THE DISTRIBUTIONS OF DISSOLVED AND SUSPENDED
VANADIUM IN SAANICH INLET, BRITISH COLUMBIA

by

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ABSTRACT

This study investigated the distribution of dissolved and suspended vanadium in Saanich Inlet, British Columbia, and the possible effects of scavenging by hydrous manganese and iron oxides. Water samples were collected from September 1973 to July 1974 and were tested for salinity, temperature, dissolved oxygen, dissolved and suspended vanadium, suspended manganese and suspended iron.

A technique involving ion exchange to isolate vanadium followed by a catalytic colorimetric determination was developed and applied to the dissolved and suspended vanadium analyses.

The data showed that, during the fall of 1973 and again in July 1974, there were positive correlations between the suspended vanadium and suspended manganese distributions, suggesting that vanadium was being scavenged by the manganese oxides during these periods. No such correlation was found between the suspended vanadium and suspended iron distributions. The anoxic deep waters generally contained less dissolved vanadium than the oxygenated waters above sill depth. This deficiency in the deep waters may have been due to co-precipitation with ferrous sulphides or adsorption by detrital silicate or organic particles.

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INTRODUCTION

The possibility that low levels of vanadium may be bene-
ficial or essential to life has stimulated the development of
analytical techniques sensitive enough to determine vanadium in
biological materials and sea water samples. Henze (1911)
reported 42,000 ppm of vanadium in the blood of an ascidian.
The concentration of vanadium in most animals and plants is
about 0.13 ppm whereas in the tunicate marine worms it is as
high as 1.5 ppm. It has been suggested that marine muds or sea
water are the probable sources of the vanadium and that oils
containing vanadium were possibly formed from ascidians
(Vinogradov, 1934). Vanadium also has been found to be an
essential element for the green alga Scenedesmus obliquus
(Arnon and Wessel, 1953) although there is no proof that vana-
dium is an essential micronutrient in higher plants.

The few studies of vanadium in ocean waters that have
been made in recent years (Riley and Taylor, 1972; Sugawara and
Okabe, 1966; Okabe and Morinaga, 1970; Morris, 1975) indicate
that, for the most part, there are no discernible geographical
or depth related patterns in the vanadium distribution although
very minor variations in the vanadium content between water
masses may be produced by biological activity (Morris, 1975).
Krauskopf (1956) concluded that the concentration of vanadium
in the oceans was probably controlled by organic processes.
However, he noted that in oxygenated sea water, adsorption by
hydrous iron and manganese oxides could also be a controlling
factor, a view which appears to be supported by the results of

Riley and Sinhaseni (1958) and Willis and Ahrens (1961) who observed that vanadium concentrations in manganese nodules were enriched by a factor of about 2×10^5 over normal sea water concentrations. This suggested that adsorption by manganese oxides could be one of the factors controlling the vanadium distribution in Saanich Inlet, which, at various times of the year, has very high concentrations of suspended manganese (Berrang and Grill, 1974). The objective of the field work carried out in this study was to determine if there was any relationship between the distributions of vanadium and the manganese oxides in the waters of Saanich Inlet.

The analytical procedure employed in this study consists of a combination of ion exchange sorption, to isolate vanadium from interfering elements (Riley and Taylor, 1968), and a colorimetric determination based on the catalytic method of Fishman and Skougstad (1964). This method, because of its high sensitivity, requires a relatively small sample volume compared to the other previously reported studies (Chan and Riley, 1966; Muzzaralli, 1971; Chau and Chan, 1970; Crump-Wiesner and Purdy, 1966; Kiriyama and Kuroda, 1972; and Morris, 1975).

GENERAL DESCRIPTION OF STUDY AREA

Saanich Inlet is a fjord-type inlet located on the south-east coast of Vancouver Island (Figure 1). It has a length of about 25.7 km, a width which varies from 0.4 to 7.6 km, and a maximum depth of about 230 m.

