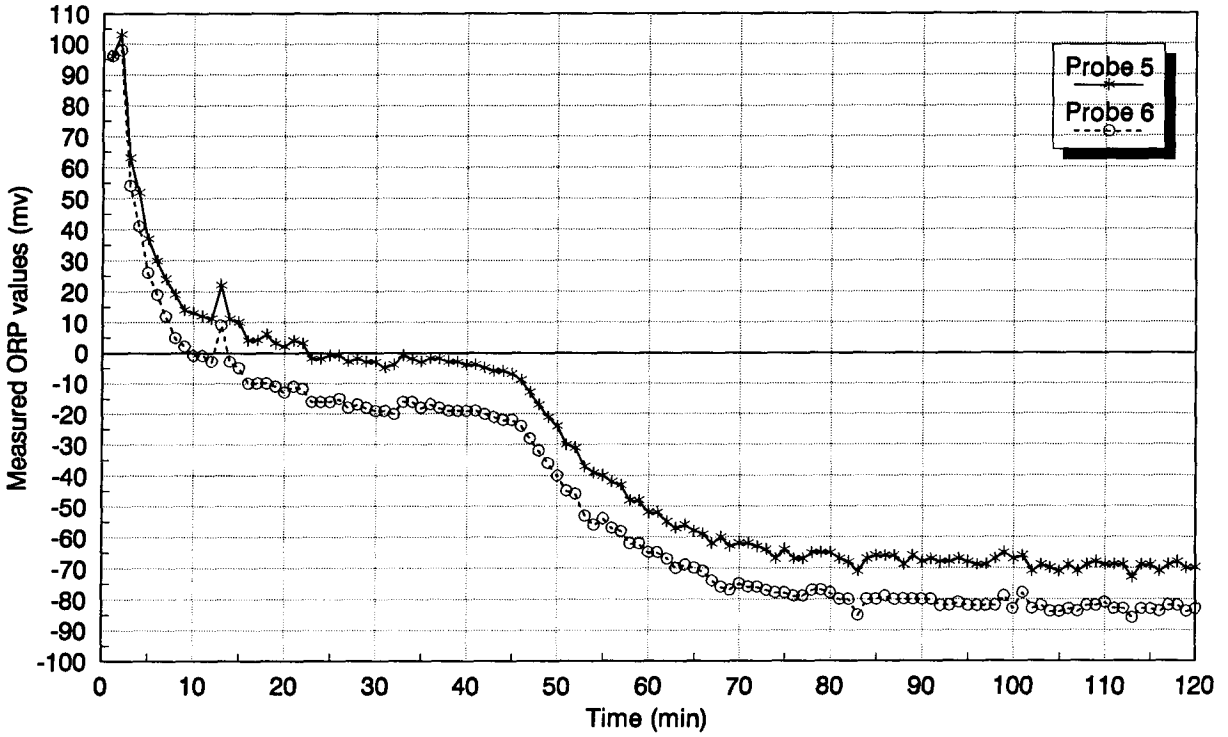


Figure B-2: Anoxic batch test 2.2 (ratio 1)

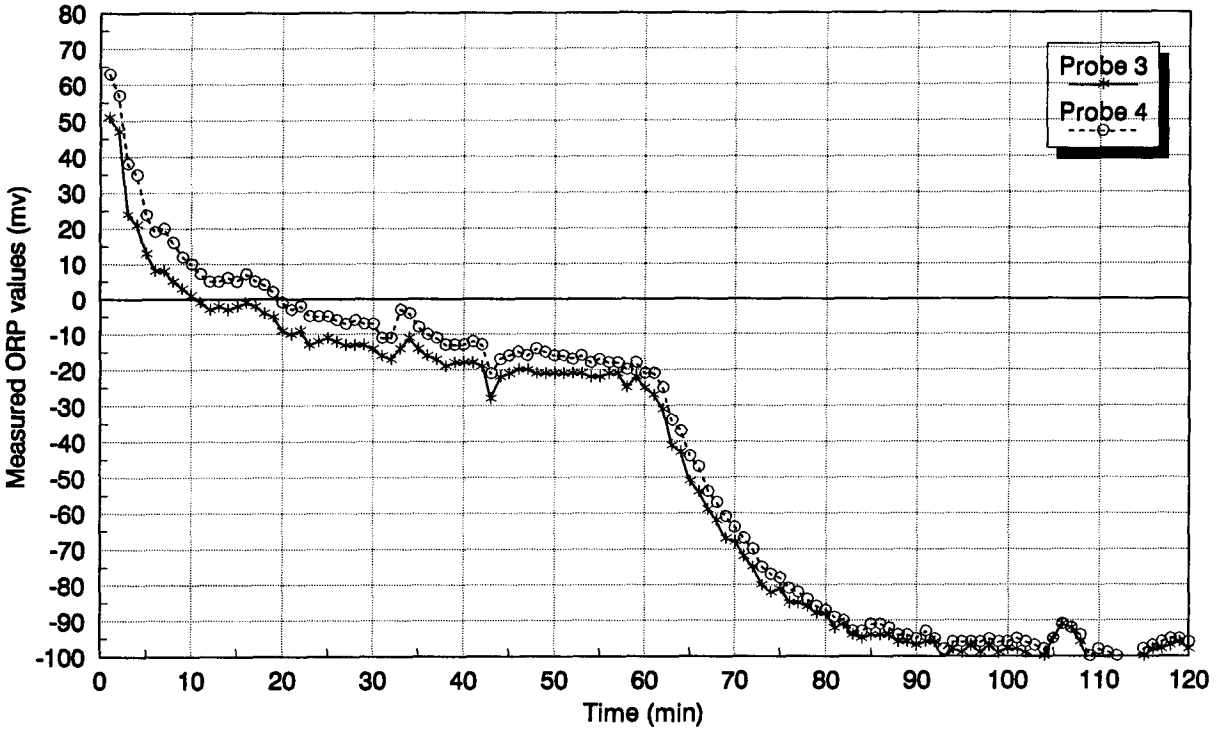


Figure B-3: Anoxic batch test 2.3 (ratio 2)

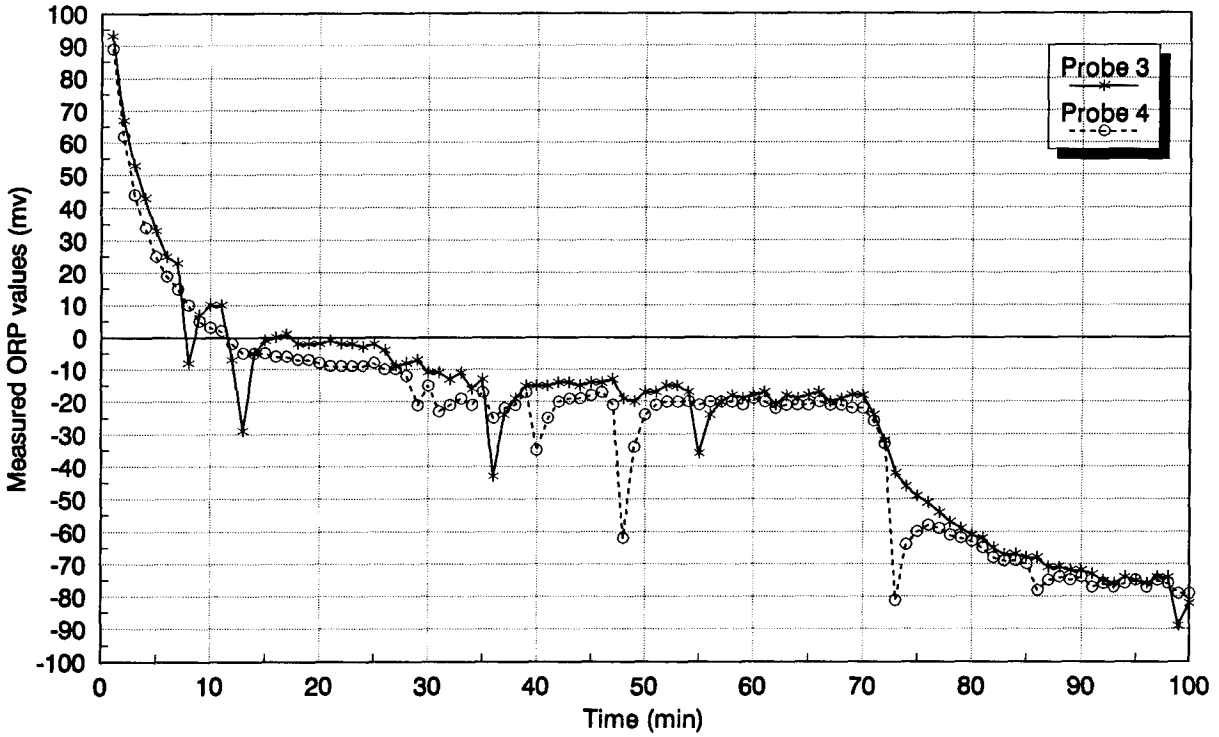


Figure B-4: Anoxic batch test 2.4 (ratio 3)

