THE VOLTAMMETRIC DETERMINATION OF COPPER

AND LEAD IN SEAWATER: APPLICATIONS TO

INDIAN ARM AND BURRARD INLET

by

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ABSTRACT

An anodic stripping voltammetric technique was de-
veloped for the simultaneous determination of Cu and Pb
in seawater.   Mercuric ion added to the sample is plated
out with the metals of interest onto a highly polished
glassy carbon electrode. The thin mercury films obtained
by this procedure gave excellent resolution and sensitivity
although a non-linear response resulted in the case of Cu,
presumably as a result of saturation of the mercury, at
concentrations in excess of 4 µg/l.

The technique was applied to a short term study of
the distribution of Cu and Pb in Indian Arm and Burrard
Inlet. Large fluctuations in the concentrations of both
metals were observed during the sampling period, July to
October, 1972. Although dissolved Pb concentrations were
lower than might be expected near a large urban area,
there was, nevertheless, an overall enrichment of the
subsurface waters of the inlets relative to Georgia
Strait by as much as an order of magnitude. Dissolved
Cu concentrations were not, however, significantly higher
than those reported for other B.C. coastal waters.

Although study of metal speciation by the method
employed here was limited by the excess of mercuric ions
added to the samples and interferences from surface

active agents, evidence was obtained indicating that a

portion of Cu in some British Columbia coastal seawater

samples is complexed with dissolved organic matter. The

experimental conditions indicate that these complexes

are either inert to displacement by mercuric ions or have

a high degree of specificity for Cu.

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1. INTRODUCTION

Trace metals play an important role in the biochemistry of the marine environment. Because many are required for the proper growth and survival of marine organisms and almost all are toxic at sufficiently high concentrations, the trace metal content of natural waters is one of the factors that must be considered in assessing its environmental quality. This study describes a method for determining two trace metals, Cu and Pb, in seawater and examines their distribution in a near shore marine environment.

Although the average concentration of Cu in seawater is normally only about 3 μg/l [Goldberg, 1965], it is, nevertheless, an essential micronutrient to all marine organisms. Many are affected by small fluctuations in its concentration and others, though insensitive to the range of Cu concentrations normally encountered in seawater, are adversely affected by abnormally high levels [Steemann Nielsen and Wium-Anderson, 1970; Erickson et al., 1970]. It has been demonstrated that chelation of Cu by organic compounds affects its biological availability, indicating that it is not just the amount of Cu present but also its chemical speciation that is important [Barber and Ryther, 1969; Lewis et al., 1972].

Though less frequently determined, the concentration
of Pb observed in seawater (0.02 - 0.3 µg/l) is generally
an order of magnitude lower than that of Cu.   Lead
apparently is not an essential micronutrient but it is
toxic to most organisms at sufficiently high levels.   There
have been indications of an increase in the Pb content of
surface waters particularly near urban areas where it is
a common air pollutant [Bryce-Smith, 1971], suggesting a
need for more extensive studies of the Pb distribution in
the sea and especially in near shore waters.

Spencer and Brewer [1970] have reviewed the different
analytical techniques that have been applied to the determin-
ation of trace elements in seawater.   The most commonly used
techniques, atomic absorption spectrophotometry and color-
imetry, are not sufficiently sensitive for direct measure-
ments at the levels (10^{-7}M or lower) at which trace metals
occur in seawater.   As a result, various time consuming
preconcentration procedures that increase the possibility
of contaminating the sample are required.

Only a few techniques permit analysis of Cu and Pb
at the concentrations at which they normally occur in
seawater without extensive preconcentration.   Neutron
activation, which requires access to a reactor facility
[Schutz and Turekian, 1965] can be used for the direct
determination of Cu; Pb, however, cannot be measured with-

out preconcentration. Isotope dilution procedures are perhaps the most precise of those available and have been successfully used to determine Pb in seawater [Chow, 1968]. An extraction step is required but, since quantitative recovery of the metal is not necessary, sample preparation is considerably simplified. The requirement for a mass spectrometer, however, limits the extensive use of the technique.

Anodic stripping or inverse voltammetry (ASV) is the technique which has been adopted for use in this study. Preconcentration is accomplished by plating out the metals of interest onto an electrode immersed in a small volume of sample. The concentration of the metals is determined by the magnitude of the current when the metals are subsequently reoxidized. Simultaneous concentration and measurement of both Cu and Pb can be carried out in the same sample. It is the simplest of available techniques in terms of instrumentation and sample preparation and has the advantage of being capable of use at sea. In addition, since ASV is sensitive to metal ion activities, it offers the possibility of providing information about their speciation.

This study describes the development of an analytical method employing ASV for the determination of Cu and Pb in seawater and its application to the study of the distribution and speciation of these metals in

Burrard Inlet and Indian Arm. Evidence was sought for a possible enrichment of these metals in this system as compared to Georgia Strait. Enrichment might be expected on the basis of the proximity of this system to Greater Vancouver and the associated urban and industrial inputs.

2. ANODIC STRIPPING ANALYSIS OF COPPER AND LEAD IN SEAWATER USING A MERCURY PLATED GLASSY CARBON ELECTRODE

2.1 Introduction to the Technique

Anodic stripping voltammetry (ASV) has become widely used for the analysis of low levels of many metals. Although not yet extensively applied to the determination of trace metals in seawater, its use is becoming increasingly more common because of its relative simplicity and great sensitivity. The increased sensitivity of ASV as compared to other voltammetric techniques is obtained through concentrating the metal or metals of interest in or on an electrode held at a reducing potential for a fixed period of time. The current is then recorded as a function of time (potential) as the metal is oxidatively stripped from the electrode with a rapid, linearly varying anodic potential sweep. Mercury is the most commonly used electrode material, though solid electrodes have also been employed. A typical response for Cu and Pb in 0.5 M NaCl obtained in this study is shown in Figure 2.1. The peak potential is characteristic of a given ion (or oxidation process) and the peak height is proportional to the concentration of the ion in solution. Shain [1963]
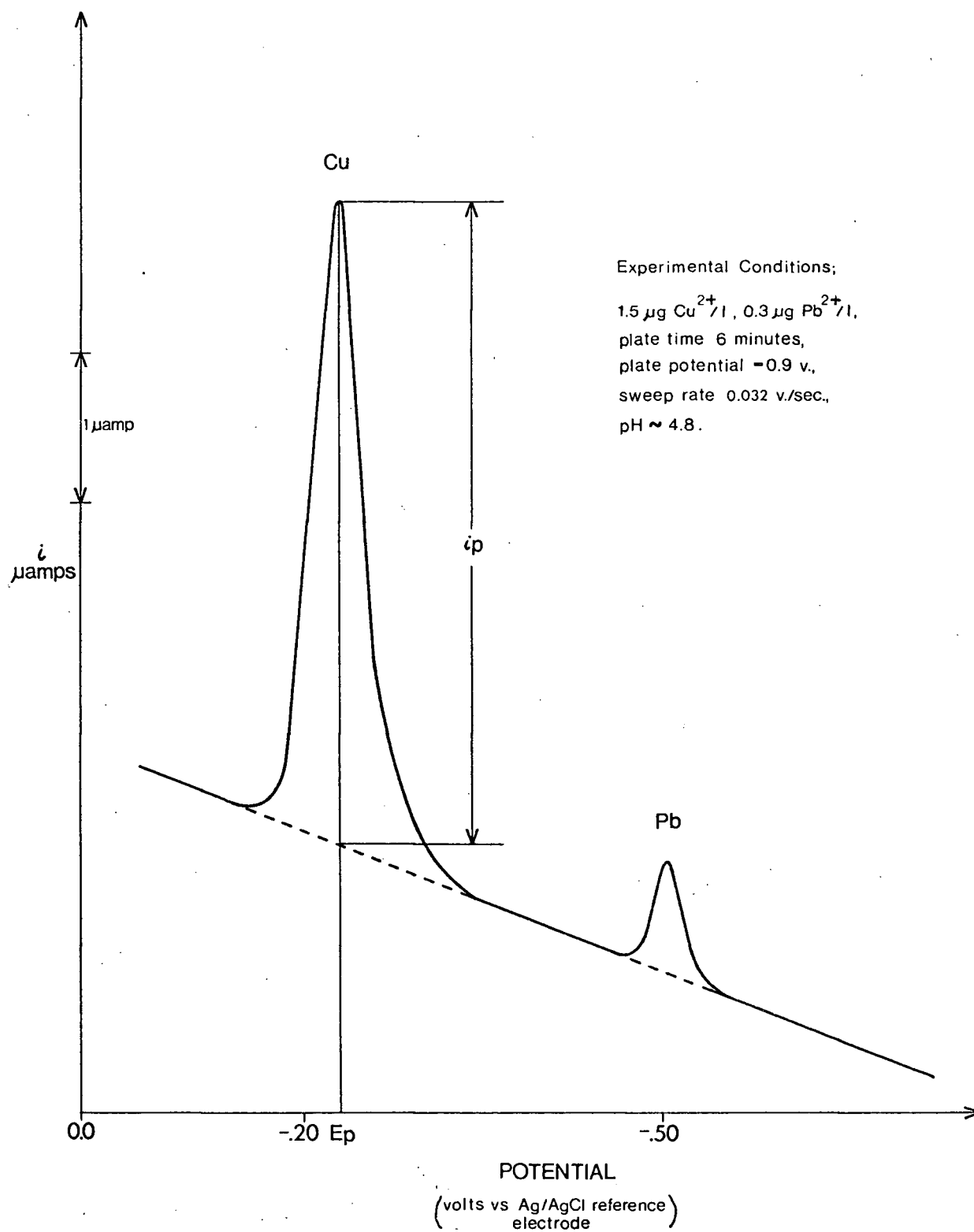
Figure 2.1   A typical ASV response curve for Cu and Pb in a 0.5 M NaCl solution

and Barendecht [1967] have reviewed the theory and procedures
in considerable detail.

In applications to the marine environment, the hang-
ing mercury drop electrode (HMDE) has been most frequently
used [Whitnack and Sasseli, 1969; Zirino, 1970; Macchi,
1965]. It has the advantages of simplicity of operation
and preparation as well as adequate sensitivity. Because
of the relatively large volume to surface ratio, however,
there is a tailing effect, due to the slow diffusion of
the metal out of the drop, that results in poor resolution
and lowered sensitivity.

Thin film mercury electrodes overcome many of these
problems by optimizing the surface to volume ratio.
Unfortunately, preparing thin film electrodes using normal
techniques is quite difficult and reproducible results
are not easily attained. Matson et al. [1965] developed
a composite mercury-graphite electrode (CMGE) in which
mercury was plated out onto a wax impregnated graphite
rod. Although the mercury was present as a large number
of very small droplets, the stripping response of the
electrode agreed quite well with that predicted for thin
film electrodes [De Vries and Van Dalen, 1964]. Matson
[1968] and Fitzgerald [1970] have both demonstrated the
applicability and the advantages of this electrode in
the study of Cu, Pb, Cd and Zn in seawater. Because of

the small diameter of the mercury droplets (generally less than 10 μm), diffusion of metal out of the mercury is extremely rapid and excellent sensitivity and resolution are obtained. The electrode does have an inherent instability, however, which seems to be a result of the high porosity of graphite. As a result, the graphite must be periodically reimpregnated with wax. The mercury "film" needs frequent replating as it is subject to alteration and contamination with use. Oxidation of the mercury in air and absorption of organics have been suggested as possible causes of this deterioration [Hume and Carter, 1972].

Florence [1970] has recently introduced a new method of preparing a thin film mercury electrode. Using highly polished glassy carbon sealed into a glass tube, Florence developed a technique whereby a thin mercury film was plated onto the glassy carbon "in situ." Sufficient mercuric ion was added to the test solution and the mercury and metal of interest were plated out simultaneously. The electrode was cleaned between runs simply by wiping with a damp tissue, insuring a fresh film for each run. The films obtained in this manner were very thin (0.01 - 0.001 μm) and gave excellent resolution and sensitivity. Because of the superior electrical qualities and very low porosity of glassy carbon, no instability was noted over a period

of several months. In a later publication, Florence [1972] demonstrated the applicability of his method to trace metal determinations in seawater. The method of electrode preparation used in this study is an adaptation of Florence's technique.

In ASV, it is necessary to stir the solution during the plating step to decrease the thickness of the diffusion layer and increase the flux of metal ions to the electrode. Two approaches can be taken. In the first, which involves plating out all the metal in the solution, fluctuations in stirring rate are unimportant. However, in the more common and practical approach in which only a small fraction of the metal is plated out, the stirring must be done in a reproducible manner to ensure a constant flux of electroactive material to the electrode. A consideration particularly pertinent to shipboard analysis by the latter approach is that the method of stirring must be insensitive to the vibration and tilting inherent in work at sea. Few methods satisfy these criteria. Rotation of the electrode, the technique employed by Florence [1970], produces a very well defined and efficient convection pattern but is too sensitive to external movement to be suitable for shipboard analysis. A stream of N_2 gas has been used in almost all work with the CMGE to provide the necessary convection. This method provides reproducible results, is well suited to field studies and minimizes the possibilities

of contamination. There is a limit to the flow rates which can be used, however, due to the danger of frothing. At the flow rates normally used in seawater, the convection set up is not very efficient and long plating times are generally required. An alternate method, the one used in this study, involves circulation of the sample through a closed system. This approach has been used previously by Koster and Ariel [1971], who found that it provided reproducible results over a wide range of flow rates. Circulation of the sample through a closed system was found in the present study to provide a more efficient mixing of the solution than that obtained by gas bubbling and to be equally well suited to analysis at sea.

2.2 Description of the Method

Briefly, the method that has been developed for use in this study involves the following basic procedure. A sufficient amount of a mercuric chloride solution is added to the seawater sample being analysed to give a final mercury concentration of approximately 10^{-5} M (roughly 1000 times the concentration of the metals to be determined). The sample is then pumped in a closed system through a cell with gas purging for a sufficient length of time to allow removal of oxygen and temperature equilibration. Next, the purging gas is passed over the solution while

the metals are plated out. When the plating is completed, the pump is turned off and the solution allowed to come to rest. The stripping step is then accomplished by applying a linear anodic potential sweep and recording the current as a function of the applied potential. The Cu and Pb concentrations are calculated after subsequent runs using the method of standard additions.

The effects of the various experimental parameters were evaluated to determine optimal operating conditions for seawater analysis.

2.3 Experimental

(A) Apparatus

A Chemtrix model SSP-2A polarographic analyzer equipped with a storage oscilloscope was used in all work. Additional capacitors were added to the sweep time circuit to allow sweep rates as low as 7.4 mv/sec. Current vs. potential scans were recorded with a Hewlett-Packard Model 7035B X-Y recorder.

The electrolysis cell (Figure 2.2) was machined from a polypropylene rod and had a useable volume of approximately 50 ml. Threaded plugs were used to provide exchangeable connections. The inlet and outlet fittings on the cell were connected through a tubing pump which circulated the sample in such a way that the solution entered the cell

Ag/AgCl Reference Electrode

Pt Wire Counter Electrode

Glassy Carbon
Electrode

Gas Out

Gas In

Cap

Teflon Separating Tubes

Flow to
Pump

3"

Fritted Glass for Gas Dispersion

¼"
Scale

Mercury

Glassy Carbon
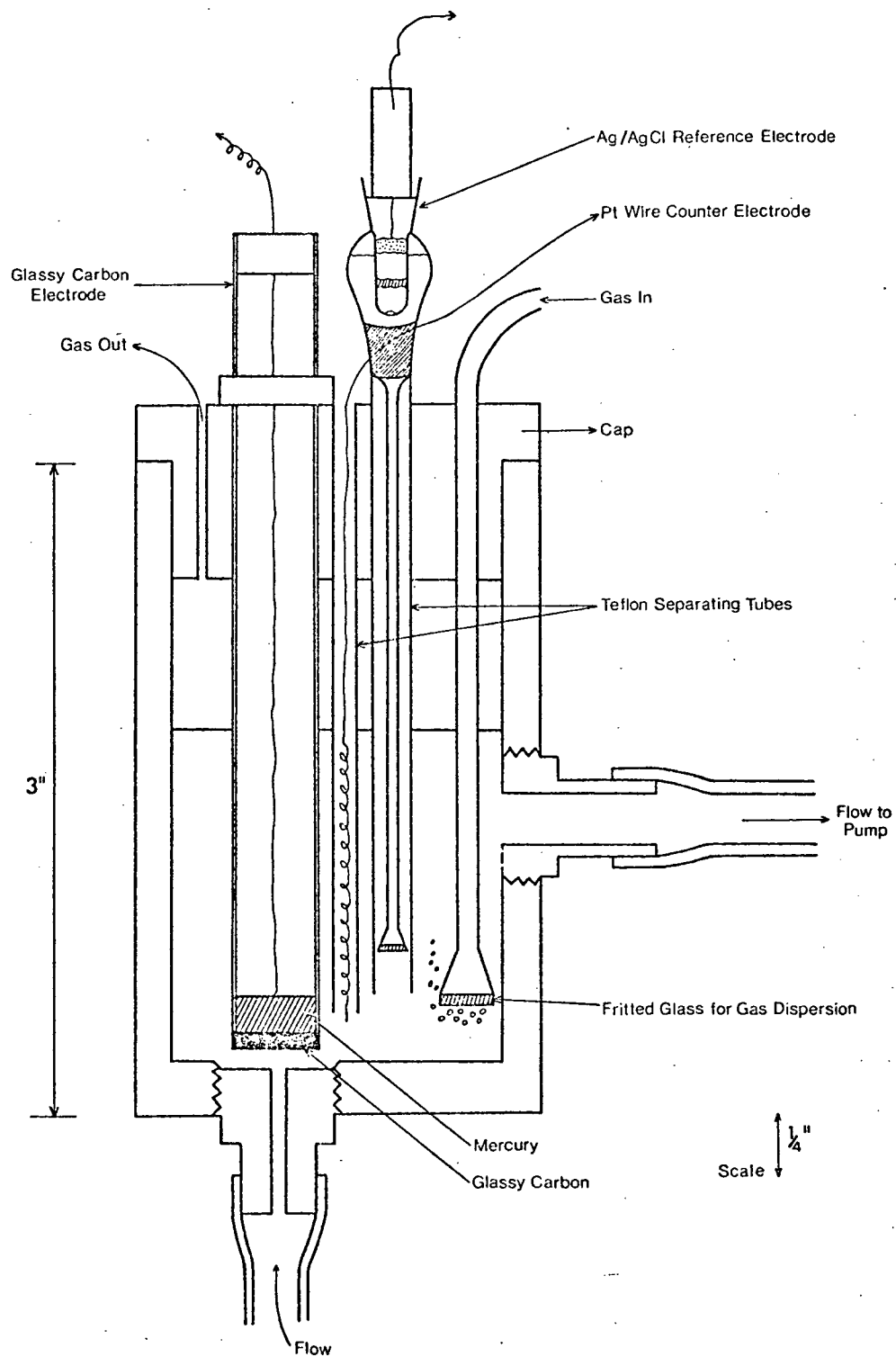
Flow

Figure 2.2   Detail diagram of the voltammetric cell

from the bottom. The 1/16" diameter opening in the entrance plug constricted and accelerated the flow at this point so that there was a jet-like inflow of solution directed at the electrode surface. The glassy carbon electrode was centered directly above this opening.