Aside from direct runoff from the sides, the only source of fresh water is the Goldstream River, which discharges into the inlet at its extreme southern end. Herlingveaux (1962), who estimated this discharge at 0.85 m^3/sec, indicated the bulk of the freshwater input is derived from the Cowichan and Fraser Rivers and is introduced as a result of tidal exchanges at the entrance.

Saanich Inlet is connected to the open sea through Satellite Channel, Haro Strait, and the Strait of Juan de Fuca. However, a sill, which is located at the entrance and which rises to within about 70 m of the surface, prevents the water below this depth from being freely exchanged with that in the approaches. Thus, because of the relatively small runoff and the resulting weak estuarine flushing mechanism, the waters below sill depth are always markedly oxygen deficient. Below 150 m, where there is little or no dissolved oxygen for much of the year, hydrogen sulfide is usually present during late spring and early summer (Richards, 1965).

Then, in the late summer or fall, when the runoffs of the Cowichan and Fraser are both low (Herlingveaux, 1962), an inter-mediate water mass formed in Haro Strait by the mixing of warm, low salinity water from the Strait of Georgia with colder,

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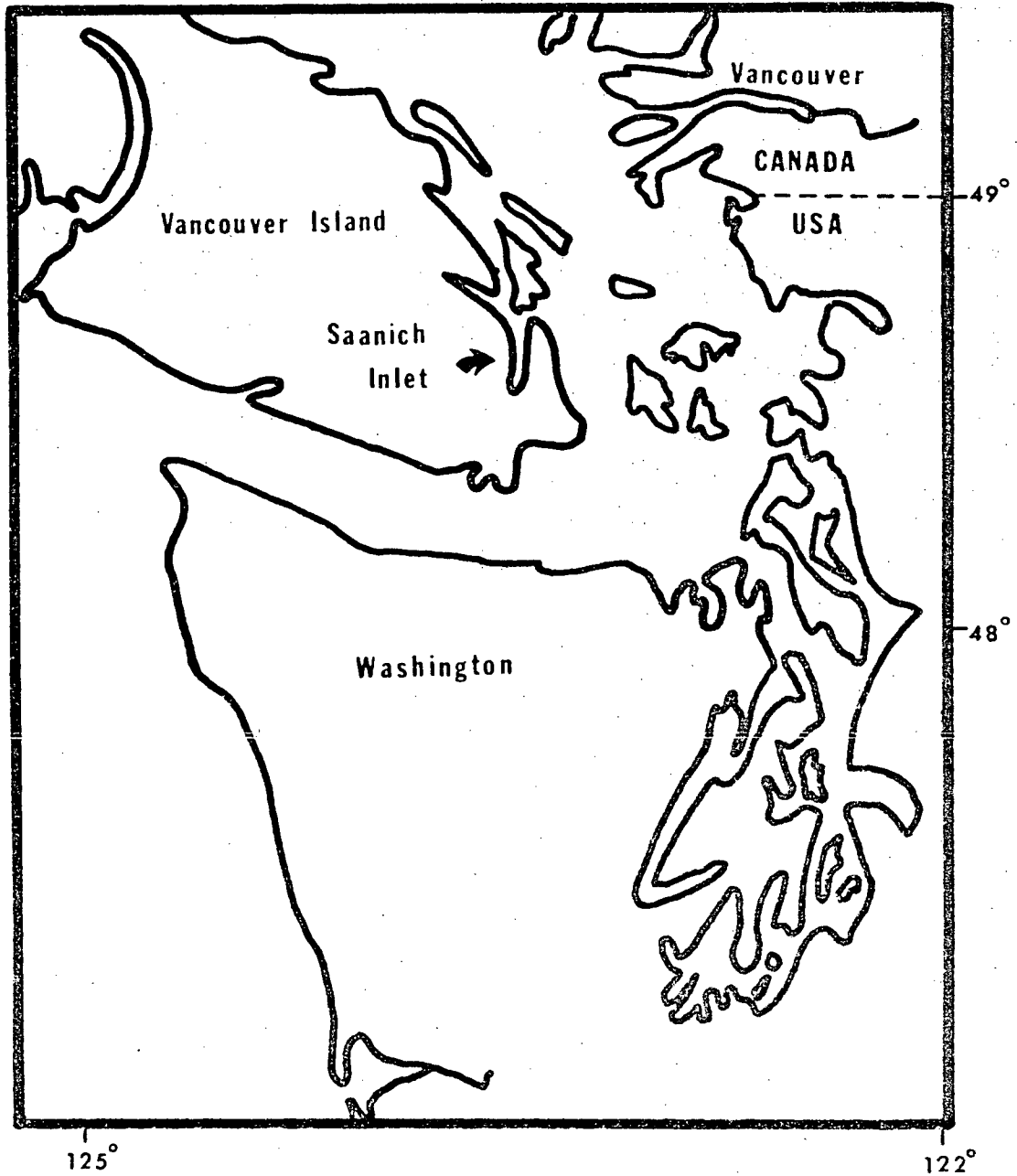
Figure 1.   Location of Saanich Inlet