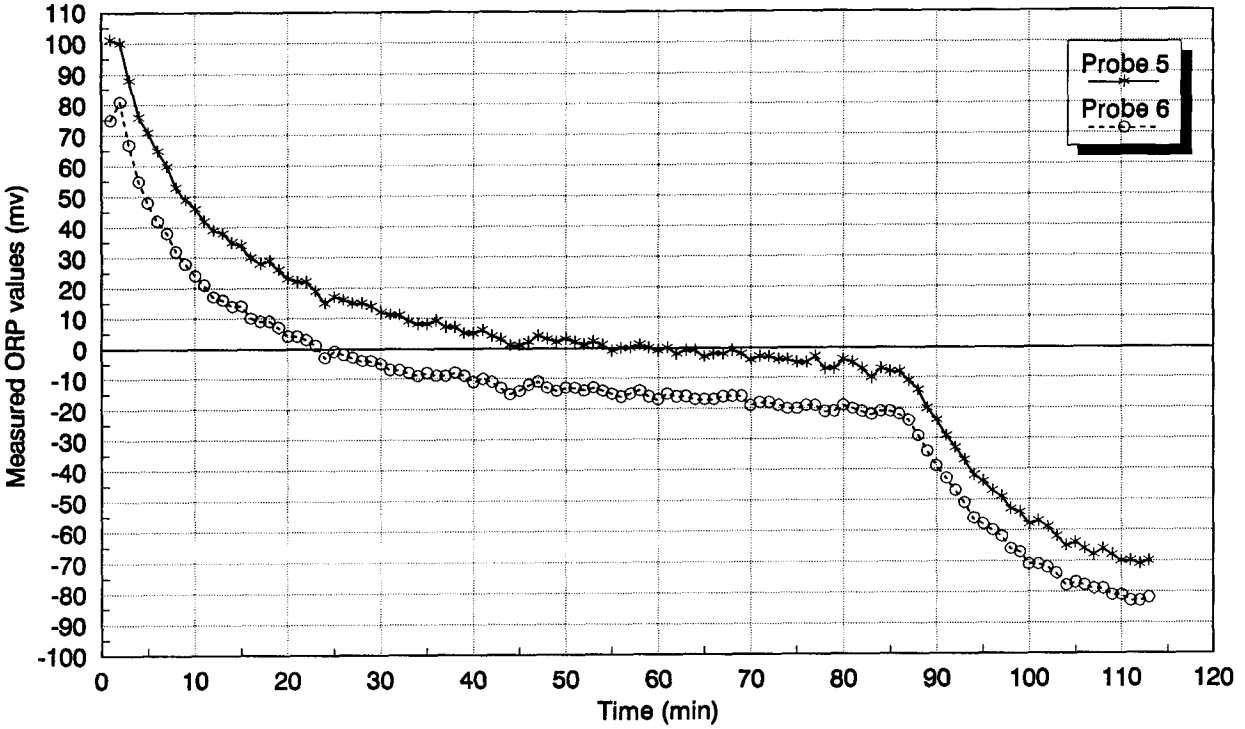


Figure B-5: Anoxic batch test 2.5 (ratio 4)

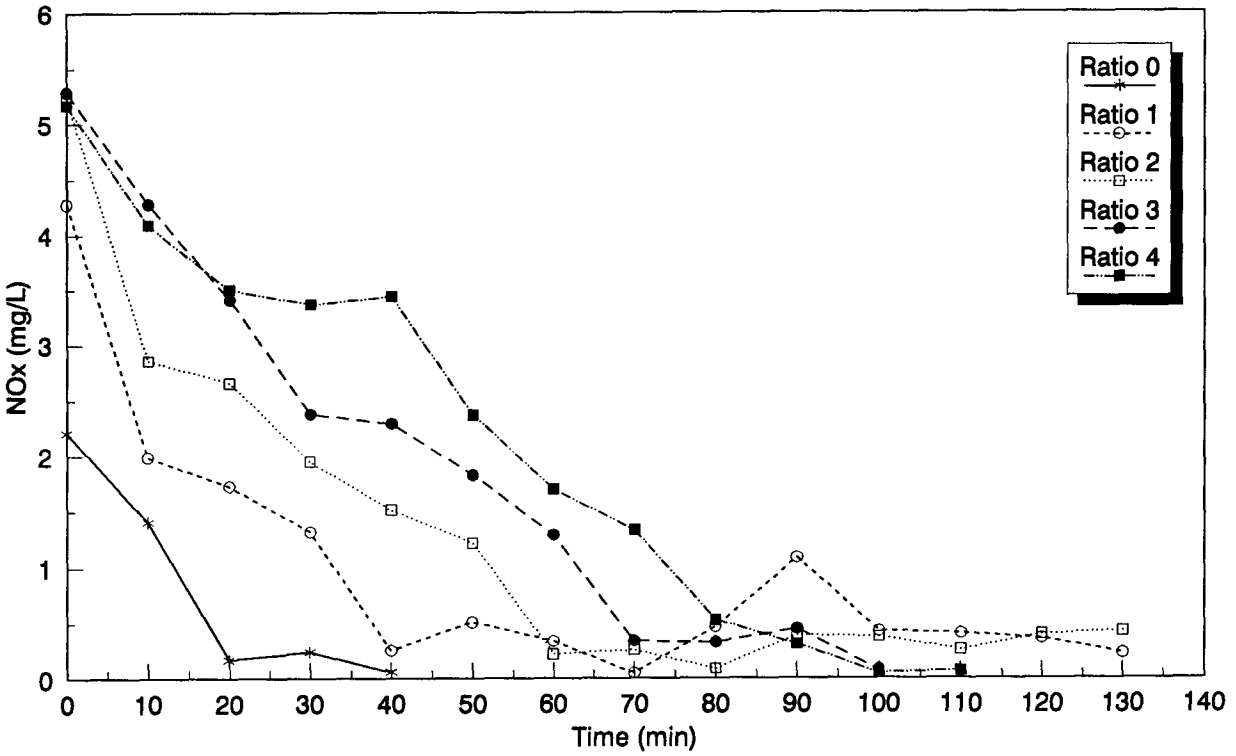


Figure B-6: NOx test results (anoxic test 2)

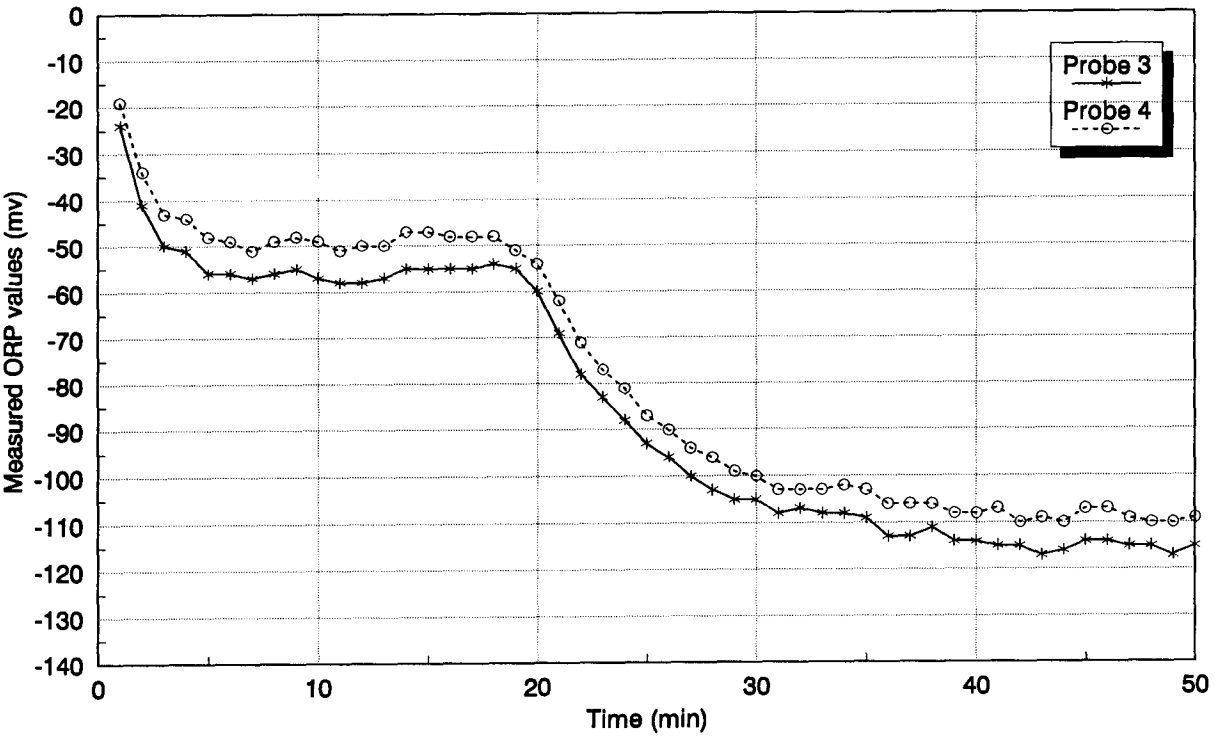


Figure B-7: Anoxic batch test 3.1 (ratio 0)