A special cell constructed from Teflon was used for pH studies. It was of similar design but had a useable volume of about 200 ml to allow for a thermometer and a glass pH electrode.

A Cole-Parmer Masterflex tubing pump (head #7015) employing Tygon tubing (special formulation R#3603, 3/16" I.D. x 3/32" wall) was used for circulating the solution through the cell.

Cylinder grade N_2 (Canadian Liquid Air) or a mixture of 99.2% N_2 and 0.8% CO_2 (Canadian Liquid Air) was used without purification for deaeration of the samples. Prior to bubbling through the cell, the gas was saturated with water by passage through a 0.5 M NaCl solution.

Glassy carbon electrodes were prepared by sealing wafers of 0.63 cm diameter glassy carbon (Beckwith Carbon Corp.) into a 30 cm length of Pyrex glass tubing with epoxy resin. The glassy carbon was then polished metallographically, the final polish using a 0.01 µm alumina slurry. Electrical contact was made with a Pt or Cu wire dipping into sufficient Hg to cover the surface to a depth

of a few centimetres. It was necessary to soak the electrode in dilute HCl for several hours prior to use to remove contamination picked up in the polishing process.

The potential values reported in this study are with respect to a Metrohm model EA 425 Ag/AgCl narrow taper reference electrode (saturated KCl filling solution, potential -0.043 volts vs. saturated calomel electrode at 25° C). A coiled Pt wire was used as the counter electrode.

Distilled water that had been passed through a mixed bed ion exchange column prior to use was used in the preparation of all standard solutions and to rinse the cell between samples. A stock Cu standard solution was prepared from reagent grade $CuSO_4 \cdot 5H_2O$ to give a final Cu concentration of 100 mg/l. The Pb standard was prepared from reagent grade $PbCl_2$ and had a final Pb concentration of 478 mg/l. A substandard of 0.10 mg/l Cu and 0.096 mg/l Pb was prepared fresh from the stock solutions prior to a series of analyses. A 10^{-3}M standard mercury stock solution was prepared from reagent grade $HgCl_2$. Reagent grade HCl was diluted to give 2N and 6N solutions. Artificial seawater was prepared according to the recipe of Lyman and Fleming [1940] with the omission of $SrCl_2$.

The pH was estimated with an Orion Model 801 pH meter and Corning 476022 glass electrode. Control of the

pH at values above 4.8 was achieved by using mixtures of N_2 and CO_2. The use of N_2 alone slowly increased the pH of seawater samples while a mixture of 99.2% and 0.8% CO_2 lowered the pH of seawater to approximately 7.0. Lower pH's were obtained by mixing N_2 with a regulated flow of pure CO_2 (Canadian Liquid Air, medical grade). Equilibration of seawater with pure CO_2 lowered the pH to approximately 4.8. Further decrease in the pH was obtained by adding 0.1 ml aliquots of 2N or 6N HCl.

(B) Investigation of Experimental Parameters

No measureable change was detected in the Cu or Pb concentration of solutions left in the polypropylene cell for periods of up to 1 hour, the maximum length of time a sample might be in the cell during the course of a routine analysis. The Teflon cell gave no increase over a period of 3 hours. The blank values for the standard Hg solution and 6N HCl used in acidification were below detection limits. New Tygon tubing introduced significant amounts of Pb and especially Cu into the samples even if rinsed repeatedly with deionized water. Several rinses with EtOH and 1% HCl proved effective in removing the contamination.

There are several possible effects that might interfere with either the deposition and/or dissolution of the metal. Surface active agents can both decrease the rate

of deposition and alter the subsequent stripping response.
Although it may be assumed that surface active agents are
present in most natural waters, repeated analysis of the
same seawater solutions normally gave reproducible results,
indicating that they do not seriously affect the precision
of the measurements. Interferences can also arise from
other metals being stripped out of Hg at similar potentials
as Cu or Pb as well as from the formation of intermetallic
compounds. Many intermetallic compounds are known to
exist [Barendecht, 1967] but the factors influencing their
formation and subsequent electrochemical behaviour are
still obscure. Formation is enhanced by high metal concen-
trations in the amalgam [Kozlovsky and Zebreva, 1972]
and ASV, particularly with thin Hg films, is very suspect
in this respect. Matson [1968] found that Ni and Zn form
a compound which strips out of Hg at the same potential
as Cu. Since both Ni and Zn are present in seawater at
about the same concentration as Cu, a potential such that
neither metal will be plated out (i.e., more positive
than -1.0 v) should be used. Other intermetallic compounds
may also exist and, thus, the possibility of such inter-
ferences cannot be completely excluded. Baier [1971]
demonstrated that Sn is stripped from Hg into seawater at
the same potential as Pb. The extent of interference is
strongly pH dependent, being negligible at pH's of less

than 5 but significant at a normal seawater pH if the concentrations of Sn and Pb are of the same magnitude.

None of the metals normally found in seawater interfere with the Cu response. The V interference in the determination of Cu reported by Smith and Redmond [1971] was not observed in this study, even with V concentrations an order of magnitude greater than that normally found in seawater.

1. <u>Peak Height (i_p) vs Metal Concentration</u>:

It is essential when using the method of standard additions for calibration that there be a linear relationship between the stripping current peak height and the concentration of metal in the solution. Such linearity was repeatedly observed for Cu and Pb in both 0.5 M NaCl and acidified seawater (Figure 2.3). The Pb peak height was proportional to the Pb concentration throughout the range studied (≤ 5 µg/l). The Cu response was linear up to a concentration of approximately 4 µg/l; above this, however, the slope of the response curve decreased with increasing concentration. The solubility of Cu in Hg is reported as only 0.002% at 20°C [Stephen and Stephen, 1963]. Even taking into account increased solubility with increased temperature, this suggests that the Hg film will be supersaturated whenever the Cu concentration exceeds <u>ca</u>. 0.1 µg/l. The degree of saturation may be the determining factor in the linearity of the Cu response.
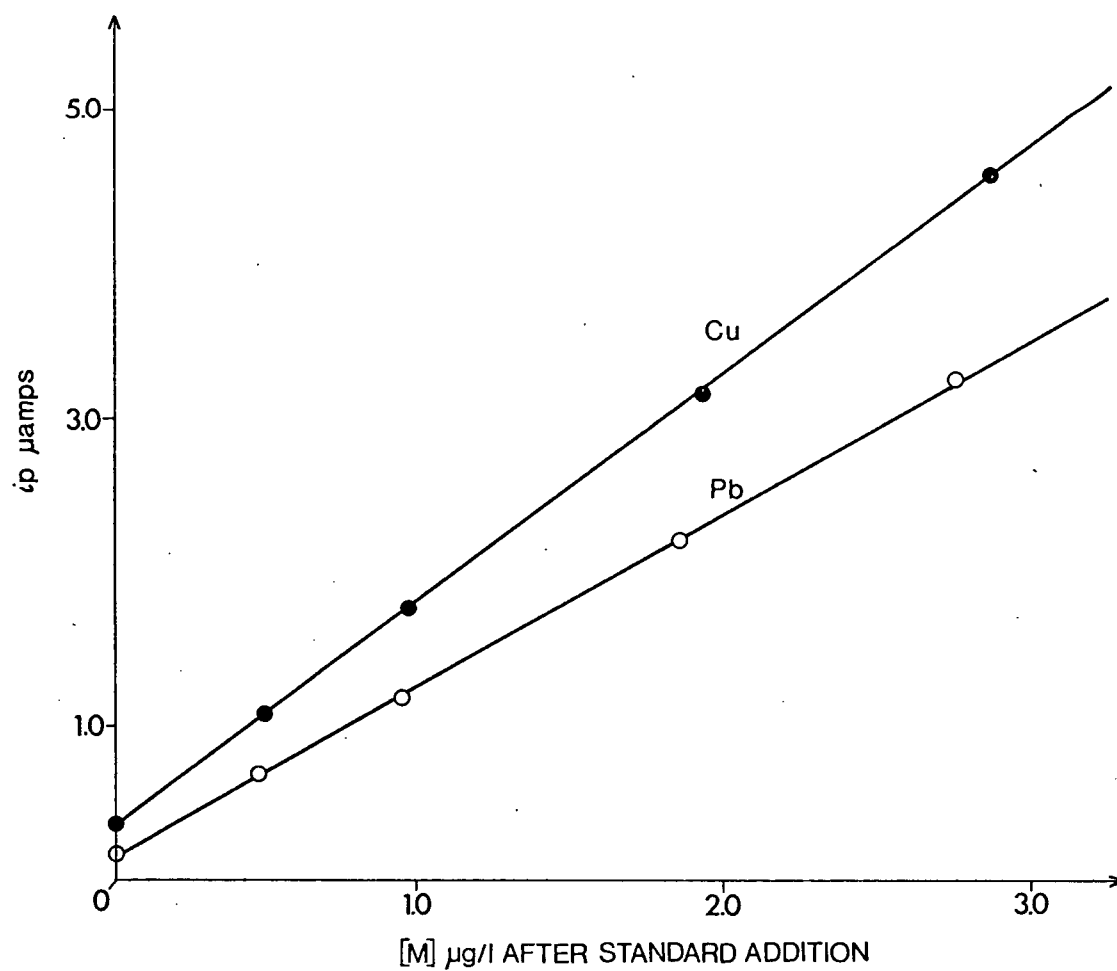
Experimental Conditions;
Aged seawater, pH 2.0, Plate time 6 minutes, Plate potential −0.9v., Sweep rate 0.032 v/sec.

Figure 2.3 Calibration curves for Cu and Pb in seawater

2. i_p vs Pumping Rate:

Although i_p increases with increasing pumping rate for both Cu and Pb (Figure 2.4), high pumping speeds also reduce tubing life. Pumping at a speed which gave a flow rate of 180 ml/min, the tubing could be used for more than 100 hours without apparent deterioration; above 600 ml/min there was notable deterioration after only 20 hours of use. Pumping also heats the solution and, as the reduction current of a metal ion at a stationary planar electrode varies by approximately 1.2%/°C [Heyrovsky and Kuta, 1966], large temperature differences between successive plating steps will appreciably affect the magnitude of i_p and the precision and accuracy of measurements. In order to extend tubing life while maintaining adequate sensitivity and precision, the sample was degassed at a flow rate of 445 ml/min for 10 minutes and the flow then decreased to 180 ml/min during the plating period. This normally resulted in a temperature of between 30 and 34°C that was maintained to within about 1°C over the span of six or seven consecutive plating and stripping steps. As shown in Figure 2.5, the temperature change over a series of plating and stripping steps depended on the initial temperature and on the length of the plating period.
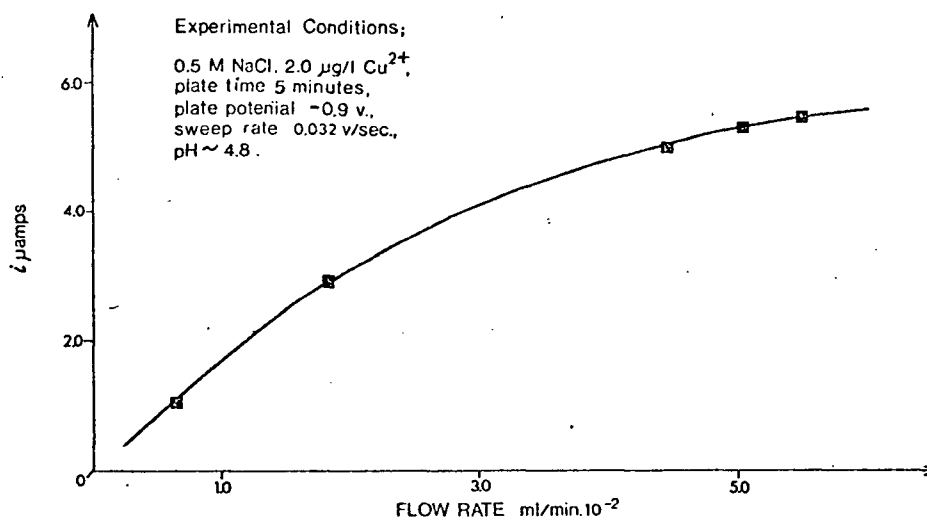
Figure 2.4 The variation of i_p with flow rate for Cu in
0.5 M NaCl
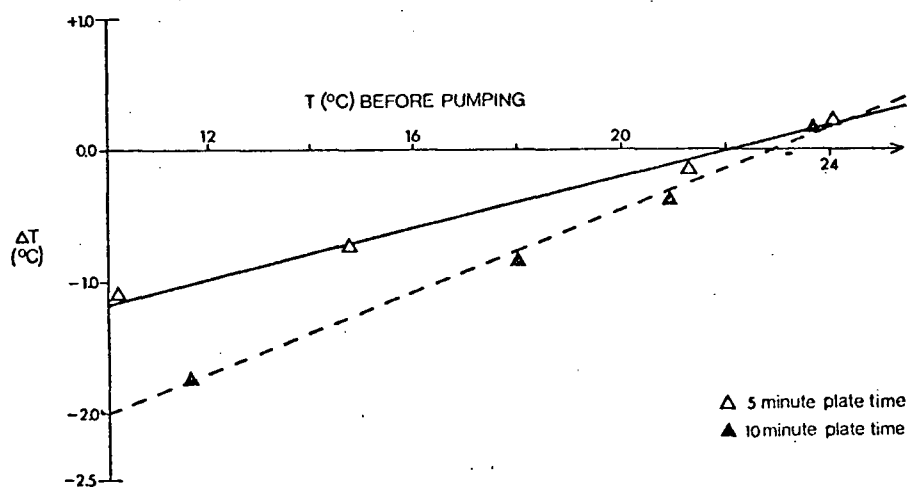
Figure 2.5 The effect of the initial solution temperature
on the temperature change during serial
analysis

3. i_p vs Sweep Rate:

The i_p of both Cu and Pb was found to be directly proportional to the sweep rate throughout the range tested (7.4 - 50 mv/sec). However, the slope of the baseline current resulting from discharge of the electrical double layer about the electrode also increases with increasing scan rate, excluding the use of very fast scans. A sweep rate of 32 mv/sec was used for most of the analyses reported in this study.

4. i_p vs Plating Time:

The i_p of both Cu and Pb was proportional to the plating time in the range 3 to 15 minutes. It was found that under normal conditions a plating time of 8 minutes was adequate for the simultaneous determination of Cu and Pb but that longer plating times were necessary when metal concentrations were less than 0.1 µg/l.