higher salinity water which has upwelled off the Washington-Oregon coast (Waldichuk, 1957), penetrates the approaches to Saanich Inlet and flows over the sill into the basin, re-oxygenating the bottom water. Anderson and Devol (1973) proposed that the flushing water enters Satellite Channel at discreet time intervals and moves as boluses along the channel and into the basin on the flood tide.

SAMPLING METHODS

Water sampling was carried out at five stations in Saanich
Inlet and one in Satellite Channel (Figure 2) during a series of
five cruises between early September 1973 and late July 1974.
The positions of these stations are listed in Table I and shown
in Figure 2.

Table I

Station	Longitude	Latitude	Depth(m)
Saanich 1	123° 32' 28" W	48° 31' 55" N	190
Saanich 2	123° 30' 80" W	48° 33' 50" N	220
Saanich 3	123° 30' 00" W	48° 35' 60" N	235
Saanich 4	123° 30' 30" W	48° 38' 92" N	190
Saanich 5	123° 30' 00" W	48° 41' 13" N	105
Saanich 6	123° 27' 15" W	48° 32' 27" N	105

Table II lists the cruise dates, cruise numbers and the
stations sampled on each cruise.

Table II

Cruise Number	Date	Stations Sampled
73/35	September 5, 1973	1 & 3
73/46	November 15, 1973	3
74/1-A	January 8, 9, 10, 1973	1 to 6
74/15	April 29 - May 1, 1974	1 to 6
74/26-A	July 29, 30, 1974	1 to 6

Cruise 74/1-A was performed on the vessel C.F.A.V. "Laymore".
All other cruises were performed on the oceanographic vessel
C.S.S. "Vector".