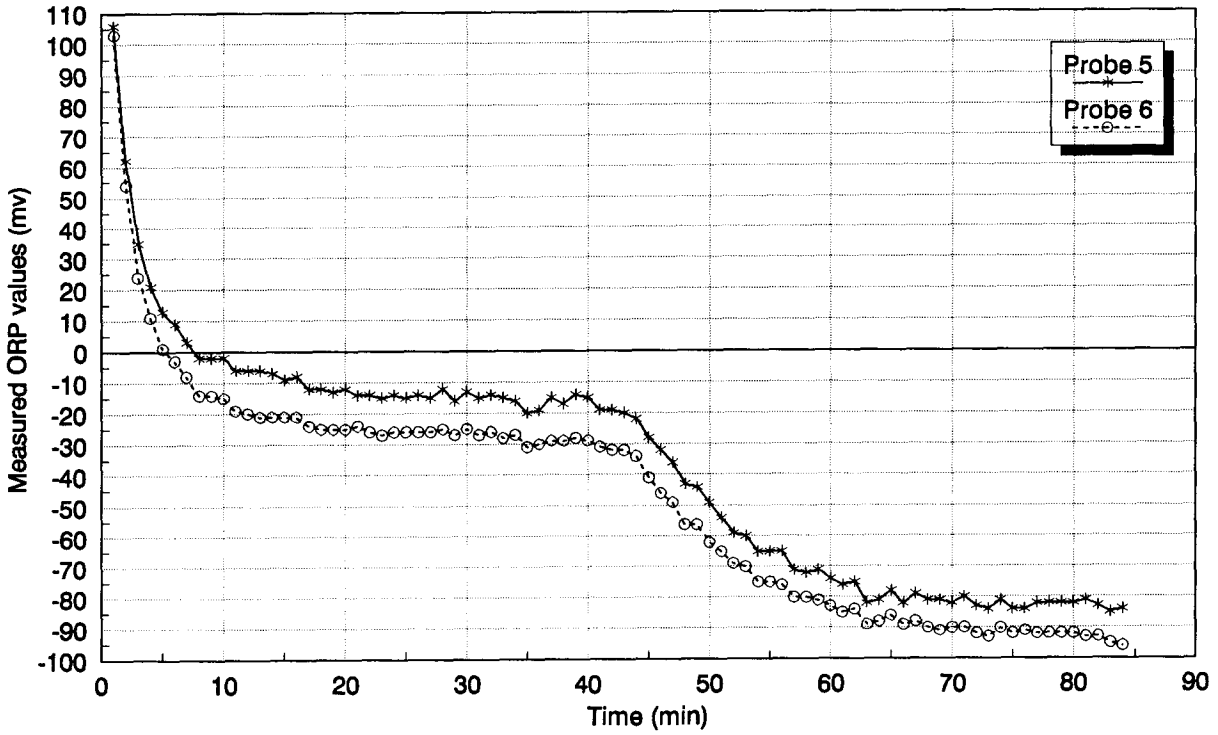


Figure B-8: Anoxic batch test 3.2 (ratio 1)

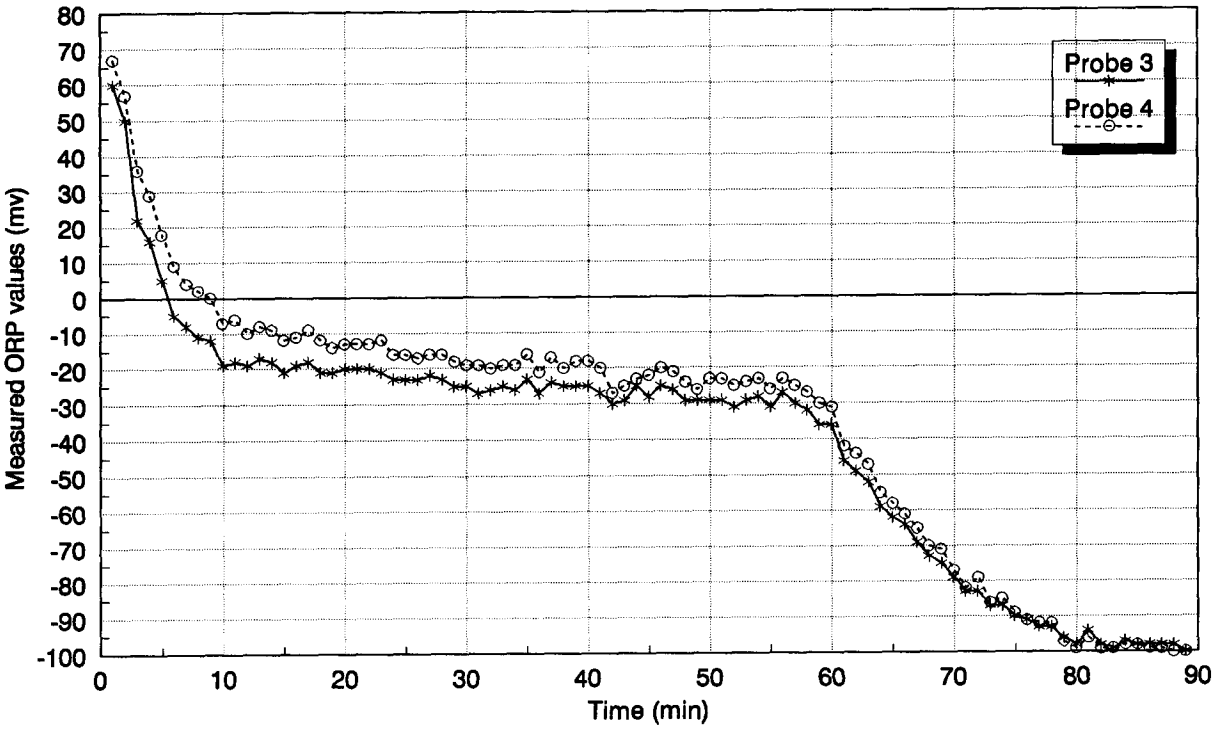


Figure B-9: Anoxic batch test 3.3 (ratio 2)