5. i_p vs pH:

The magnitude of i_p for both Cu and Pb in seawater is pH dependent, increasing markedly as the pH is lowered from 8 to approximately 5. In artificial seawater, it remains essentially constant below this (Figure 2.6). In natural seawater, however, the Cu current sometimes increased further at pH's of less than 5. Such anomalous behaviour is discussed later in Section 4. In the analysis
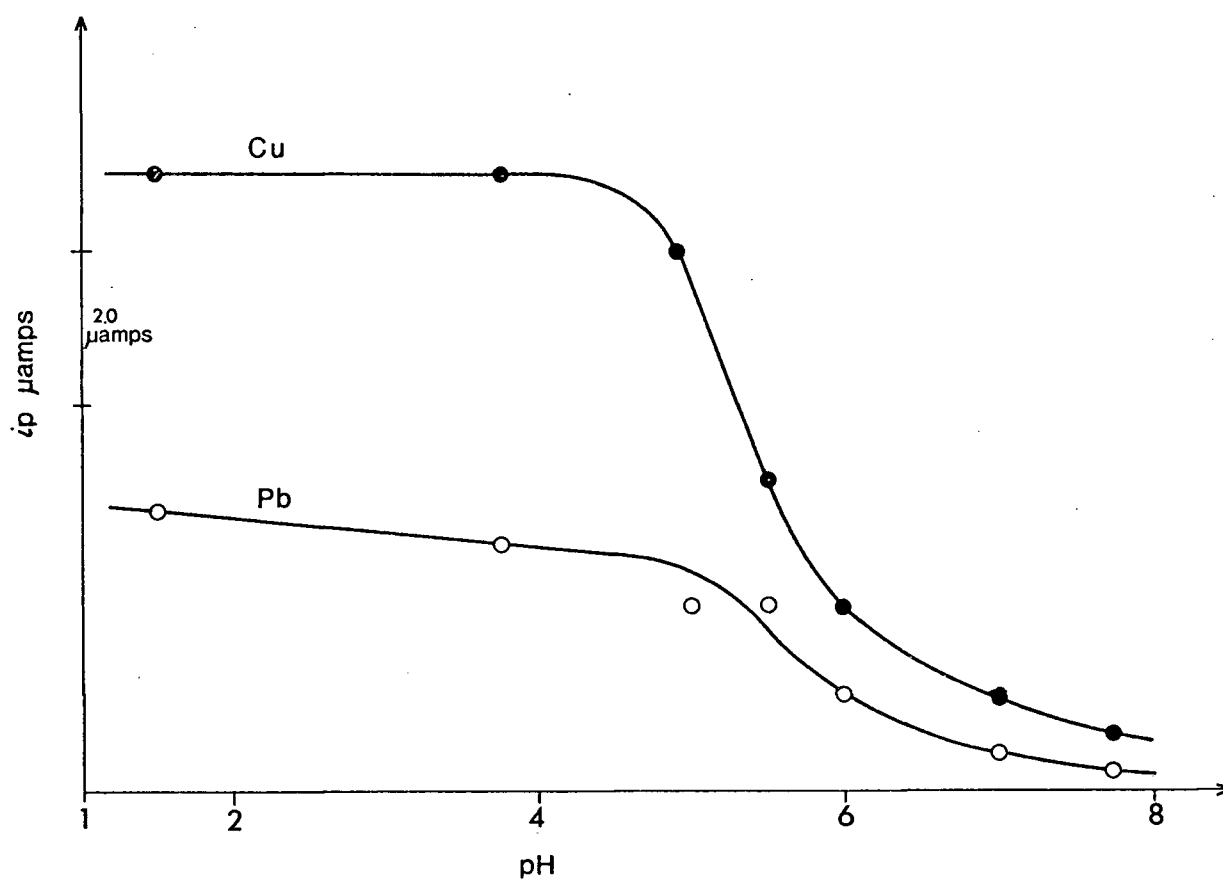
Experimental Conditions;
Plate time 5 minutes, Plate potential −0.9v., Sweep rate 0.032 v/sec., UV irradiated artificial sea water

Figure 2.6   The variation of i_p with pH for Cu and Pb
              in artificial seawater

of seawater, decreasing the pH therefore increases sensitivity and, since hydrogen ions will tend to displace metals from labile complexes, possibly provides a better estimate of the total metal in the sample. The use of a low pH also decreases the possibility of Sn interfering in the Pb determination.

6. i_p vs Mercury Concentration:

The variation of i_p for Pb and Cu with the mercury concentration of the sample is given in Table I. There is a very abrupt decrease in the i_p below a Hg concentration of approximately 3×10^{-6}M. This agrees quite well with the results obtained by Florence [1970], who calculated that this cut-off point corresponds to a Hg film thickness of only 4Å or roughly a monolayer of Hg atoms. Calculations based on the stripping current for Hg obtained in this study give a similar result. Florence [1970] suggested that this was evidence that the Hg was present as a discrete film and not a number of very small droplets.

7. i_p vs Plating Potential:

The variation of i_p with the plating potential for Cu and Pb in 0.5 M NaCl is shown in Figure 2.7. A steady state peak current is reached at a plating potential between 300 and 400 mv cathodic to the peak potential of the metal. In seawater, steady state values often were not obtained with plating potentials as low as -1.2 volts,

TABLE I

RELATIONSHIP BETWEEN i_p AND THE MERCURY CONCENTRATION

$10^5 \, C_{Hg}2+(moles.1^{-1})$	$(i_p)_{Cu}$ [a]	$(i_p)_{Pb}$ [a]	$(i_p)_{Pb}$ [b]
nil	0.25	0.00	1.1
0.1	0.50	0.20	1.5
0.2	2.50	0.70	5.20
0.4	4.60	1.10	5.80
0.9	4.75	1.20	6.21[c]
2.0	5.00	1.40	6.87
5.0	5.30	1.50	7.42[d]

[a] $3\mu g/1 \, Cu^{2+}$ and $0.5\mu g/1 \, Pb^{2+}$ in 0.5 M NaCl, plate time 6 minutes, plate potential -0.9 volts, v = 0.032 v/sec

[b] from Florence [1970]

[c] Hg concentration $1.0 \times 10^{-5}M$

[d] Hg concentration $10.0 \times 10^{-5}M$

COPPER

Experimental Conditions;
1.5 ug Cu^{2+}/l,
plate time 6 minutes,
sweep rate 0.032 v/sec.

0.5 M NaCl

0.5 μamps

i_p

seawater

0
−.2
−.4
−.6
−.8
−1.0
−1.2

PLATE POTENTIAL
(volts vs Ag/AgCl reference electrode)

LEAD

Experimental Conditions;
0.3 ug Pb^{2+}/l,
plate time 6 minutes,
sweep rate 0.032 v/sec.

0.5 M NaCl

0.2 μamps

i_p

seawater

0
−.2
−.4
−.6
−.8
−1.0
−1.2

PLATE POTENTIAL
(volts vs Ag/AgCl reference electrode)
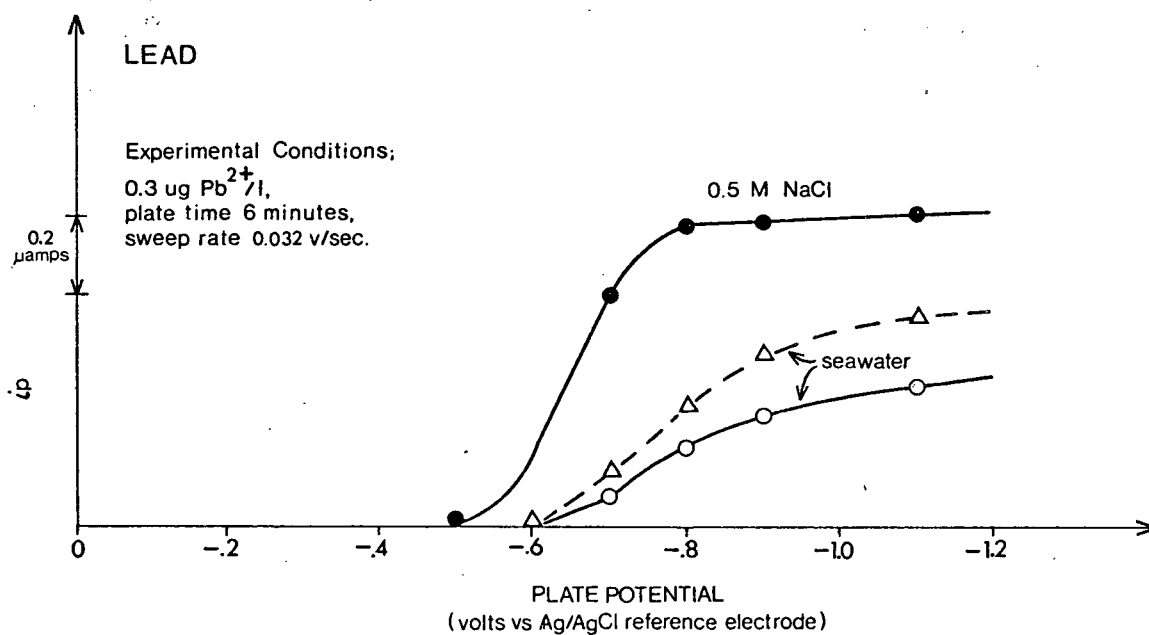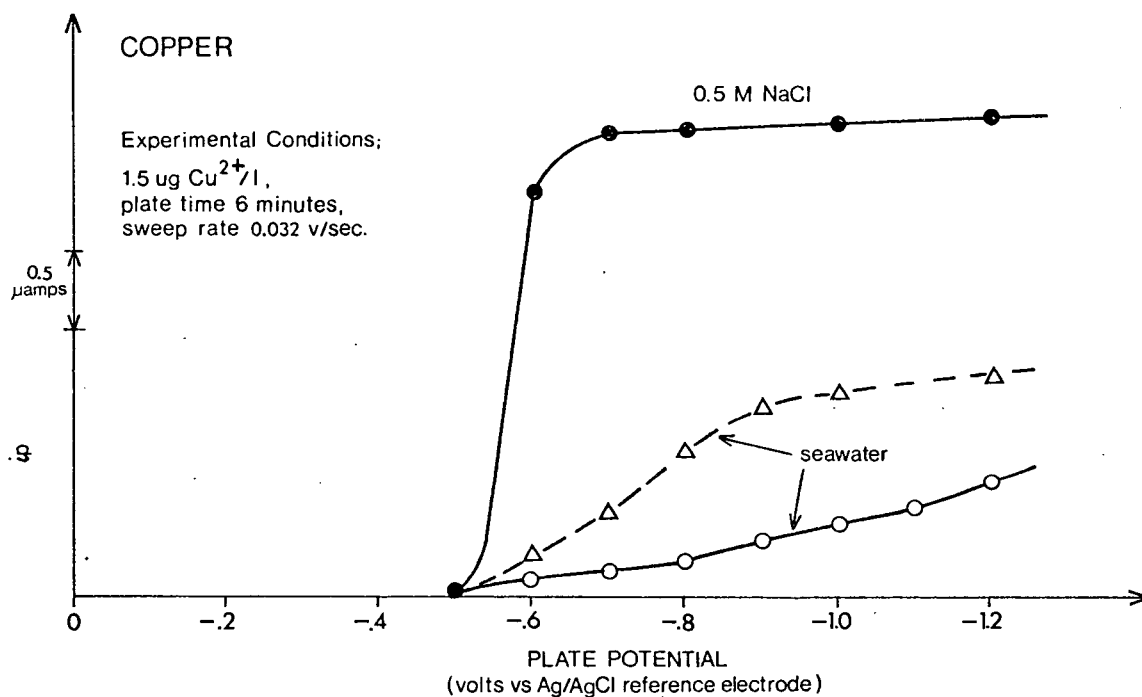
Figure 2.7   The variation of i_p with plate potential for
Cu and Pb in 0.5 M NaCl and aged seawater

even in acidified samples. This effect is discussed in terms of speciation of the metals in Section 4. The use of potentials more cathodic than -1.0 volt in acid solutions is limited by hydrogen ion reduction and by the possibility of Ni-Zn intermetallic compound interferences in the Cu response. A plating potential of -0.9 volts was used in all the analyses reported in this study.

(C) Standard Procedure

The following is the procedure which was finally adopted for the analysis of seawater samples:

1. The cell is rinsed twice with deionized water and then once with the sample. The surface of the glassy carbon electrode is thoroughly wiped with a damp tissue, rinsed with deionized water and then placed in the cell.

2. An aliquot of the sample is pipeted into the cell (35 - 45 ml). After adding 0.5 ml of standard 0.001 M $HgCl_2$ solution and 0.3 ml of 6 N HCl (which lowers the pH of the sample to approximately 2), the solution is pumped through the cell at a rate of 445 ml/min for 10 minutes while bubbling N_2 through the sample.

3. After deaeration, the purging gas is passed over the solution and the pumping rate is reduced to 180 ml/min.

4. The potential of the glassy carbon electrode is adjusted to -0.9 volts vs the Ag/AgCl reference electrode and the plating step timed with a stop-watch.

5. After plating for 5 minutes, the pump is turned off and the solution allowed to equilibrate for 45 seconds. The potential is then swept anodically at a rate of 0.032 v/sec, the current being recorded as a function of potential on the X-Y recorder. After the Cu peak has been recorded, the recorder is switched to standby and the current followed on the oscilloscope until the Hg has been completely stripped off. The contact to the glassy carbon electrode is then removed.

6. The glassy carbon electrode is removed from the cell and cleaned as before.

7. This first run gives an estimate of the concentrations of both Cu and Pb in the sample and conditions the electrode (the first run always differs slightly from subsequent ones). Steps 3, 4, 5 and 6 are repeated using longer plating times if necessary.

8. After satisfactory completion of step 7, an aliquot of the substandard solution is added to the sample. A volume of 0.2 ml of the solution containing 0.1 mg Cu/l and 0.096 mg Pb/l proved adequate for most levels of the metals encountered in this work.

After adding the spike, the solution is purged with N_2 again for 2 minutes, pumping the solution at a rate of 180 ml/min to mix the added metal and remove O_2 introduced with the spike.

9. Steps 3 through 6 are then repeated. The concentration of the metals in the original solution is then calculated from the difference in the peak heights of the spiked and unspiked samples according to the formula:

$$C_o = (i_1 V_s C_s)/(i_2 V_s + V\Delta i)$$

where C_o is the concentration of the unspiked sample

         i_1 is the peak height of the metal in the unspiked sample

         V_s is the volume of the spike

         C_s is the concentration of the spike

         i_2 is the height of the peak in the spiked sample

         Δi $= (i_2 - i_1)$

         V is the volume of the original solution + cell dead volume + the volume of the Hg standard and acid added to the sample.

The cell contains a dead volume (i.e., a volume of solution remaining in the cell and tubing after draining). This was found to be approximately 0.8 ml and was determined

periodically. The dead volume is added to the volume of
sample added to obtain the total volume of sample in the
cell. Correction for the dilution of the sample by additions
of Hg standard and acid was made to obtain the concentration
in the original sample.

The method of standard additions is valid when the
peak height is proportional to the metal concentration.
Although this is not true for Cu concentrations in excess
of 4 μg/l, the concentrations encountered in this study
were always less than this and rarely greater than 1.5 μg/l.
The use of a standard additions technique is advantageous
in that rigid control of experimental parameters is not
required throughout a whole series of analyses.

2.4 Precision

Precision was determined by replicate analyses of
an aged, filtered seawater sample that had been collected
in Georgia Strait at 100 m and stored in a 5 gallon Pyrex
carboy at ca 5°C. The results are given in Table II.

The standard deviation of the Pb determinations
corresponds to the approximate detection limit of the
method and also to the lower limit of Pb concentrations
reported for seawater [Chow, 1968]. The concentration of
both Cu and Pb in this sample roughly corresponds to
the average levels of these metals encountered in this
study.

TABLE II

PRECISION OF Cu AND Pb DETERMINATIONS AS DETERMINED BY REPLICATE
ANALYSES[a]OF AN AGED, FILTERED SEAWATER SAMPLE

Sub-Sample	[Cu] µg/l	[Pb] µg/l
1	0.52	0.18
2	0.56	0.23
3	0.49	0.19
4	0.55	0.30
5	0.60	0.26
6	0.53	0.24
7	0.51	0.21
Mean	0.54	0.23
Standard Deviation	0.04	0.04
Relative Standard Deviation	7%	17%

[a]experimental parameters as described in the standard pro-
cedure with a plate time of 7 minutes

2.5 Comparison of the Response with Theory

De Vries and Van Dalen [1964, 1965] have developed
a mathematical model for the current-potential curves obtained
in ASV with planar, thin-film mercury electrodes. It was
assumed that equilibrium exists between the oxidized and
reduced forms of the metal during the dissolution step,
that the electrode reaction is reversible and diffusion
controlled and that the concentration of the oxidized species
in the solution at the start of the anodic sweep is homo-
geneous. The resulting equations showing the effect of film
thickness and sweep rate on the current wave were in excellent
agreement with observed results. In a later publication
[1967], a generalized solution was given for the case of
very thin films (i.e., less than 1 μm which yielded the
following expressions:

$$i_p = 1.1157 \times 10^6 (n^2 A C_r{}^\circ L v) \tag{1}$$

$$n(E_p - E\tfrac{1}{2}) = -1.43 + 29.58 \log(H) \tag{2}$$

$$nb\tfrac{1}{2} = 75.53 \tag{3}$$

where
i_p is the peak current in amperes

  n   is the number of electrons involved in the
       reaction

  A   is the area of the electrode in cm^2

C_r° is the concentration of the metal in the Hg film (moles $.1^{-1}$)

L   is the thickness of the Hg film in cm

v   is the sweep rate in volts/sec

E_p is the potential of the peak current in mv

$E\frac{1}{2}$ is the half wave potential for the electrode reaction in mv

H   is a dimensionless parameter = $L^2\sigma/D_r$

σ = $(nF/RT).v$

D_r is the diffusion coefficient of the metal in Hg in cm^2/sec

(F/R) = 8.02×10^4 deg. $volt^{-1}$

T   is the temperature in °K

$b\frac{1}{2}$ is the width of the peak at half the peak height in mv.

As predicted by equation 1, the i_p of both Cu and Pb was found to be a linear function of the sweep rate over the range tested. Comparison of the calculated response using equations 1, 2 and 3 and the observed Pb response is given in Table III. It is apparent that there is excellent agreement between the response calculated for a two electron, diffusion controlled oxidation and that observed for the Pb oxidation in seawater.

In seawater, cupric ions undergo a two step reduction [Odier and Plichon, 1971]:

TABLE III

COMPARISON BETWEEN THE OBSERVED AND CALCULATED RESPONSE FOR Pb
IN SEAWATER SOLUTIONS.[a]   A SUBSCRIPT C REFERS TO A
CALCULATED VALUE AND A SUBSCRIPT o REFERS
TO AN OBSERVED VALUE

$C_r^{o}M$ [b]	$(i_p)_c$	$(i_p)_o$	$(i_p)_c/(i_p)_o$	$(E_p)_c$	$(E_p)_o$	$(b\frac{1}{2})_c$	$(b\frac{1}{2})_o$
0.03	0.63	0.70	0.90	-.51	-.50	38	~40
0.05	1.14	1.20	0.95	-.51	-.50	38	~40
0.08	1.71	1.80	0.95	-.51	-.50	38	~40
0.15	3.25	3.25	1.00	-.51	-.50	38	~40

[a] Results for acidified seawater (pH = 2.0) with: L = 5 x 10^{-7} cm; H = 2.4 x 10^{-8}; $E_{\frac{1}{2}}$ = -0.40 v; v = 0.032 v/sec; T = 34°C

[b] Calculated from the area of the Pb and Hg stripping peaks

$$Cu^{2+} + 2Cl^- + e = CuCl_2^- \qquad E_{\frac{1}{2}} > 0.0 \text{ v}$$

$$CuCl_2^- + e = Cu^\circ + 2Cl^- \qquad E_{\frac{1}{2}} \sim -0.20 \text{ v}$$
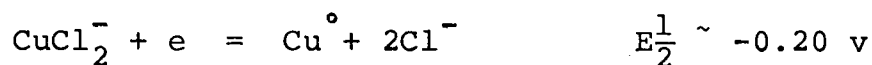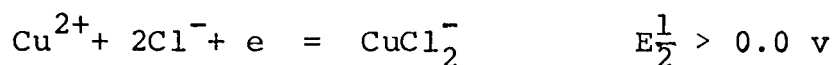
The observed stripping peak for Cu in seawater should correspond to the reverse of the second reduction. Table IV, where the theoretical response for a reversible, diffusion controlled, one electron oxidation is compared with that experimentally observed, indicates that the observed value of $b_{\frac{1}{2}}$ is variable, decreasing with increasing peak height. At high values of i_p, $b_{\frac{1}{2}}$ approaches a limiting value approximately half that predicted, closely corresponding with the theoretical value for a two electron oxidation. In order to determine whether the oxidation of Cu in seawater is in fact a 2 step reaction, sufficient Cu was added to a seawater sample to allow observation of the oxidation wave when the metal was plated directly onto glassy carbon in the absence of Hg. Two stripping peaks were observed, the first corresponding to that observed in the presence of Hg. The second peak, which presumably corresponds to the oxidation of Cu(I) to Cu(II), occurs at a potential that is masked by the oxidation of Hg when Cu is stripped from an amalgam.

TABLE IV

COMPARISON BETWEEN THE OBSERVED AND CALCULATED RESPONSE FOR Cu
IN SEAWATER SOLUTIONS.[a] A SUBSCRIPT c REFERS TO A
CALCULATED VALUE AND A SUBSCRIPT o TO
AN OBSERVED VALUE

c_r^o M [b]	$(i_p)_c$	$(i_p)_o$	$(i_p)_c/(i_p)_o$	$(E_p)_c$	$(E_p)_o$	$(b\frac{1}{2})_c$	$(b\frac{1}{2})_o$
0.06	0.33	0.64	0.52	-.43	-.30	76	~55
0.20	1.02	2.00	0.51	-.43	-.24	76	~40
0.30	1.55	3.10	0.50	-.43	-.23	76	~40

[a]Results for acidified seawater (pH = 2.0) with: L = 5 x 10^{-7} cm; H = 1.2 x 10^{-8}; $E\frac{1}{2}$ = -0.2 volts; v = 0.032 v/sec; T = 34°C

[b]Calculated from the area of the Cu and Hg stripping peaks

The observed Cu peak potential is anodic to that predicted by equation 2 for a one electron reduction. In a kinetically controlled reduction, the half wave potential is shifted to a more anodic potential than that for the simple diffusion controlled case [Heyrovsky and Kuta, 1966]. Since reduction to the cuprous oxidation state occurs in the presence of sufficient complexing agent, the potential of the oxidation of Cu(0) to Cu(I) in seawater would be expected to depend on the concentration of chloride ions. The observed peak potential is in fact observed to vary with the chloride ion concentration, shifting anodically with decreasing chloride (Figure 2.8). In addition, the peak potential shifts anodically with increasing Cu concentration (Figure 2.8). Both observations are consistent with the hypothesis that diffusion of chloride ions to the electrode has a rate limiting effect on the oxidation process.

If the oxidation is kinetically controlled, the equations derived for a reversible, diffusion controlled oxidation would not be applicable. This would account for the lack of agreement between the observed and calculated stripping response for Cu in seawater.
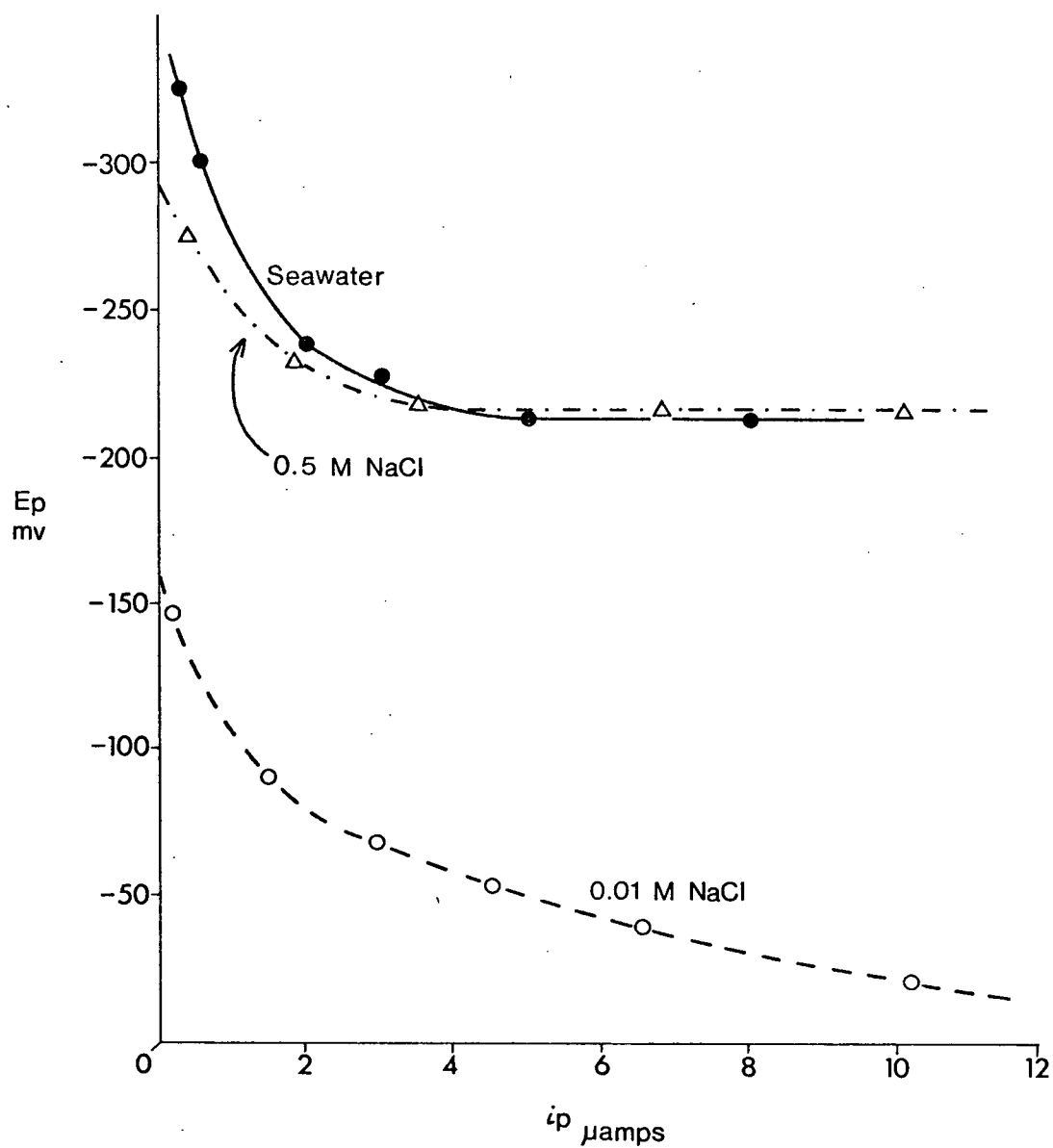
Figure 2.8   The variation of the Cu peak potential with
              i_p and chloride concentration

2.6 Multiple Peaks

Occasionally, a doublet or a shoulder was observed
in the stripping current for Cu instead of one distinct
and sharp peak as expected. Both Matson [1968] and
Fitzgerald [1970] reported similar behaviour for both Cu
and Pb. Matson attributed the anomalous Cu response to
deterioration of the electrode. Reimpregnating the graphite
rod with wax was found in most cases to remedy the situation.
Hume and Carter [1972] found that the appearance of a Pb
doublet was also a function of the electrode surface. If
a large portion of the graphite surface were left uncovered
by the Hg, doublet peaks resulted from metal stripped from
both the Hg and the graphite.

The presence of more than one Cu peak or an unsymmetrical
peak in the present work was found, in some cases, to be a
function of the glassy carbon surface. If different electrodes
were used in the same solution, one might give a doublet
while the other would not. If the electrode that gave the
doublet was then repolished, a single sharp peak was obtained.
The surface may become pitted after repeated use due to
electrochemical oxidation in the presence of O_2, although
there was no microscopically visible difference in the
surface of a freshly polished electrode and one that had
been in use for several months. In these cases, the surface
film may consist of many Hg droplets, resulting in the

stripping of metal that has been deposited both in Hg and directly onto glassy carbon, as suggested by Hume and Carter. The peak potential for the Pb stripping peak from glassy carbon was found to be identical to that from Hg, explaining why doublets were not observed in the Pb response even under circumstances where doublets were observed for Cu.

In many instances, however, the presence of a distorted or doublet Cu peak was found to be independent of the electrode used. As noted before, the Hg appears to be supersaturated with respect to Cu increasing the likelihood of intermetallic compound formation. The presence of an extra peak or a distorted peak in the Cu response may thus reflect the presence of an intermetallic compound oxidized at a potential similar to that of Cu or the oxidation of Cu which has not dissolved in Hg and is present either on the surface of the Hg or covered by a thin film of saturated Cu-Hg amalgam. Kozlovsky and Zebreva [1972] have attributed the appearance of a new peak in stripping analysis to the oxidation of intermetallic compounds which have accumulated on the surface of the electrode.

3. THE DISTRIBUTION OF COPPER AND LEAD IN INDIAN
ARM AND BURRARD INLET

3.1 Introduction

Burrard Inlet and Indian Arm comprise a continuous
system that forms the southernmost inlet on the mainland
British Columbia coast (Figure 3.1). Burrard Inlet is
narrow and relatively shallow, having an average depth of
less than 30 m inside the sill at First Narrows (Figure
3.2). The lower portion of the inlet serves as the main
harbour for the city of Vancouver, while the entire inlet
is bounded by the urban areas of Greater Vancouver. In
contrast, the shoreline of Indian Arm is virtually
uninhabited.

Indian Arm extends approximately 22 km due north
into the Coast Mountains from its connection with Burrard
Inlet (Figure 3.2). It has the physical features common
to most fjords on the British Columbia coast; a shallow
sill near the entrance separates a deep central basin from
the adjoining waters. The entrance sill has a limiting
depth of 26 m and the central basin, averaging over 200 m
in depth, has a maximum depth of 224 m. Seasonal varia-
tions in water properties have been studied by Gilmartin
[1962] who observed that there is a characteristic
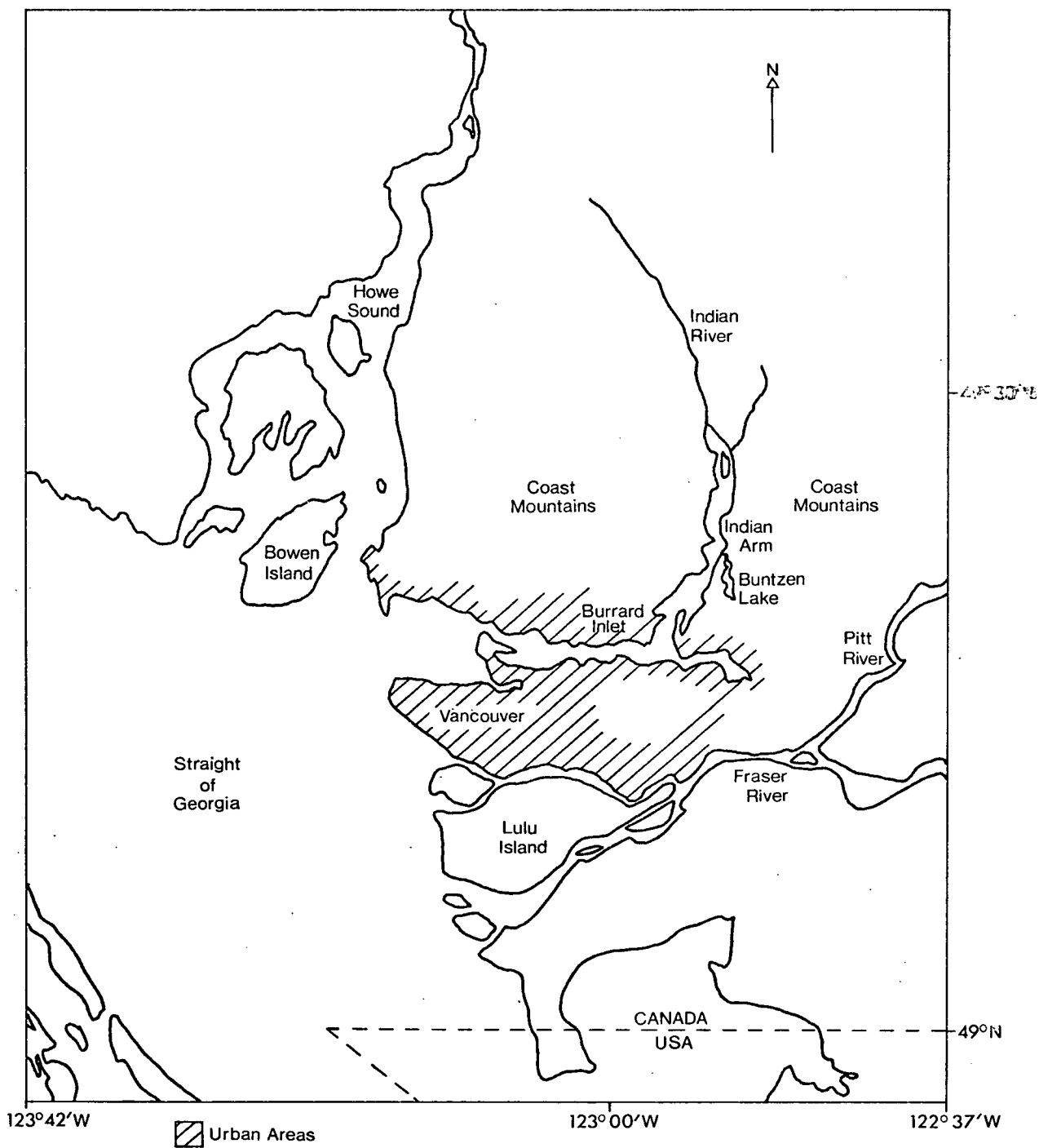
Figure 3.1   Location of Burrard Inlet and Indian Arm
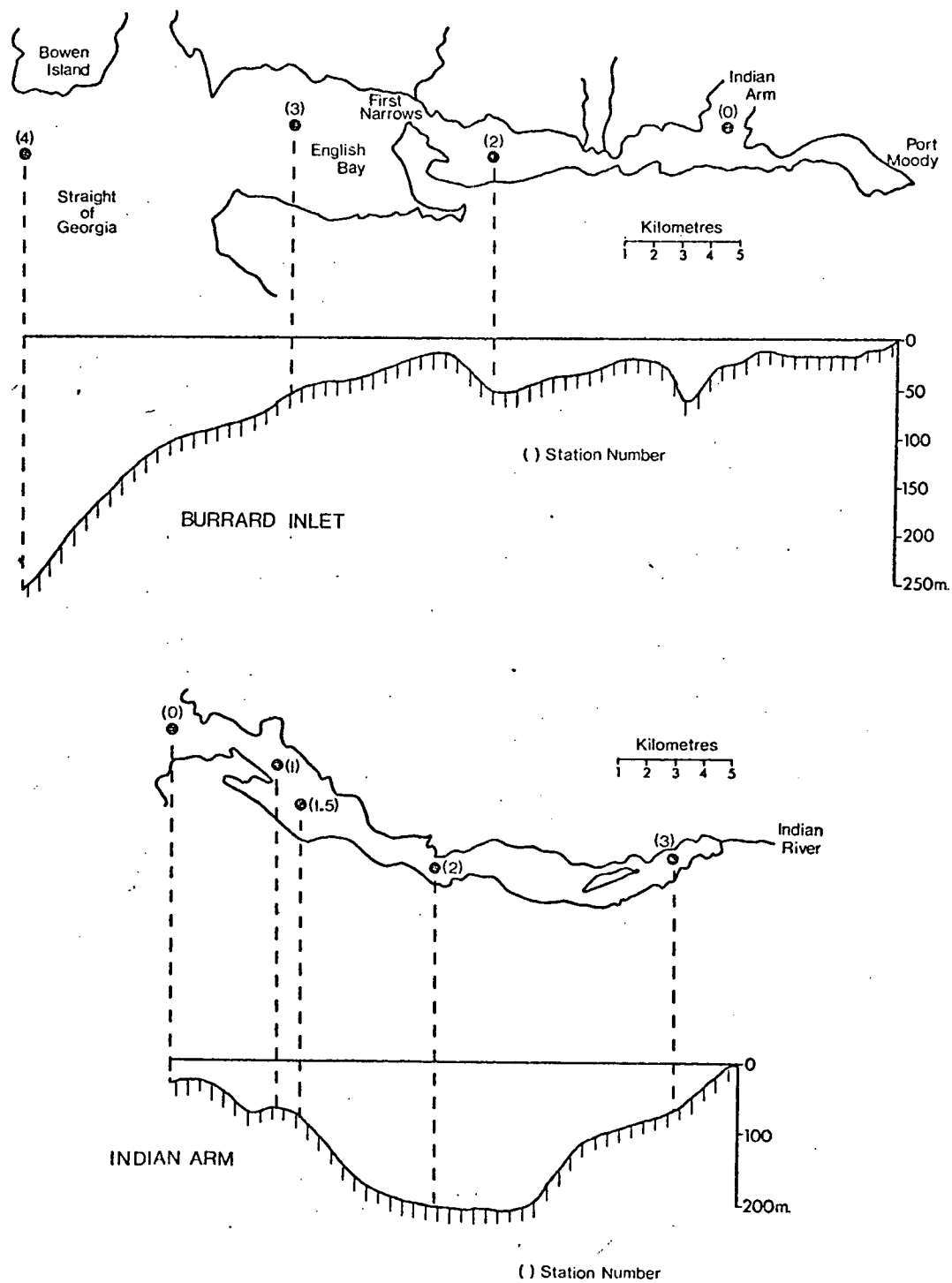
Figure 3.2 Station location maps and longitudinal sections for Burrard Inlet and Indian Arm

estuarine type of two layer circulation with a thin layer
of relatively brackish water flowing out of the system at
the surface and, below this, a compensating inflow of
denser, more saline water. The shallow approaches in
Burrard Inlet restrict the free exchange of deep water
between Indian Arm and Georgia Strait.