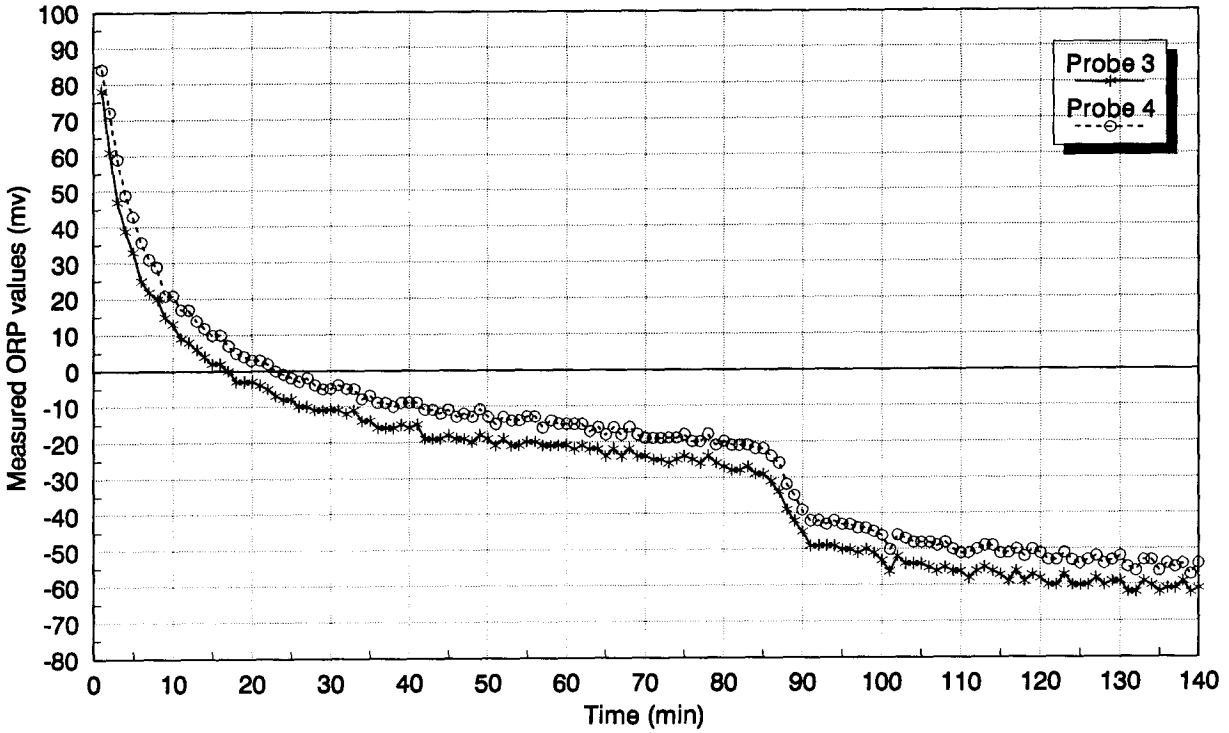


Figure B-10: Anoxic batch test 3.4 (ratio 3)

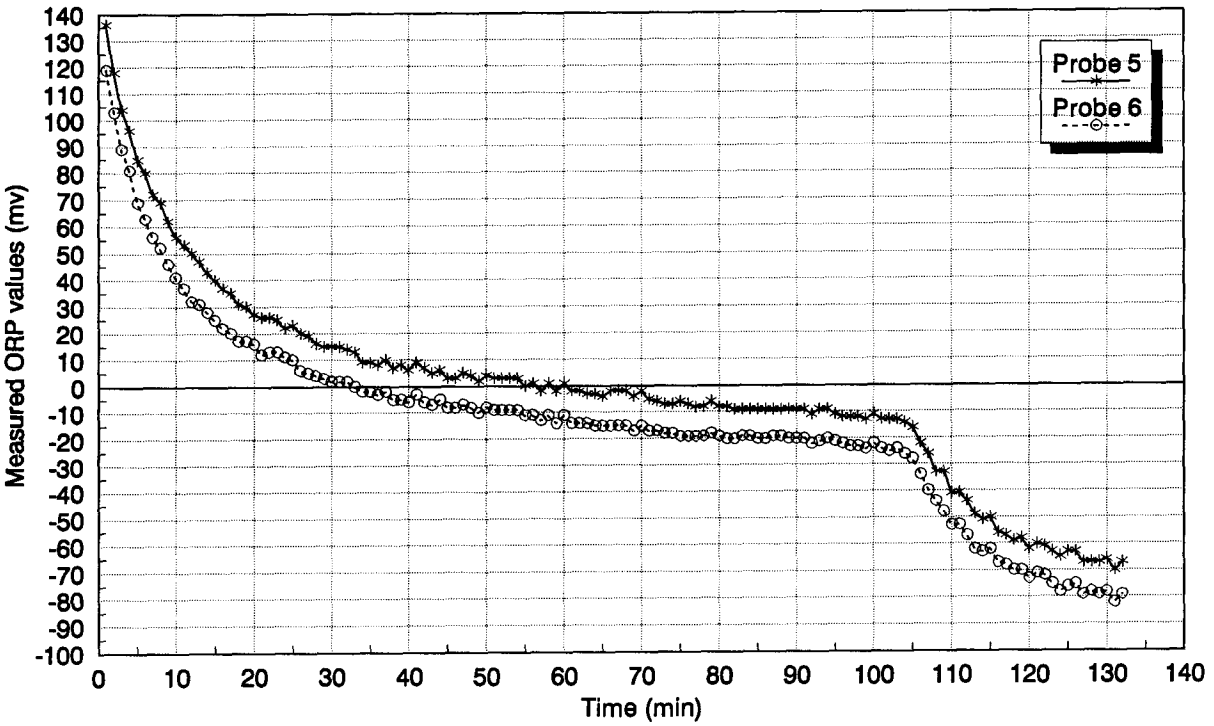


Figure B-11: Anoxic batch test 3.5 (ratio 4)

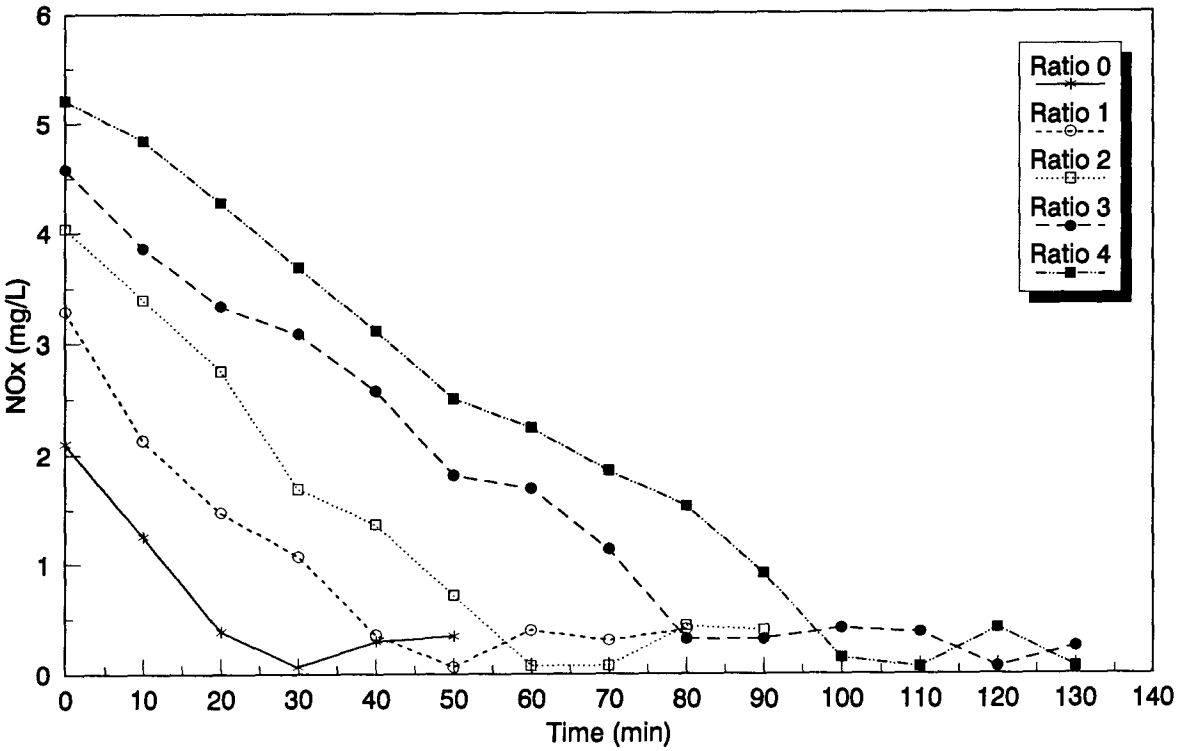


Figure B-12: NOx test results (anoxic test 3)