3.2 Sampling Procedures

All sampling in Indian Arm and Burrard Inlet was
carried out from the oceanographic research vessel C.S.S.
Vector at the stations shown in Figure 3.2. Water samples
were collected either with 1.2 litre polypropylene N.I.O.
bottles or five litre PVC Nisken bottles. The water collected
in the Nisken samplers was used only for intercomparison
and storage tests.

Temperature observations and the samples for dissolved
metal, oxygen and salinity determinations were all taken
from the same water sample. The dissolved oxygen and
salinity samples were withdrawn immediately after collection
and the remaining water then transferred to 500 ml poly-
ethylene bottles until filtered. Filtration was carried
out under reduced pressure through membrane filters (0.2 μm
average pore diameter) which were soaked for 1/2 hour in a
1% HCl solution and then rinsed several times with deionized
water before use. The first 100 ml of filtrate was used

to rinse out the filter flask and then discarded. Storage
bottles for the metal samples and the glassware involved
in filtration were cleaned with hot 6N HCl prior to a
cruise and then rinsed several times with deionized water
and once with the sample prior to use.

3.3 Storage Methods

Since it was not always feasible to analyse the metal
samples immediately after collection, the effect of storage
was investigated. Samples collected with a 5 litre Nisken
bottle and filtered as described in the previous section were
analysed on board ship within 3 hours of collection and the
remaining sample stored in different ways and analysed at
various times after return to the laboratory. Changes observed
in the concentrations of Cu and Pb as a function of time
and method of storage are given in Figure 3.3. The concen-
tration of both metals decreased significantly with time in
unacidified samples even when frozen, presumably through
adsorption onto the walls of the container. No loss was
found if the samples were acidified with HCl to a pH of
approximately 2 and stored in polypropylene bottles.
Robertson [1968] observed that other trace metals behave
similarily.

All data reported in this study were obtained using
100 ml filtered samples that were acidified with 0.5 ml of
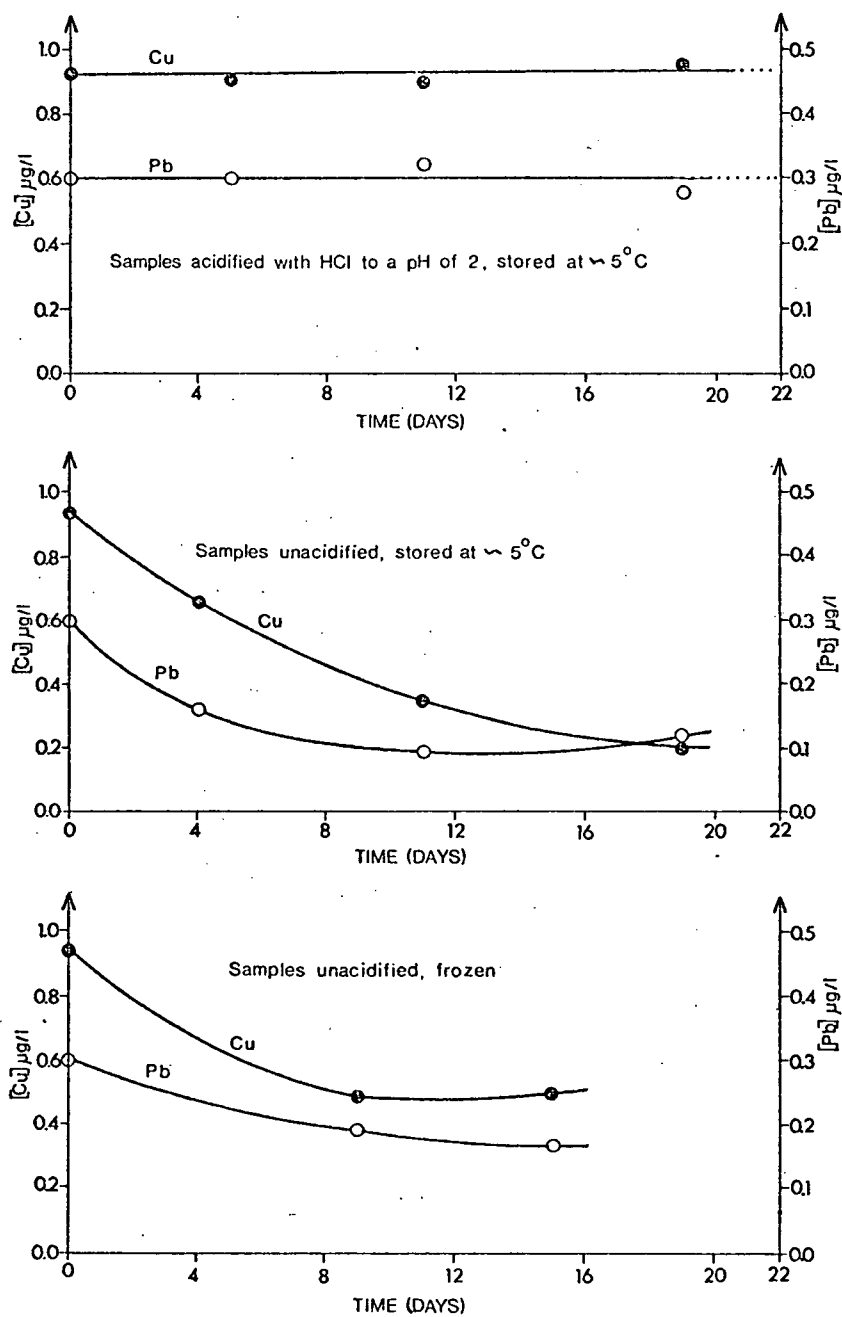
Figure 3.3   Storage effects on the Cu content of seawater
samples stored in 125 ml polypropylene
containers

6N HCl and stored in 125 ml polypropylene bottles at approximately 5°C until analysed.

3.4 Analytical Methods

1. Dissolved Cu and Pb: Seawater samples were filtered and stored as described above and analysed for Cu and Pb by the standard procedure given in Section 2.3. Samples were generally analysed within 10 days of collection.

2. Dissolved Oxygen: Dissolved oxygen was determined on board ship by standard Winkler titration using the modified reagents described by Carrit and Carpenter [1966].

3. Salinity: Salinity was estimated with an Auto-Lab Model 601 MK3 Inductive Salinometer (Extended Range Model).

3.5 Intercomparison of Techniques

The chemical species in which Cu occurs in solution in seawater have not been definitely established and there is no assurance that different analytical procedures all measure the same forms of dissolved Cu. As a consequence, it may not always be meaningful to compare values obtained by different techniques.

The voltammetric method developed in this study was compared to another method which is currently being employed

for the routine analysis of Cu and several other trace metals in seawater at the University of British Columbia. This technique [E.V. Grill, unpublished procedure] involves a solvent extraction preconcentration followed by atomic absorption spectrophotometric analysis. The preconcentration consists of chelating the metals in 2 litres of filtered seawater with diethyl dithiocarbamate (DDC) at a pH of 6 and extracting the sample 3 times with isoamyl acetate; the metals are then back extracted from the organic phase into a 20 ml aqueous phase with acidified Cl_2 water. The above operations are carried out on board ship immediately after filtering. The acidified aqueous extract, which is stored in acid rinsed polypropylene bottles and returned to the lab, is further concentrated prior to analysis by reformation of the metal diethyl dithiocarbamates and extraction into 5 ml of methyl isobutyl ketone (MIBK). Copper is then determined by flame atomic absorption measurement of the MIBK solution.

On two separate occasions, water samples collected at a variety of depths were filtered and separated into 2 aliquots and then analysed by the two different methods. The results are given in Table V. The first set was obtained using samples that were stored unacidified in 1 gallon polyethylene carboys at 5°C and analysed 5 days after collection. The second set was run on board ship immediately after filtration.

TABLE V

COMPARISON BETWEEN THE CONCENTRATION OF Cu IN SELECTED SEA-
WATER SAMPLES AS DETERMINED BY ASV AND BY ATOMIC
ABSORPTION ANALYSIS WITH SOLVENT
EXTRACTION PRECONCENTRATION.[a]

I. Water collected October 12, 1972 at station Indian 2.

| Depth (m) | [Cu] µg/l | | $(\frac{[Cu] \text{ solv.extr.}}{[Cu] \text{ ASV}})$ |
	ASV	Solvent Extraction	
10	0.60	0.55	0.92
20	0.57	0.53	0.93
50	0.60	0.53	0.88
75	0.46	0.42	0.91
100	0.43	0.45	1.05
150	0.47	0.42	0.89
200	0.40	0.40	1.00
		Mean Ratio	0.94

II. Water collected and analysed October 24, 1972 at station
Pacific 2 (48° 00' N, 128° 00' W).

| Depth (m) | [Cu] µg/l | | $(\frac{[Cu] \text{ solv.extr.}}{[Cu] \text{ ASV}})$ |
	ASV	Solvent Extraction	
10	0.36	0.37	1.03
50	0.24	0.24	1.00
500	0.24	0.22	0.92
1000	0.55	0.46	0.84
2000	0.36	0.33	0.92
2300[b]	2.96	2.82	0.95
		Mean Ratio	0.94

[a]Analyst, F.A. Whitney

[b]Sample apparently contaminated in collection

The results obtained by the two methods agree in most cases to within 10%, though the values obtained by ASV tend generally to be slightly higher than those obtained by extraction. This could reflect a real difference in the amount of metal measured by the two methods or an analytical bias related to the particular techniques and analysts involved. Since the true value for the metal content of the samples is not known, it is not possible to determine whether one of the methods is more accurate than the other or whether either measures the total dissolved Cu. The close agreement does suggest though, that both methods detect roughly the same forms of the metal in natural seawater.

3.6 Experimental Observations

Stations in the system were sampled three times in the period July to October, 1972. Table VI lists the dates, cruise numbers and the stations sampled. The observations from these cruises are tabulated in the Appendix.

TABLE VI

SAMPLING IN INDIAN ARM AND BURRARD INLET

Cruise	Dates	Stations Sampled
72/29	July 17, 1972	Indian 0,1,2,3: Burrard 2,3,4
72/35	Sept. 5, 1972	Indian o,1,2,3: Burrard 2,3,4
72/39	Oct. 12, 1972	Indian 1.5, 2, 3
72/41	Oct. 25, 1972	Burrard 4

The station at Burrard 4 was taken as a control, assuming the subsurface water at this station to be typical of Georgia Strait water and of the subsurface water entering Burrard Inlet and subsequently Indian Arm.

The lowest concentrations of both metals were observed in the subsurface waters at Burrard 4 during July and September, while the highest levels were encountered in the subsurface waters of the harbour and Indian Arm during the same period. The concentration of Cu at the stations sampled ranged from 0.19 to 2.20 μg/l, although values were generally less than 1.0 μg/l (Appendix). The range in Pb concentrations was from less than 0.05 to 0.83 μg/l (Appendix). The distributions of Cu and Pb observed at Burrard 4 and Indian 2 are compared in Figures 3.4 and 3.5. It is apparent that both metals tend to have parallel distributions at each of the stations.

3.7 Discussion

The marked tendency for Cu and Pb to covary, both spatially and temporally, suggests that their distributions are generally controlled by similar factors. Although these may be of a biological, chemical or physical nature, the most important factor in at least some cases appears to be the general circulation of water in the system.

The increasing salinity in the subsurface waters at Burrard 4 during successive cruises (Figure 3.6) indicates

O July   ● September   △ October

a) INDIAN 2   b) BURRARD 4

DEPTH (m)

[Cu] μg/l   [Cu] ug/l
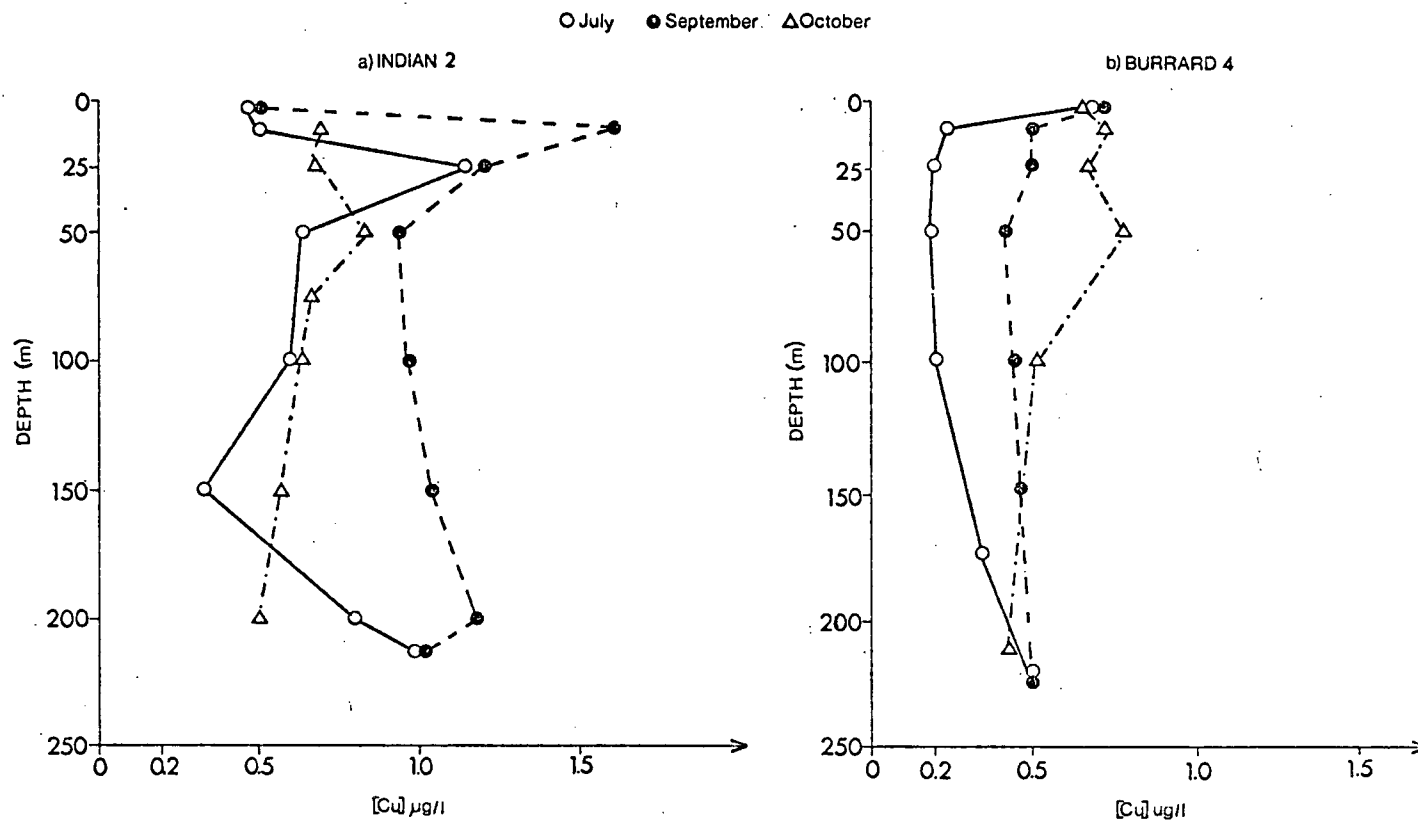
Figure 3.4   The Cu distribution at stations Indian 2 and Burrard 4 during July, September and October, 1972
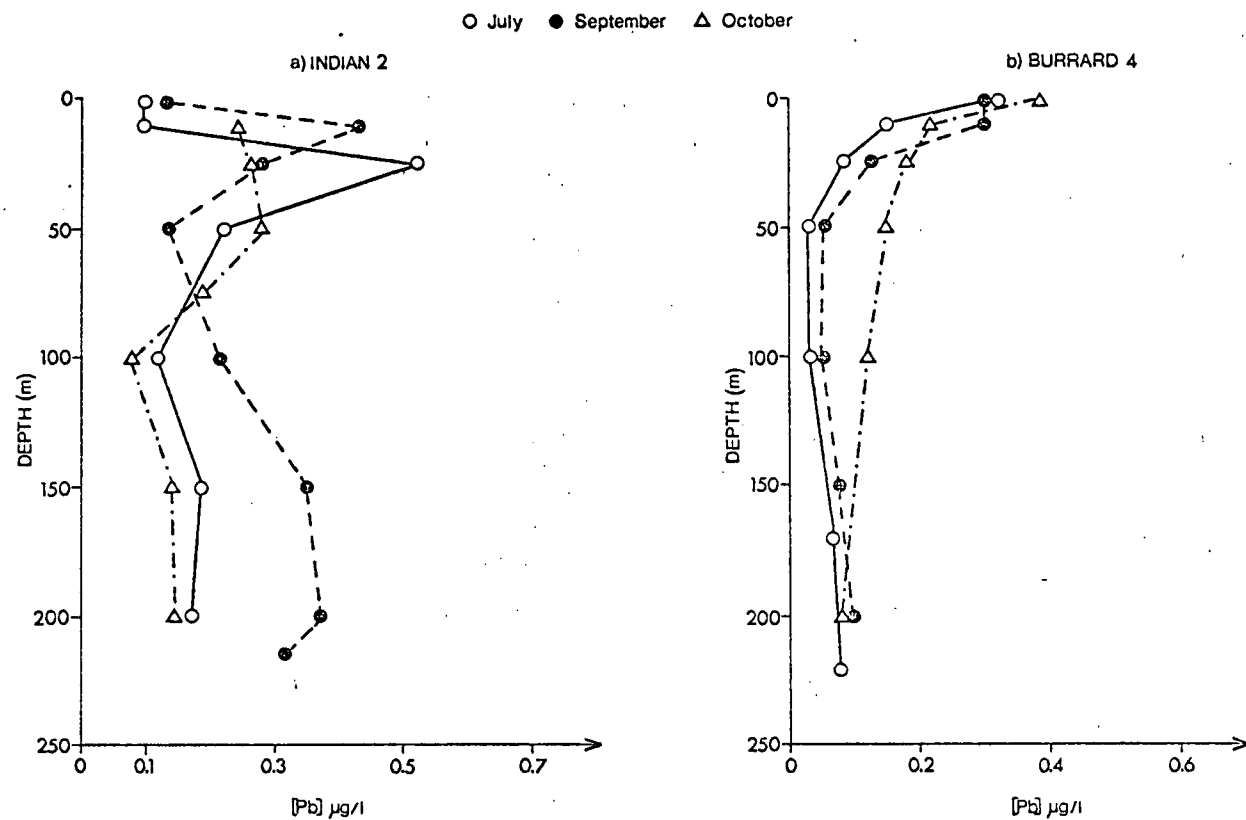
Figure 3.5   The Pb distribution at stations Indian 2 and Burrard 4 during July,
September and October, 1972

an intrusion of more saline Juan de Fuca Strait water into
the Strait of Georgia [Waldichuk, 1957]. A corresponding
increase in the Cu and Pb concentrations at this station
suggests that the intruding water had a higher metal content
than that resident in Georgia Strait. This increase is
particularly evident in the Cu distribution (Figure 3.4).
However, the Cu concentrations did not exceed 0.80 μg/l
and are consistent with reported concentrations of less
than 1.0 μg/l in the North Pacific and in other British
Columbia coastal waters [Tatomer, 1972, E.V. Grill, personal
communication].

The dissolved Pb concentrations of the subsurface
water at Burrard 4 are generally less than 0.10 μg/l and
approach the lower limit of detection for the method.
These values are only slightly higher than the Pb concen-
trations of 0.02 - 0.04 μg/l observed in the open ocean
below 1000 m [Chow, 1968] and are in good agreement with
the values observed by Baier [1971] at stations near the
mouth of Georgia Strait.

During July and September, there was an increase
in the Cu and Pb content of the subsurface waters on passing
from Georgia Strait into Burrard Inlet and Indian Arm and
a reversal of this trend at the surface (Figures 3.7 and
3.8), gradients which are also apparently closely related
to general circulation patterns. The surface water in the
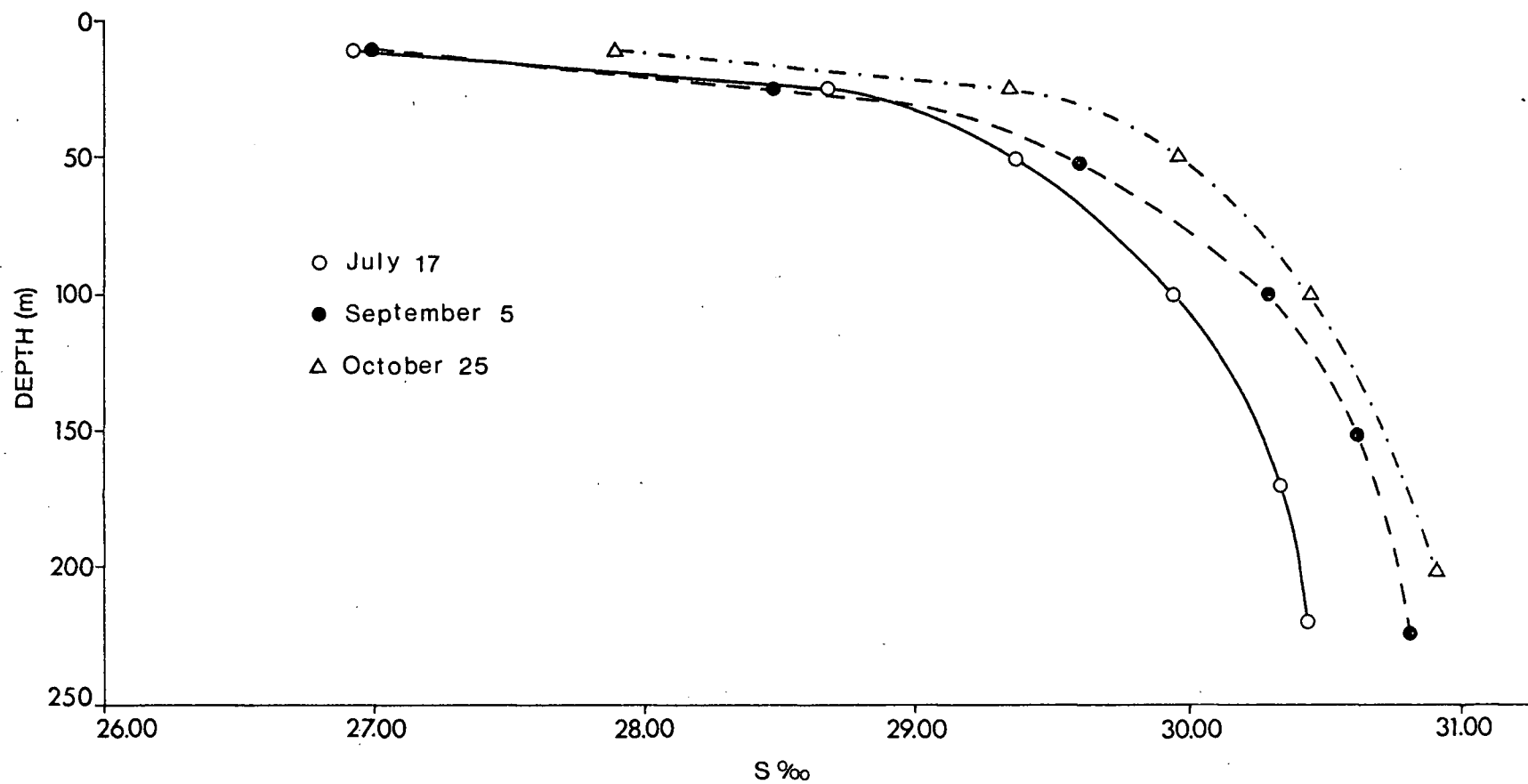
Figure 3.6   Variations in salinity with depth at station Burrard 4 during July,
              September and October, 1972
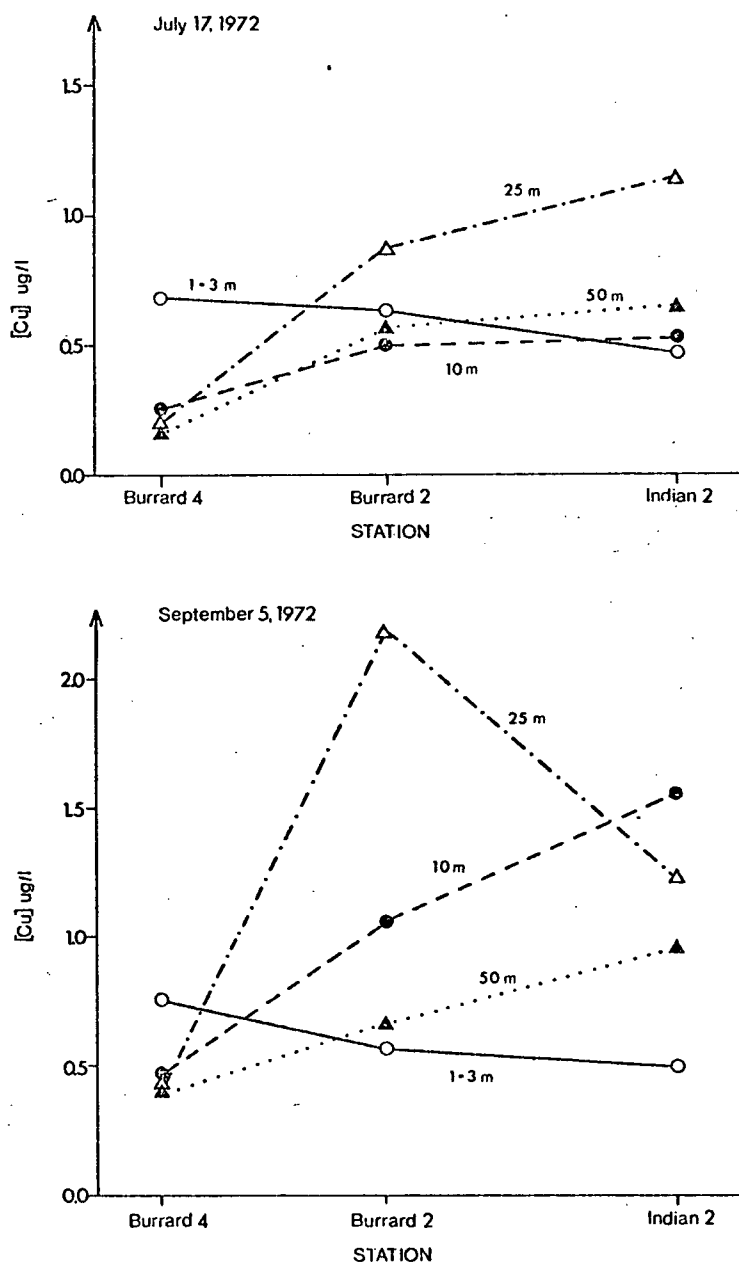
Figure 3.7 Variations in the Cu concentration in the upper
50 m at stations Burrard 4, Burrard 2 and Indian
2 during July and September, 1972
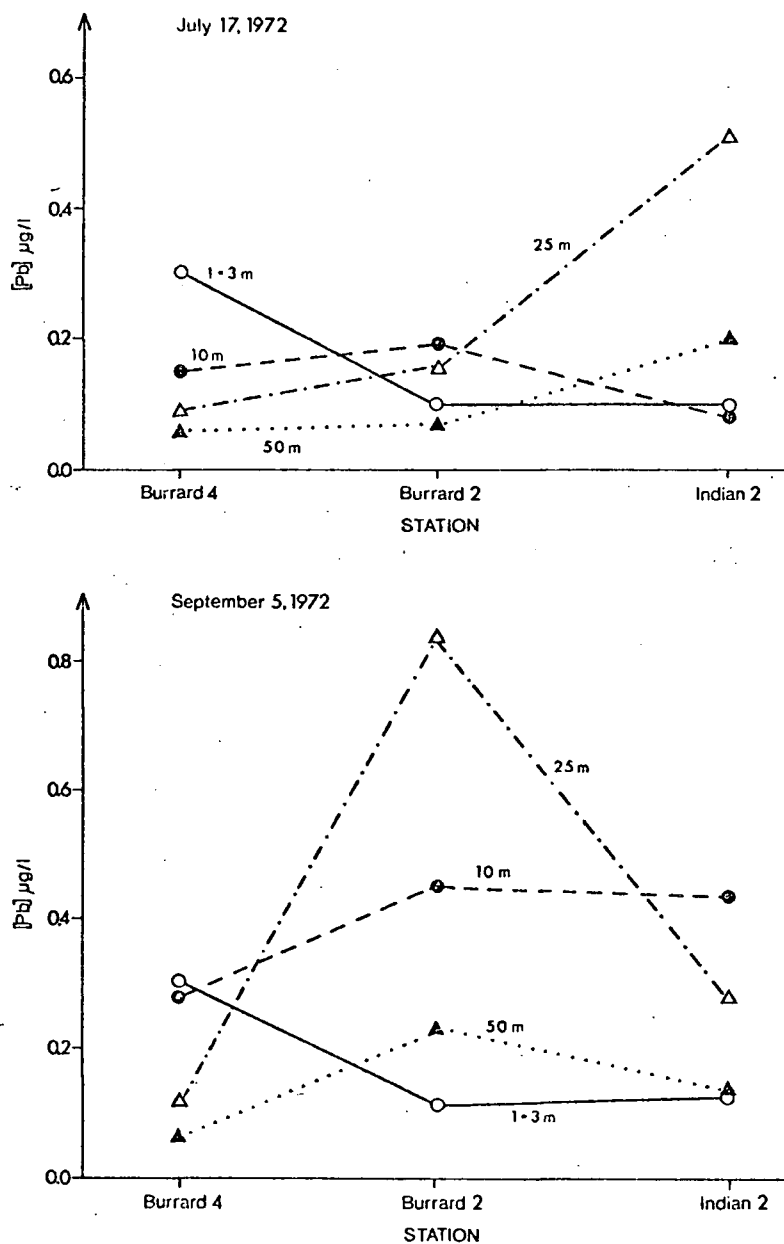
Figure 3.8   Variations in the Pb concentration in the upper
50 m at stations Burrard 4, Burrard 2 and Indian
2 during July and September, 1972

inlets is relatively brackish, flowing outwards while the subsurface water is more saline and moving towards the head of Indian Arm. When this is considered, there is an increase in the metal content for both the surface and subsurface water as it flows through Burrard Inlet where the greatest inputs might be expected.

A persistent feature of the distributions of both metals in Indian Arm were maxima between 10 and 50 m (Figures 3.4 and 3.5). Intrusions of water from Burrard Inlet into Indian Arm normally occur at depths of between 10 and 100 m and are often noticeable as tongues of highly oxygenated water extending from the mouth towards the head of the inlet [Gilmartin, 1962]. Such an intrusion is evident in the logitudinal profile for dissolved oxygen during September (Figure 3.9). The net effect of these intrusions is the addition of Burrard Inlet water, usually at an intermediate depth. The dissolved metal maxima in Indian Arm between 10 and 50 m correlates with the approximate depth of these intrusions, suggesting that Burrard Inlet water is the source of the dissolved metal maxima at these depths. As a result of mixing and the entrainment of this higher metal content water with water of lower metal content at the surface, a concentration gradient between the mouth and the head of the fjord at the depths of the intruding water would be expected. This gradient is present between stations Indian 0 and 1 in July and September but the maximum
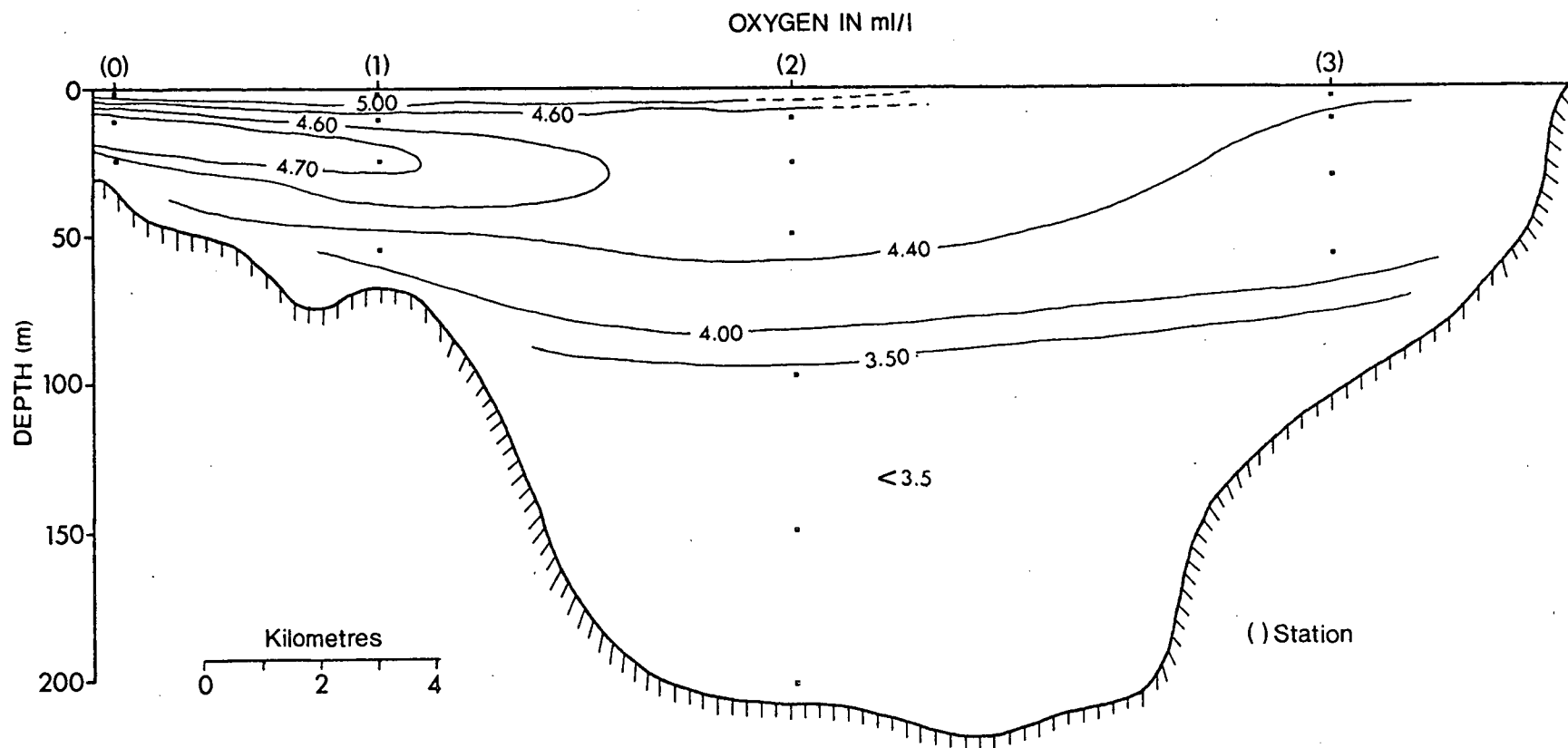
Figure 3.9   Longitudinal profile of dissolved oxygen in Indian Arm on September 5, 1972. The dots indicate sample depths

metal concentrations were observed at Indian 2 in the middle
of the inlet (Figures 3.10 and 3.11). In the absence of
additional data, it is not possible to determine if this is
the result of an earlier intrusion or of other sources of
the metals in the system.