Appendix C

Results of Carbon Addition Test 2 and Carbon Addition Test 3

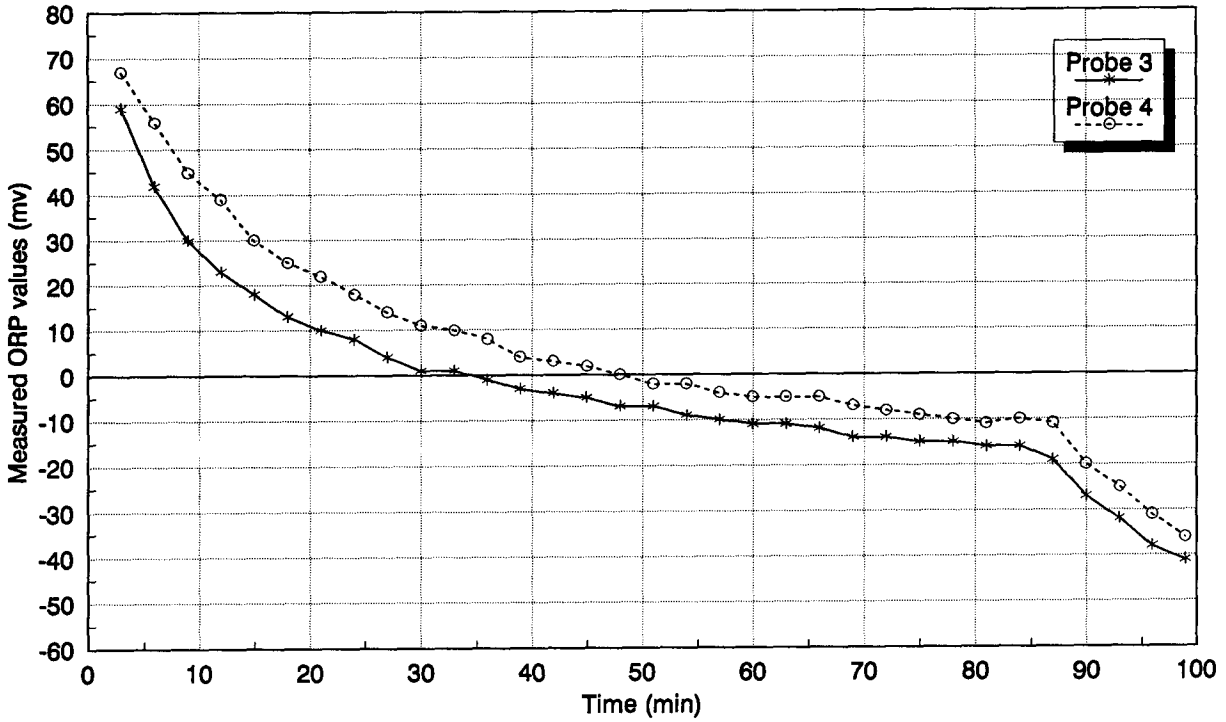


Figure C-1: Carbon addition test 2.1 (control)

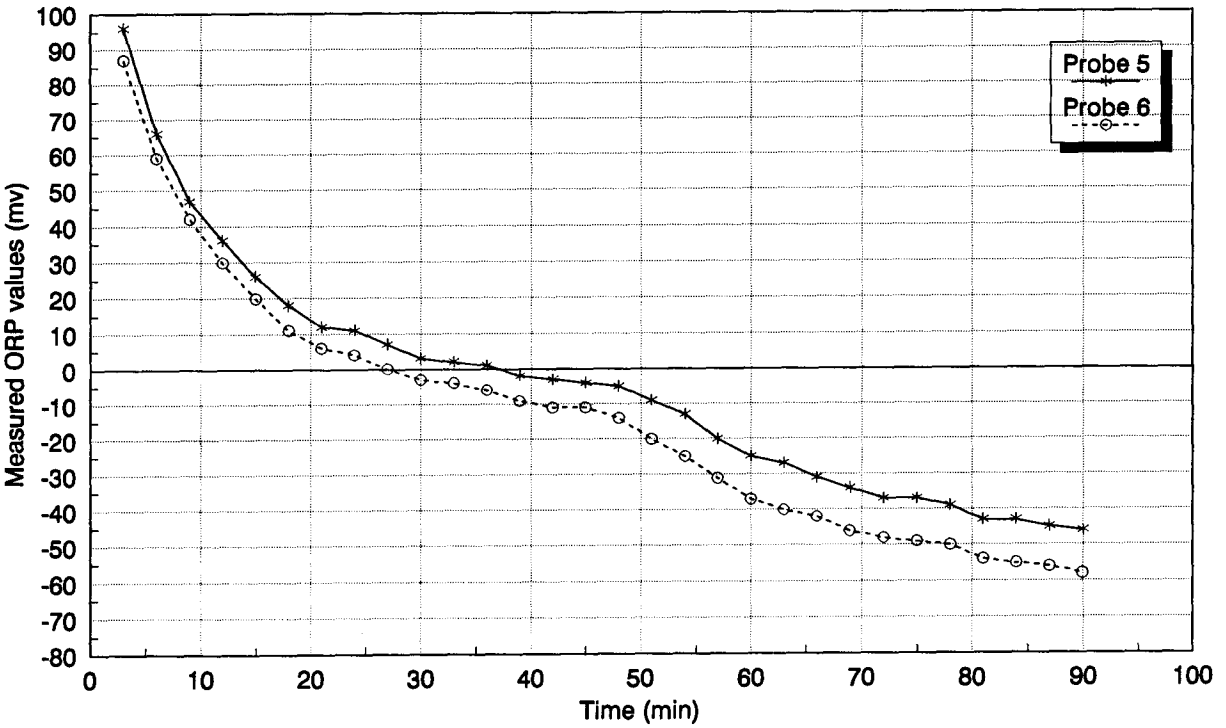


Figure C-2: Carbon addition test 2.2 (20 mg/L)

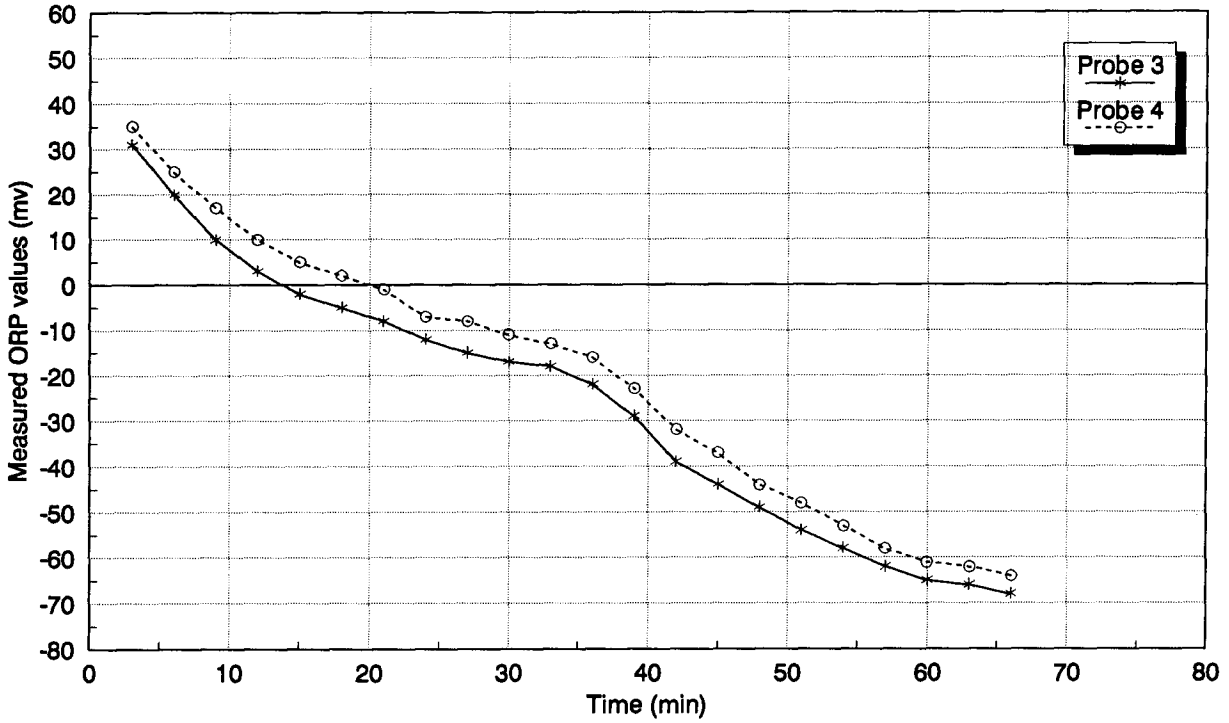


Figure C-3: Carbon addition test 2.3 (40 mg/L)