Sources of water in Indian Arm other than tidal
intrusions are the Indian River entering at the head of the
fjord and, to a lesser extent, the discharge of the Buntzen
power plant directly across from Indian 2 on the eastern
shore [Gilmartin, 1962]. Since the dissolved Cu and Pb
concentrations of the surface layer are very low, the fresh
waters derived from these sources would appear to have a
lower metal content than that of the resident saline waters.
Water introduced at these sources may, however, also contain
metal that is associated with particulate matter. If metals
were desorbed as this material sinks into more saline water,
a subsurface maxima originating near the head or middle of
the inlet might then be expected. Kharkar et al. [1968] have
shown that significant desorption of trace metals from
suspended mineral matter can occur with increasing salinity.

It is particularily evident that the metal distri-
butions are not controlled solely by physical factors when
the deep water in Indian Arm is considered. Despite the
fact that there was no apparent displacement of water in
Indian Arm below 100 m during the sampling period, large
fluctuations in metal content were observed similar to those
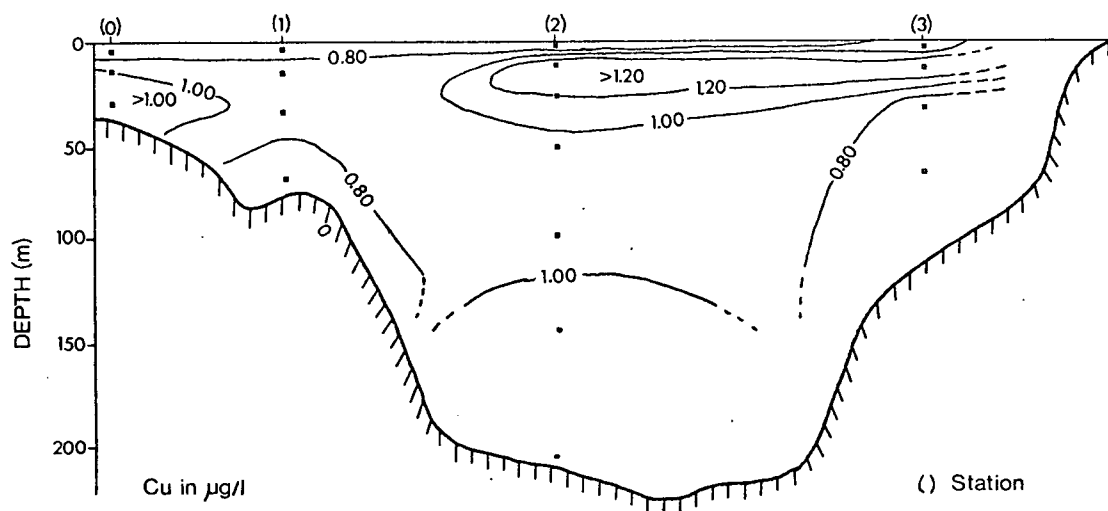
Figure 3.10   Longitudinal profile of dissolved Cu in Indian
Arm on September 5, 1972. The dots indicate sample
depths
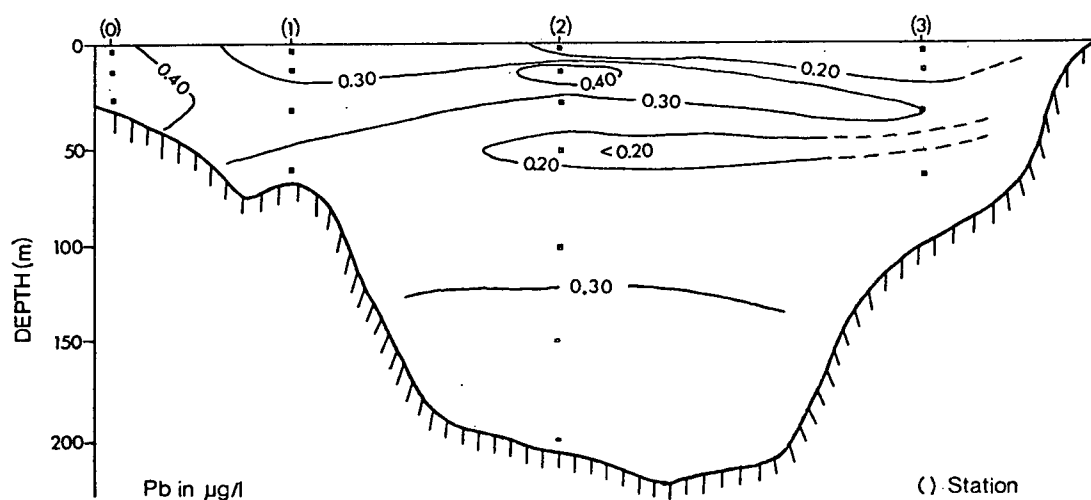

Figure 3.11   Longitudinal profile of dissolved Pb in Indian
Arm on September 5, 1972. The dots indicate
sample depths

in the upper 100 m (Figures 3.4 and 3.5). An increase in
the metal concentrations between July and September was
followed by a significant decrease in October. Since these
variations are apparently independent of inputs of higher
or lower metal content water, the controlling mechanism
must be either biological consumption or decay, or else
solution or sorption reactions involving suspended
particulate matter. The extent of the effects of biological
processes are impossible to predict at present and those of
sorption processes can vary with the concentration of
adsorbate, pH, salinity and temperature as well as the
physical characteristics of the adsorbents. The fact that
suspended mineral and detrital organic materials readily
adsorb trace metals such as Cu and Pb from seawater is,
however, well documented [Krauskopf, 1956].

The Pb concentrations observed in this system are
lower than might be expected considering its proximity to
a large urban area. Baier [1971] reported that Pb concen-
trations in and near San Francisco harbour are more than
2 µg/l and that in Lake Washington (Seattle) they are as
high as 6 µg/l. The dissolved Pb concentrations observed
in the present study are well below these levels and are
particularily low at the surface within Burrard Inlet and
Indian Arm. The results of previous studies on marine
systems have indicated that the dissolved Pb concentration

in the surface layer varies inversely with the distance
from a large urban area [Chow, 1968; Baier, 1971]. Such
a relationship does not appear to hold in the present
system where the lowest surface dissolved Pb concentrations
were observed in the harbour and Indian Arm. Baier [1971]
indicated that the particulate Pb content of nearshore
waters could exceed the dissolved content. If Pb is
introduced as a particulate aerosol, the low dissolved
levels at the surface in the harbour and Indian Arm would
indicate that the particulate metal is removed from the
surface layer before much of the Pb dissolves or is desorbed
either by the general surface flow that carried it out into
Georgia Strait or by sinking into the more saline subsurface
water. In agreement with this, the highest Pb concentrations
were at intermediate depths in the harbour and Indian Arm
and higher Pb concentrations were observed in the surface
layer at Burrard 3 and 4 than at Burrard 2 in the harbour.

3.8 Summary

        Although localized pockets of Cu enriched water
occurred at different times and locations within both Burrard
Inlet and Indian Arm, there does not appear to be an overall
significant enrichment of Cu in this system as compared to
Georgia Strait and other British Columbia coastal waters.
The observed distribution appears, to a large extent, to be

regulated by the circulation within the system but additional regulatory mechanisms can also be inferred from the large fluctuations in concentration observed in Indian Arm that are apparently independent of the circulation. Similar mechanisms appear to regulate the distribution of dissolved Pb. Although the subsurface waters in the inlets are enriched in dissolved Pb by as much as an order of magnitude compared to Georgia Strait, the dissolved Pb concentrations are lower than those reported for marine waters near other urban localities.

4. APPLICATION OF THE MERCURY PLATED GLASSY CARBON ELECTRODE TO THE STUDY OF COMPLEXED METAL IN SEAWATER

Trace metals occur in seawater in a variety of forms that can be differentiated on the basis of their chemical or physical characteristics. The simplest scheme of classification is one based on physical size in which any metal retained by a fine porosity membrane filter (normally one with a 0.45 μm average pore diameter) is termed particulate. The portion passing through the filter is arbitrarily defined to be dissolved but may in fact consist of metal that is a constituent of colloidal sized organic or inorganic material as well as molecular or ionic species that are conventially considered to be in true solution. The metal in true solution potentially consists of simple hydrated cations and of complexes formed by the cation with inorganic ligands, particularily major seawater anions, and simple organic solutes.

The methods currently available for the analysis of trace metals at the levels present in seawater do not allow one to readily differentiate between the dissolved species that are potentially present. Thus, the values reported in the literature are generally for the total or some undefined portion of the total dissolved metal content. But, as

pointed out previously, speciation of a metal may be more
important biologically (and chemically) than its total
concentration. There have been a number of reports citing
evidence for associating a fraction of Cu in seawater with
dissolved organic matter [a review is given by Seidel, 1970]
but as yet very little is known about the extent of such
interactions and the whole question of whether the metal
in solution is complexed to a significant extent with organic
matter remains largely one of speculation.

Both Matson [1968] and Fitzgerald [1970] have
attempted to examine this question by means of ASV. Matson
observed a variety of anomalies in the behaviour of the
composite mercury graphite electrode during the analysis of
seawater solutions that he attributed to organic or inorganic
complexing of the metal. Hume and Carter [1972] observed
similar anomalies but found that most were the result of
changes in the physical characteristics of the electrode
itself and concluded that it is unlikely that the technique
provided any useful quantitative information about metal ion
speciation in natural waters. Much of the problem, they
found, originates in the difficulty in distinguishing
between the interfering effects of surface active agents
that are adsorbed onto the electrode and the effects
produced by complexation of the metal. For instance, Matson
[1968] observed that the rate of increase of the peak
current with plating potential for Cu was lower in most

seawater samples compared to 0.5 M NaCl. Matson attributed

this to complexation of the metal ion. Similar results

were obtained in the present study but it was also found

that the addition of small amounts of gelatin to a 0.5

M NaCl solution produced a suppressing effect on the Cu peak

height similar to that observed in seawater (Figure 4.1).

Thus the adsorption of surface active material could be the

source of the anomalous behaviour observed in seawater.

Oxidative destruction of the organic matter in solution would

not differentiate between the two possibilities.

Matson [1968] and Fitzgerald [1970] also observed

that the peak height of the Cu stripping current was very

sensitive to changes in pH. Fitzgerald concluded that since

lowering of the pH and prolonged photo-oxidation of the sample

both had a similar effect on the measured Cu concentration,

the increase in the current as the pH is lowered is the

result of the release of metal complexed by organic compounds

present in the sample.   Similarily, Allen et al. [1970]

attributed the increase in the Pb stripping current when

samples were acidified to the release of metal from labile

organic complexes.

The variation of the Cu and Pb stripping current

observed in the present study with changing pH in irradiated,

artificial seawater is shown in Figure 2.6. Samples were

irradiated with an Ultra Violet Products Inc. PCQ 9G-1

quartz lamp (radiant output at 2537 Å; 2.5 watts) immersed
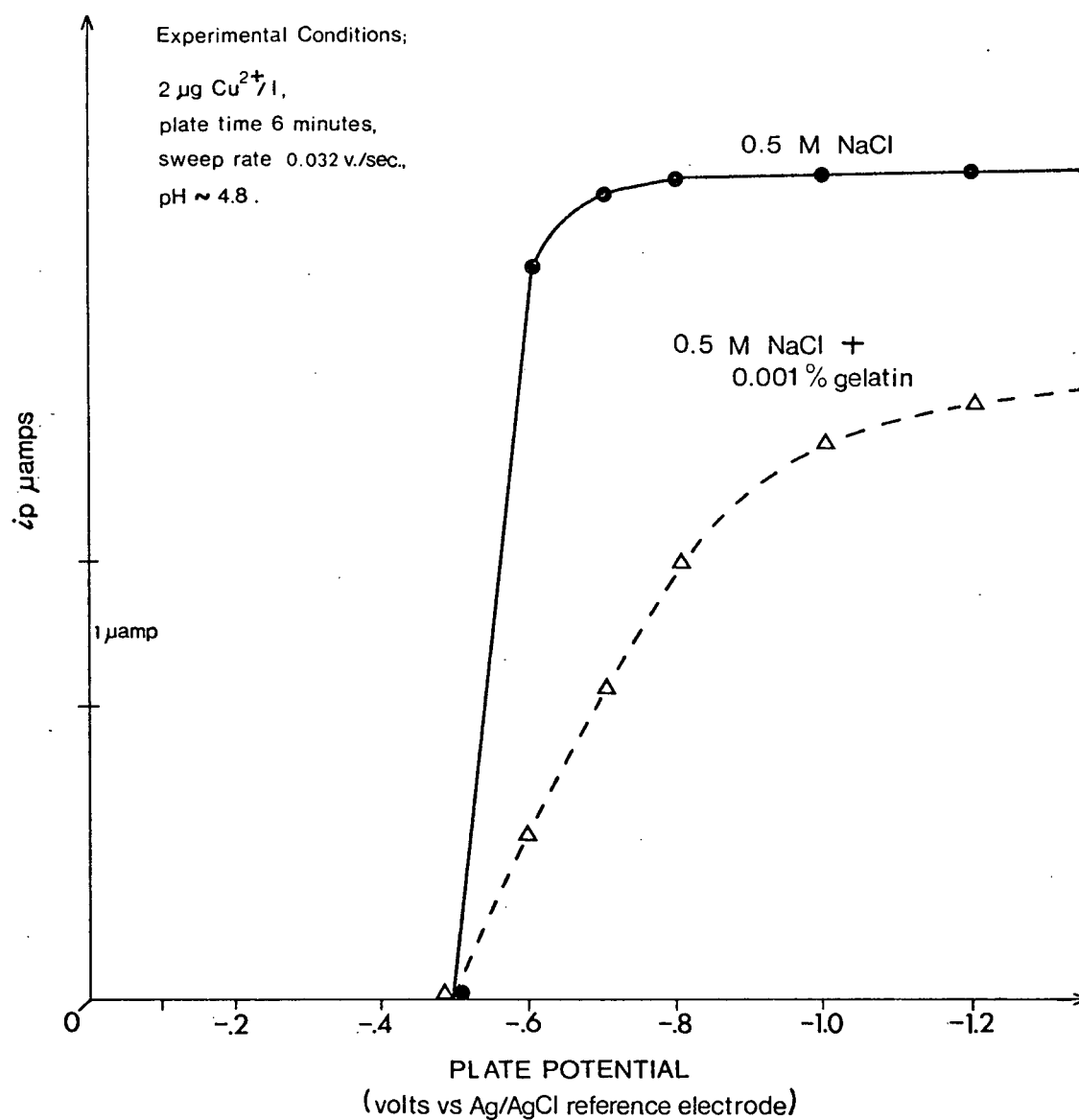
Figure 4.1 The effect of gelatin on the Cu stripping response as a function of plating potential in 0.5 M NaCl solution

in a Pyrex cylinder containing approximately 200 ml of sample. This technique is preferable to wet oxidation since no reagents are added to the samples and the pH is not appreciably altered. Fitzgerald [1970] using the same lamp, found that the rate of destruction of the organic matter followed first order kinetics. Irradiation of 70 ml samples for 4 hours destroyed 75% of the organic matter. In this work, samples were irradiated for a minimum of 10 hours. No attempt was made to determine the efficiency of the procedure. Artificial seawater which had not been irradiated with UV light, some natural seawater samples, and all seawater samples after prolonged photo-oxidation gave identical responses.

The amount of Hg plated onto the electrode was found to be independent of the pH below a pH of 7, indicating that the observed variations in the Cu and Pb stripping currents are not due to changes in the Hg film thickness. The increase in the stripping current with decreasing pH (and, thus, in the amount of metal readily reducible at the electrode) must therefore reflect changes in the degree of complexation of the metals by inorganic ligands or an alteration in electrode surface characteristics.