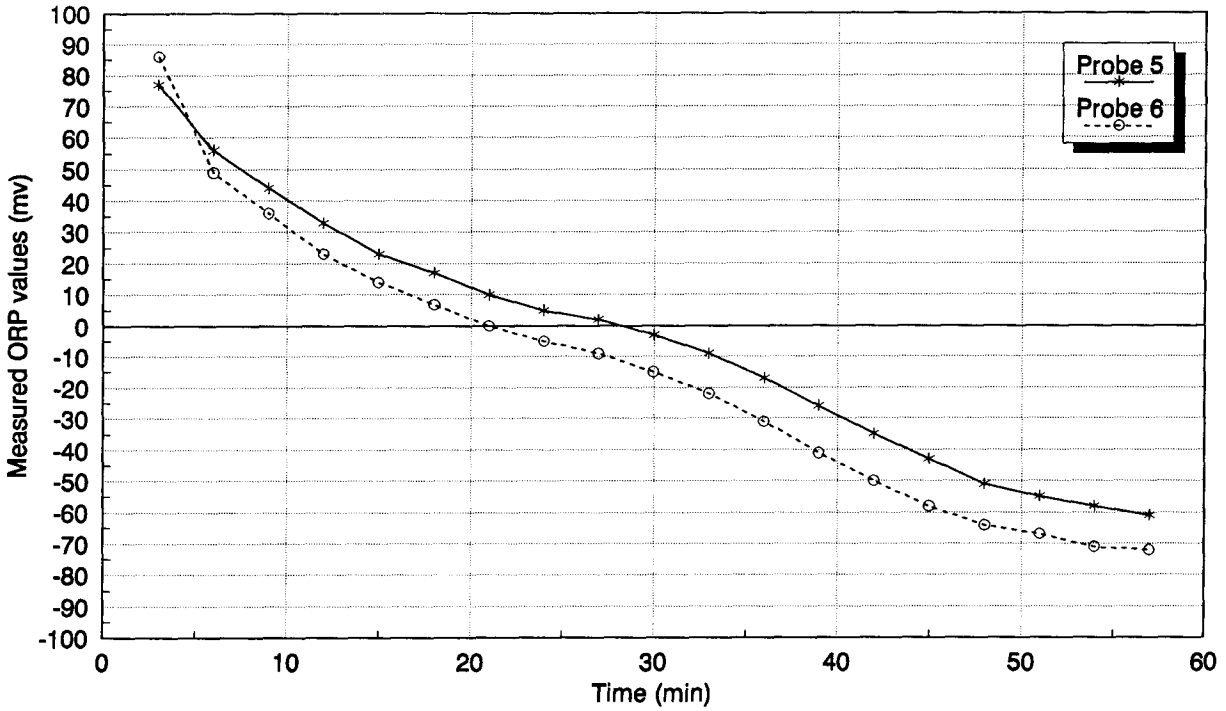


Figure C-4: Carbon addition test 2.4 (60 mg/L)

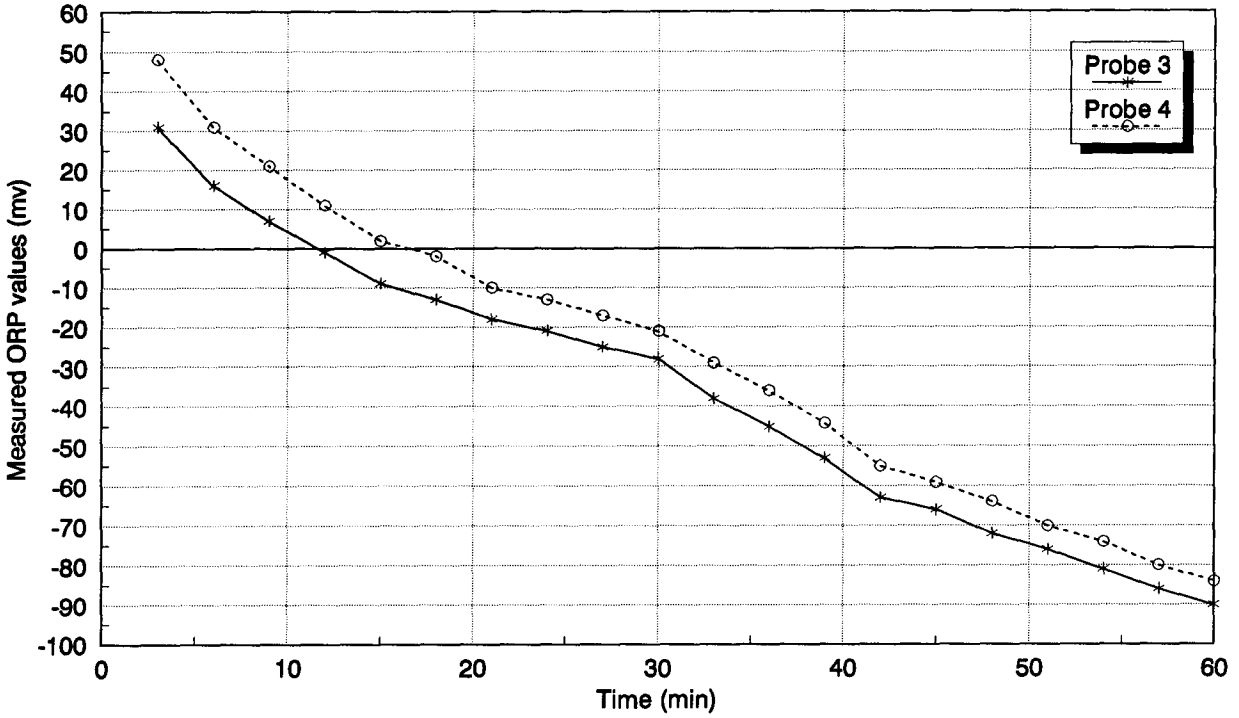


Figure C-5: Carbon addition test 2.5 (80 mg/L)

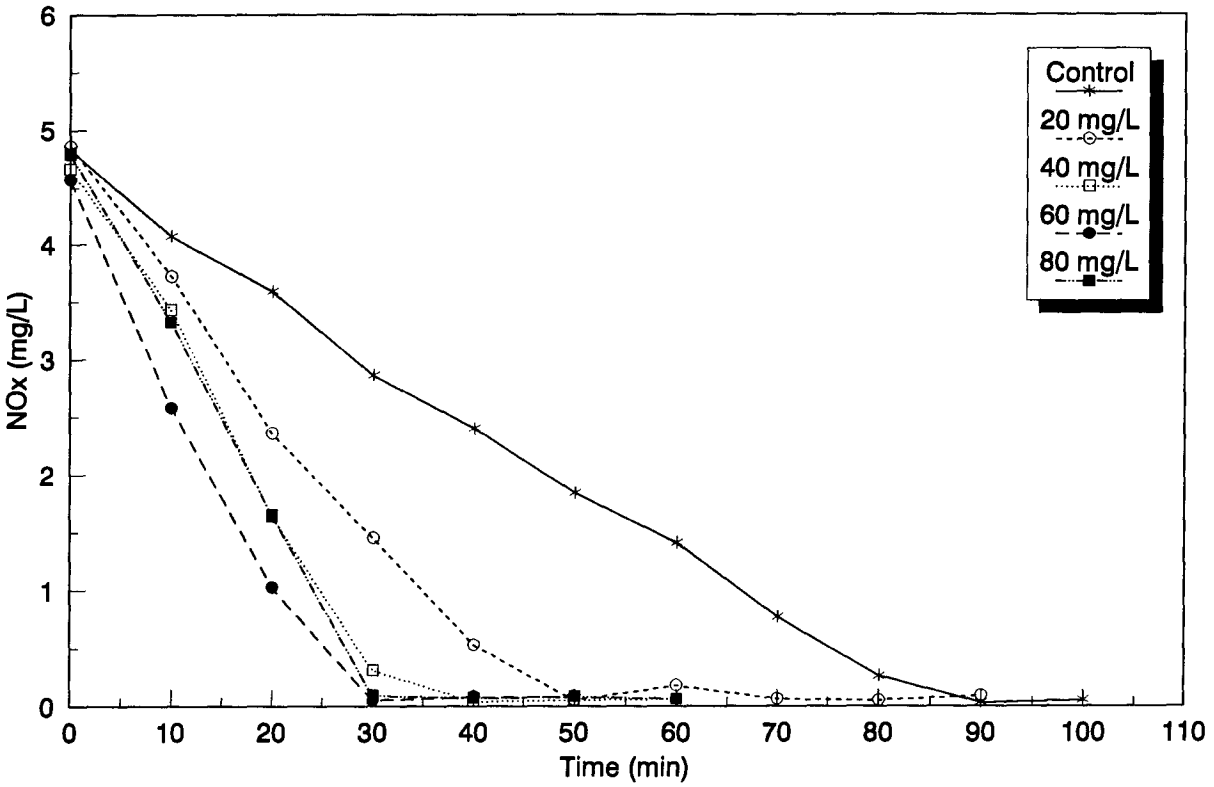


Figure C-6: NOx test results (carbon addition test 2)

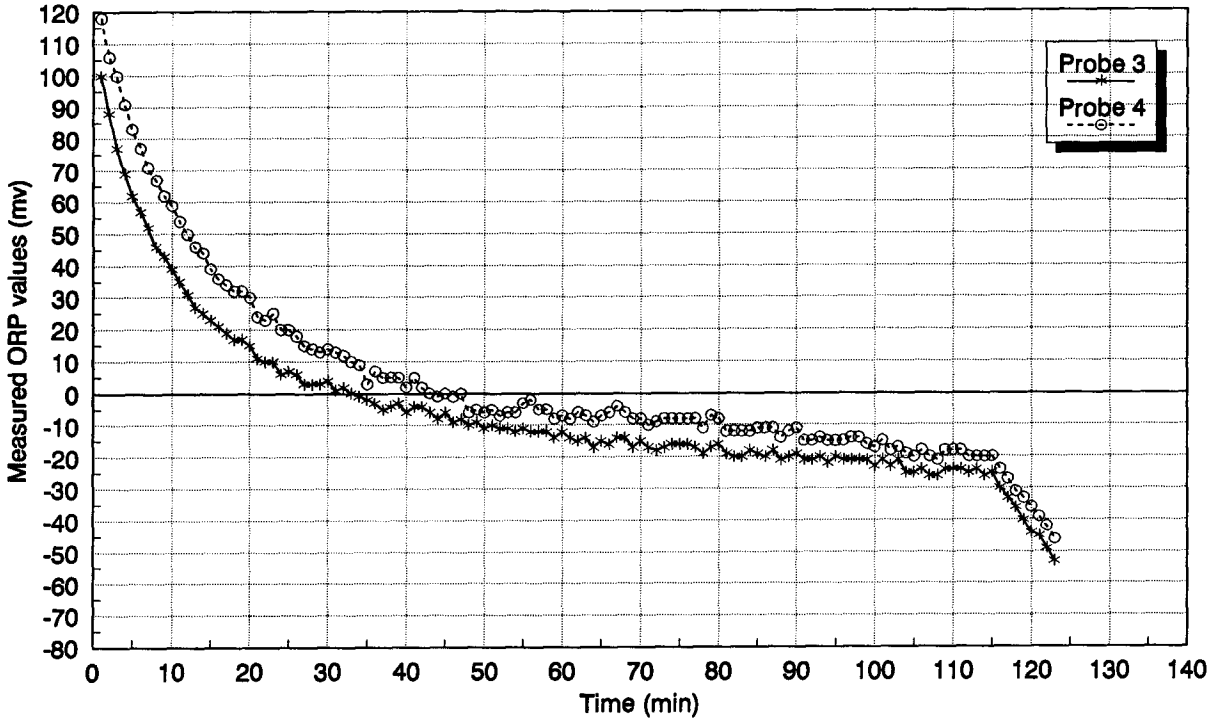


Figure C-7: Carbon addition test 3.1 (control)

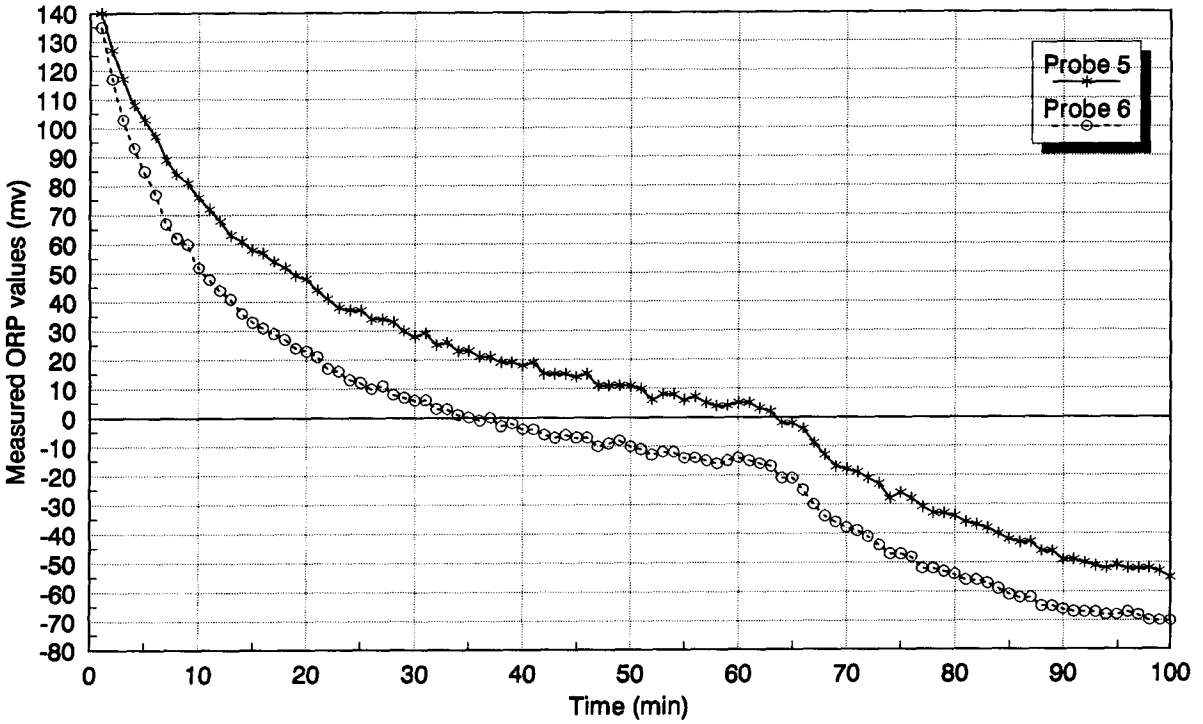


Figure C-8: Carbon addition test 3.2 (20 mg/L)

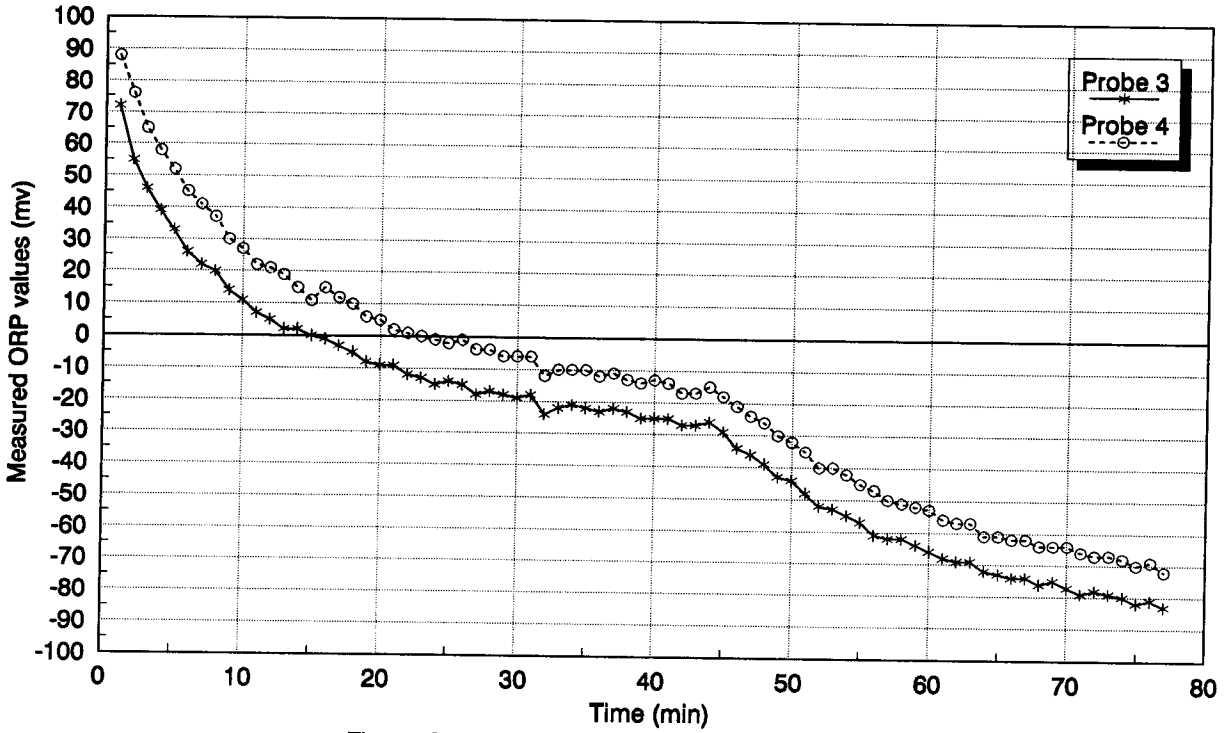


Figure C-9: Carbon addition test 3.3 (40 mg/L)