The latter possibility has been suggested by Peters and Cruser [1965]. They proposed that the decrease in the rate of reduction of Cu at a Pt electrode in chloride media at neutral or basic pH's was the result of cupric

ions being precipitated as $Cu(OH)_2$ onto the electrode surface, causing an effective decrease in the surface area. A local excess of hydroxide will exist in the reaction layer adjacent to the electrode as a result of the reduction of residual oxygen in the solution [Heyrovsky and Kuta, 1966]. Precipitation of $Pb(OH)_2$ in this reaction layer has also been suggested for the decrease in the pulse polarographic Pb current in unbuffered or basic solutions [Osteryoung and Osteryoung, 1972]. If the reduction in the stripping current were simply due to an alteration of the effective surface area, the pH dependence of all metals might be expected to be roughly the same since the deposition of a precipitate(s) on the electrode surface would have a similar effect on the reduction or dissolution of all metals. While the pH dependence of Cu and Pb observed in this study is very similar, the Cd and Zn responses reportedly differ from that observed for Cu and Pb [Zirino, 1969, Piro et al., 1969]. For these metals, a steady state current is apparently reached when the pH is lowered to approximately 7. Thus, the variations in stripping currents with pH must be, at least in part, the result of changes in the activities of individual metal ions. Zirino and Yamamoto [1972] have suggested that variations in the stripping current with pH are the result of changes in speciation in the solution as a whole; however, speciation changes in the bulk solution

cannot be distinguished experimentally from those occurring in a thin diffusion layer adjacent to the electrode.

Piro et al. [1969] demonstrated that the pH dependence of the ASV response for Zn could be markedly altered by adding several different chelating agents to seawater samples. Their results showed that chelation requires the pH to be lowered below that in the base electrolyte for the release of all the Zn, as might be expected, and that the level to which the pH must be lowered is a function of the stability of the chelate formed.

The pH dependence of the Cu and Pb stripping response with the mercury plated glassy carbon electrode was investigated in this light to determine its applicability to the detection of organically complexed metal in sea water. The stability constants of the organic chelates formed by the mercuric ion are in many cases of the same order of magnitude as those formed by Cu and Pb [Sillèn and Martell, 1964]. As a result, mercuric ions, which were added in large excess to the samples, could in some cases compete for organic ligands which normally would be bound to these metals. The present method has, therefore, only limited application, even to a qualitative study of metal complexation. Only naturally occurring complexes having a high specificity for Cu or Pb or those in which Cu or Pb are kinetically inert to displacement by mercuric but not hydrogen ions would be expected to persist under these

conditions. Such complexes do apparently exist.

Several seawater samples from Georgia Strait and Indian Arm were found to have a pH response differing from that of artificial seawater. In these cases, the Cu stripping current increased as the pH decreased to 5, as is characteristic of all seawater samples, but instead of remaining constant below this level, increased again as the pH was lowered further. An example is given in Figure 4.2. Piro's work [1969] had indicated that chelation by organics produced a similar effect on the Zn response. To determine whether the anomalous results in this case were due to chelation of Cu, the samples were analysed before and after irradiation for 10 hours with UV light. In all cases, after irradiation, the pH response returned to normal (i.e. to a response identical to that obtained with artificial seawater). While addition of small amounts of gelatin to artificial seawater did not alter the character of the pH response, an addition of 10^{-6} M EDTA produced a shift analogous to that observed in the raw seawater samples in question. An artificial seawater sample spiked with 10^{-6} M EDTA, after irradiation, gave no anomalous behaviour (Figure 4.3). These results strongly suggest that the shift in the pH response observed in some seawater samples was the result of the partial complexing of Cu by naturally occurring dissolved organic solutes.

Seawater – stored in glass carboy at 5°C
O Without irradiation
◉ After 12 hours irradiation

Experimental Conditions;

plate time 8 minutes,
plate potential −0.9 v.
sweep rate 0.032 v/sec.
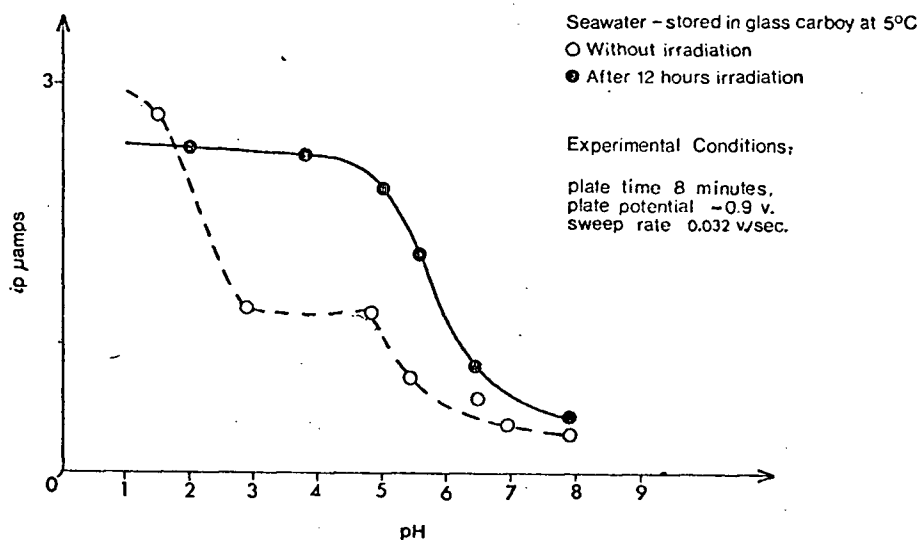
Figure 4.2 Variation of i_p for Cu as a function of pH in aged seawater before and after photo-oxidation

◉ Artificial seawater
O +10^{-6}M EDTA
▲ +10^{-6}M EDTA after 10 hours irradiation

Experimental Conditions;

plate time 5 minutes
plate potential −0.9 v
sweep rate 0032 v/sec.
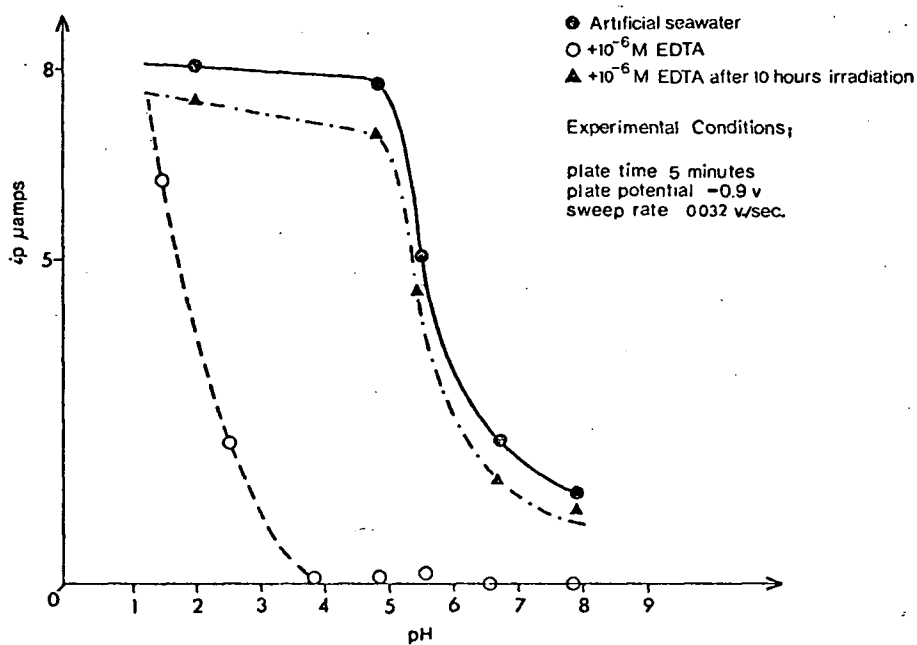
Figure 4.3 Effect of EDTA on the i_p for Cu in artificial seawater before and after photo-oxidation

No similar effect was observed in the Pb pH response. Complexation of Pb is perhaps less likely to occur since Pb concentrations on a molar scale are more than an order of magnitude lower than those of Cu. However, it is also possible that Pb was completely displaced from any complexes by mercuric ions or else that changes in the magnitude of the Pb stripping current were not large enough to be discernable at the low levels of Pb encountered in most samples.

4.1 Summary

Although it is not possible to obtain quantitative information on the speciation of Cu or Pb in seawater by the present technique, correlations between the stripping current and hydrogen ion activity can furnish some qualitative information as to the relative extent of the association of these metals with certain types of organic solutes. On the basis of the results obtained in this study, Cu in seawater at a normal pH appears to be complexed in some cases by dissolved organic matter. The large excess of mercuric ions present in the samples suggests that these complexing agents have a high specificity for Cu.

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A P P E N D I X

CRUISE: 72/29   DATE: July 17, 1972

(a) STATION: Indian 3 LOCATION: 49° 27.3' N SONIC DEPTH: 79 m
                                  122° 52.5' W

Depth (m)	Sal.°/₀₀	T°C	σ_t	O$_2$(ml/l)	Cu(µg/l)	Pb(µg/l)
1	3.910	13.78	2.38	7.90	0.41	0.13
10	21.362	10.52	16.31	5.47	0.62	0.20
30	23.473	9.51	18.09	5.25	0.93	0.26
50	25.054	7.79	19.55	5.22	0.79	0.10
70	26.799	6.76	21.04	3.67	0.59	0.10

(b) STATION: Indian 2 LOCATION: 49° 23.5' N SONIC DEPTH: 216 m
                                  122° 52.5' W

Depth (m)	Sal.°/₀₀	T°C	σ_t	O$_2$(ml/l)	Cu(µg/l)	Pb(µg/l)
1	5.180	16.79	2.86	8.10	0.48	0.10
10	21.533	10.86	16.39	5.46	0.50	0.10
25	23.470	10.10	18.00	5.17	1.14	0.52
50	25.273	7.80	19.72	5.18	0.63	0.22
100	27.303	6.89	21.42	3.69	0.60	0.12
150	27.538	6.88	21.60	3.73	0.34	0.19
200	27.573	6.86	21.63	3.65	0.81	0.17
210	27.569	6.87	21.63	3.66	1.00	0.10

(c) STATION: Indian 1 LOCATION: 49° 20' N SONIC DEPTH: 61 m
                                  122° 55.5 W

Depth (m)	Sal.°/₀₀	T°C	σ_t	O$_2$(ml/l)	Cu(µg/l)	Pb(µg/l)
1	8.079	16.60	5.11	8.00	0.43	0.08
10	22.737	11.16	17.28	5.39	0.57	0.10
30	24.208	10.32	18.54	5.00	0.77	0.18
55	26.635	7.42	20.83	4.34	0.84	0.15

(d) STATION: Indian 0 LOCATION: 49° 18.2' N SONIC DEPTH: 32 m
                                   122° 56.3' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/1)	Cu(µg/1)	Pb(µg/1)
1	14.258	15.15	10.09	8.91	0.77	0.10
10	22.065	11.19	16.75	5.34	1.07	0.25
25	24.291	10.39	18.60	5.16	0.67	0.16

(e) STATION: Burrard 2 LOCATION: 49° 17.9' N SONIC DEPTH: 59 m
                                   123° 5.5' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/1)	Cu(µg/1)	Pb(µg/1)
1	16.661	14.75	12.00	7.72	0.63	0.10
10	24.858	10.29	19.05	5.29	0.47	0.15
30	28.305	8.90	21.93	4.83	0.87	0.20
55	28.728	-	-	4.76	0.55	0.07

(f) STATION: Burrard 3 LOCATION 49° 19.05' N SONIC DEPTH: 39 m
                                  123° 12.1 ' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/1)	Cu(µg/1)	Pb(µg/1)
1	18.479	15.67	13.22	7.39	1.00	0.28
10	26.887	9.72	20.71	5.15	0.42	0.15
25	28.654	8.84	22.21	4.95	0.43	0.18
35	29.260	8.52	22.73	4.75	0.56	0.24

(g) STATION: Burrard 4 LOCATION: 49° 18.0' N SONIC DEPTH: 240 m
                                   123° 24.0' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/1)	Cu(µg/1)	Pb(µg/1)
1	15.939	-	-	7.65	0.68	0.31
10	26.929	-	-	5.80	0.23	0.15
25	28.684	-	-	5.10	0.19	0.09
50	29.372	-	-	4.92	0.19	<0.05
100	29.950	-	-	4.58	0.20	<0.05
150	30.342	8.27	23.61	4.27	0.35	0.07
220	30.450	7.90	23.75	4.27	0.47	0.09

CRUISE: 72/35 DATE: September 5, 1972

(a) STATION: Indian 3 LOCATION: 49° 27.3' N SONIC DEPTH: 77 m
                                   122.

Depth(m)	Sal.°/₀₀	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
1	18.047	16.8	12.66	-	0.84	0.19
10	24.300	9.84	18.68	4.23	1.39	0.13
30	24.999	9.07	19.34	4.29	0.72	0.29
60	25.514	7.94	19.89	4.16	0.77	0.23

(b) STATION: Indian 2 LOCATION: 49° 23.5' N SONIC DEPTH: 220 m
                                   122° 52.5' W

Depth(m)	Sal.°/₀₀	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
1	-	-	-	-	0.50	0.13
10	24.625	10.63	18.82	4.43	1.52	0.43
25	25.295	-	-	4.42	1.20	0.28
50	25.998	11.06	19.81	4.42	0.93	0.14
100	27.421	6.89	21.51	3.30	0.97	0.21
150	27.543	6.90	21.60	3.38	1.04	0.35
200	27.561	6.88	21.62	3.28	1.18	0.38
215	27.562	6.91	21.62	3.16	1.02	0.32

(c) STATION: Indian 1 LOCATION: 49° 20' N SONIC DEPTH: 67 m
                                   122° 55.5'W

Depth(m)	Sal.°/₀₀	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
1	20.686	14.27	15.17	7.02	0.75	0.29
10	24.794	-	-	4.46	0.89	0.25
30	25.745	-	-	4.72	0.94	0.33
60	26.291	10.13	20.19	4.07	0.65	0.23

(d) STATION: Indian 0   LOCATION: 49° 18.2' N   SONIC DEPTH: 32 m
                                    122° 56.3' W

Depth(m)	Sal.°/oo	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
1	24.408	14.27	18.02	5.46	0.69	0.40
10	25.339	12.05	19.05	4.84	0.99	0.40
25	25.963	11.22	19.76	4.48	1.03	0.46

(e) STATION: Burrard 2   LOCATION: 49° 17.9' N   SONIC DEPTH: 58 m
                                    123° 5.5' W

Depth(m)	Sal.°/oo	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
3	24.981	12.71	18.75	5.68	0.55	0.11
10	26.094	11.98	19.73	5.12	1.08	0.46
30	27.546	11.14	21.00	4.84	2.20	0.83
50	28.004	10.83	21.40	4.60	0.67	0.24

(f) STATION: Burrard 3   LOCATION: 49° 19.7' N   SONIC DEPTH: 40 m
                                    123° 12.1' W

Depth(m)	Sal.°/oo	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
1	21.124	15.16	15.33	7.02	1.02	0.32
10	27.498	11.98	20.81	4.95	0.56	0.15
25	28.569	–	–	4.37	0.47	0.17
35	29.287	9.77	22.57	3.95	0.43	0.23

(g) STATION: Burrard 4   LOCATION: 49° 18' N   SONIC DEPTH: 245 m
                                    123° 24' W

Depth(m)	Sal.°/oo	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
1	22.807	16.32	16.38	6.58	0.72	0.30
10	26.973	12.95	20.24	6.59	0.49	0.30
25	28.449	9.71	21.92	4.51	0.49	0.12
50	29.579	9.16	22.89	3.90	0.41	0.05
100	30.312	8.86	23.50	3.78	0.44	0.07
150	30.612	8.55	23.78	3.51	0.45	0.08
225	30.830	8.62	23.94	3.48	0.50	0.10

CRUISE: 72/39   DATE: October 12, 1972

(a) STATION: Indian 3 LOCATION: 49° 27.3' N SONIC DEPTH: 83 m
                                  122° 52.3' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/l)	Cu(µg/l)	Pb(µg/l)
10	25.526	9.97	19.62	4.28	0.54	0.05
20	25.966	9.90	19.97	3.82	0.41	0.07
30	26.147	9.78	20.13	3.73	0.87	0.13
50	26.298	9.21	20.33	3.61	0.89	0.15

(b) STATION: Indian 2 LOCATION: 49° 23.5' N SONIC DEPTH: 220 m
                                  122° 52.3' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/l)	Cu(µg/l)	Pb(µg/l)
10	25.676	10.47	19.66	4.20	0.69	0.26
20	26.246	10.84	19.97	4.00	0.67	0.23
50	26.504	10.12	20.35	4.08	0.82	0.29
75	26.909	8.30	20.93	3.39	0.66	0.19
100	27.265	6.92	21.38	3.12	0.63	0.10
150	27.495	6.93	21.56	3.16	0.57	0.17
200	27.532	6.94	21.59	3.12	0.50	0.16

(c) STATION: Indian 1.5 LOCATION: 49° 20.9' N SONIC DEPTH: 130 m
                                    122° 54' W

Depth(m)	Sal.°/°°	T°C	σ_t	O_2(ml/l)	Cu(µg/l)	Pb(µg/l)
10	26.058	10.80	19.90	-	0.80	0.54
30	26.304	10.29	20.17	4.43	0.71	0.08
50	26.495	10.14	20.34	4.54	0.90	0.28
75	26.786	9.29	20.70	3.81	0.49	0.10
100	27.314	7.04	21.41	2.97	0.46	0.21
125	27.437	-	-	2.88	0.74	0.17

CRUISE: 72/41   DATE: October 25, 1972

(a) STATION: Burrard 4   LOCATION: 49° 18' N   SONIC DEPTH: 238 m
                                     123° 24' W

Depth(m)	Sal.°/$_{oo}$	T°C	σ_t	O_2(ml/l)	Cu(μg/l)	Pb(μg/l)
3	27.319	9.73	21.04	6.84	0.64	0.38
10	27.846	9.65	21.47	6.04	0.72	0.22
25	29.346	8.79	22.76	4.03	0.66	0.18
50	29.963	9.01	23.21	3.59	0.77	0.15
100	30.459	9.27	23.55	3.63	0.48	0.12
200	30.895	8.95	23.94	3.46	0.41	0.08