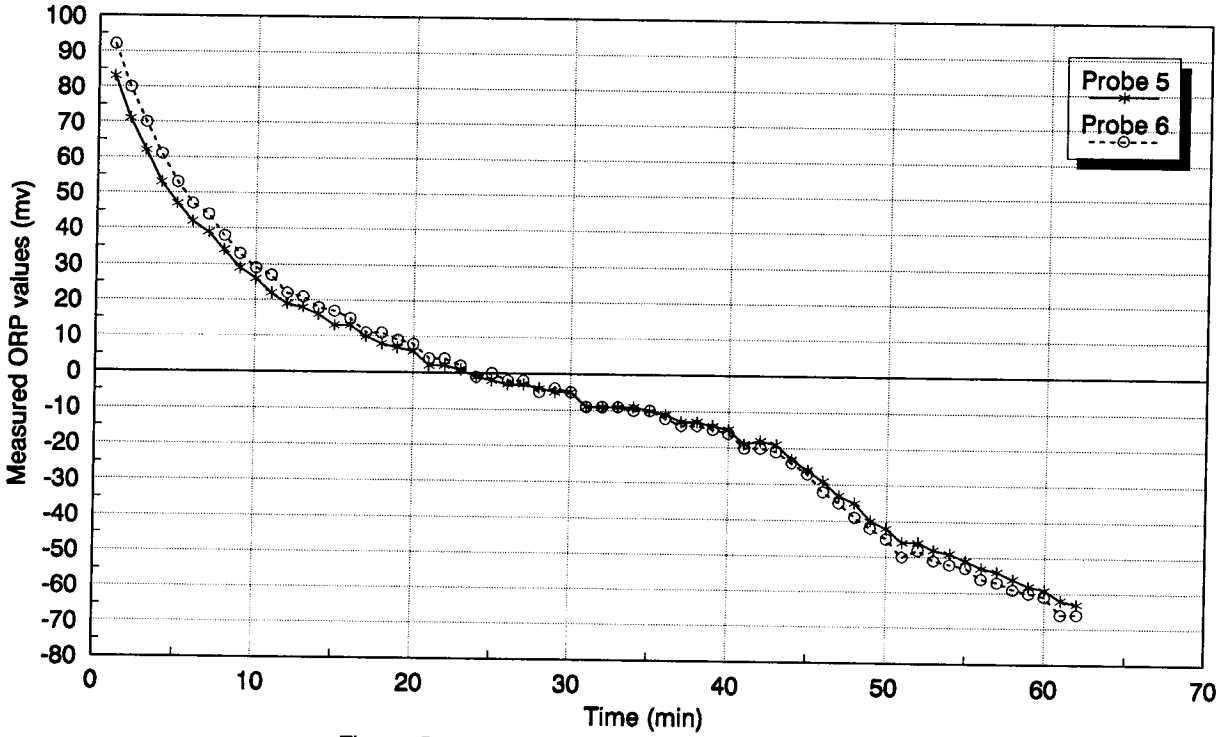


Figure C-10: Carbon addition test 3.4 (60 mg/L)

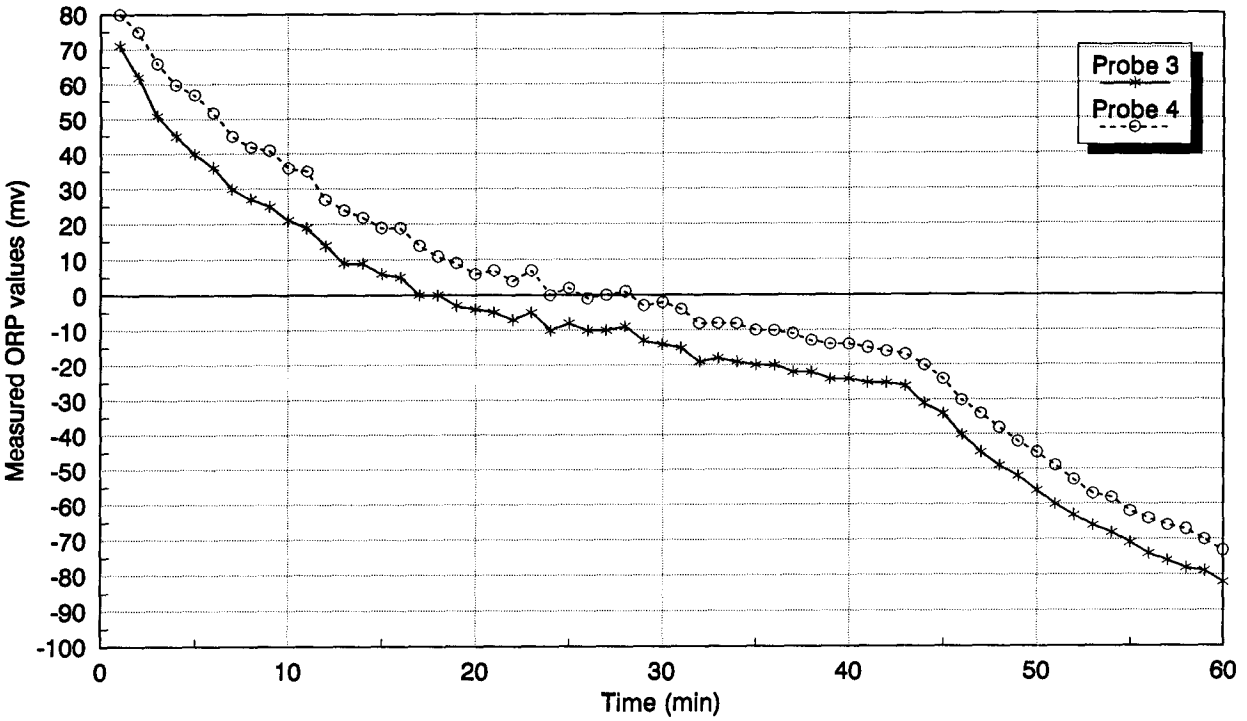


Figure C-11: Carbon addition test 3.5 (80 mg/L)

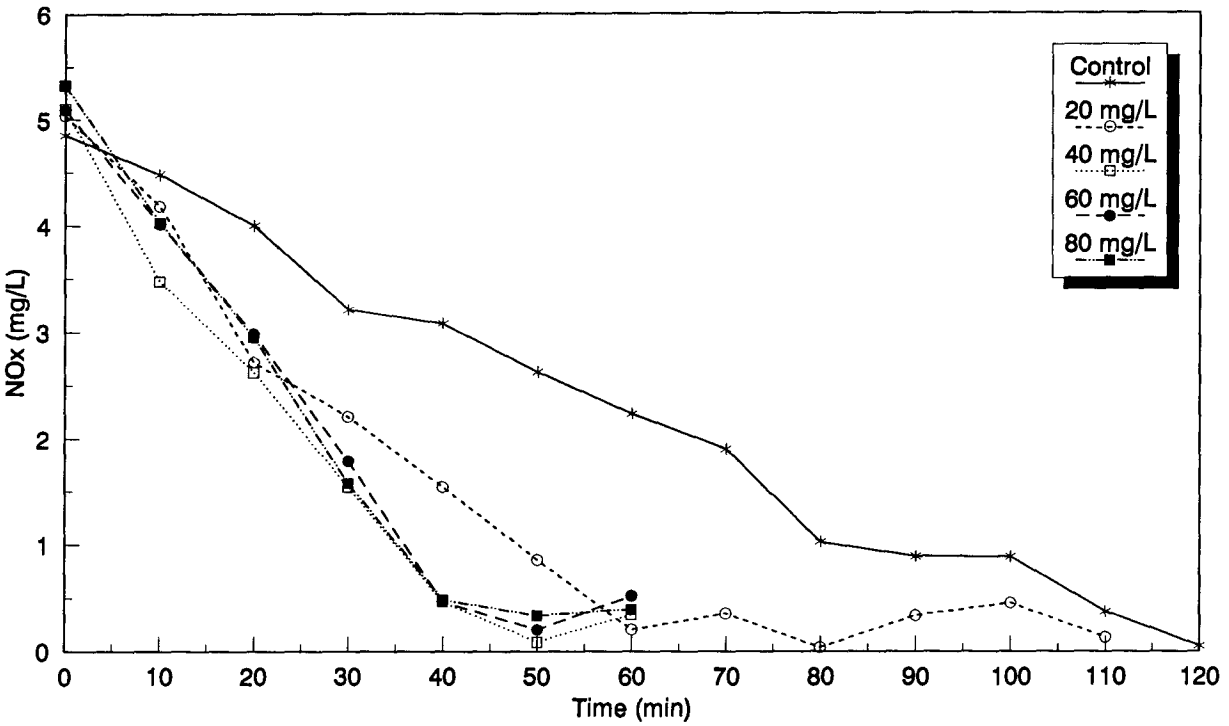


Figure C-12: NOx test results (carbon addition test 3)