Dissolved and suspended vanadium, suspended manganese and iron,
dissolved oxygen, temperature, and salinity were measured on all
cruises. The suspended matter was analysed only on those filter
samples showing strong manganese oxide staining. All other
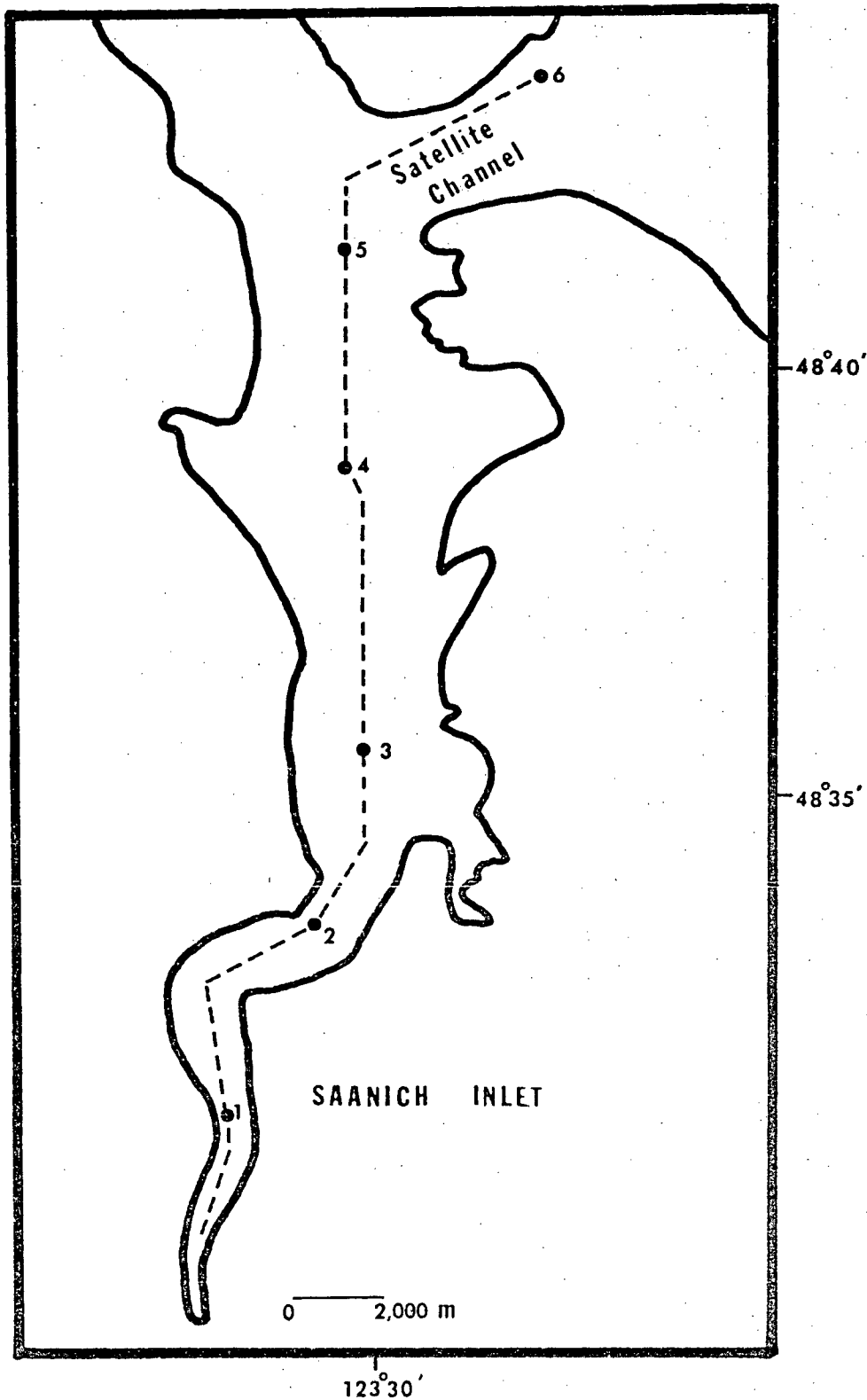
Figure 2.   Sampling Stations

tests were conducted on samples collected throughout the entire water column.

All samples, except those for suspended matter, were collected in 1 l N.I.O. sampling bottles. Aliquots were drained from the bottles for dissolved oxygen and salinity tests. The remaining water was then drained and stored in polyethylene or polypropylene containers until it could be filtered through Gelman Metricel GA-6 membrane filters with 0.45 μm pore diameter. These filters had been previously soaked in a 5% solution of KH_2PO_4 and rinsed with deionised water to leach out any metals present in the filters. The filtering was carried out under reduced pressure using a Millipore filter unit which was acid washed and thoroughly rinsed with deionised water prior to use. After filtration, the filtrate was transferred to an acid cleaned storage bottle, its pH adjusted to about 2 by the addition of 1 ml of 6 N HCl, and then it was placed in cold storage until analysis could be performed in the shore lab. Chau and Chan (1970) reported that there is no loss of vanadium from sea water stored in polyethylene or polypropylene containers at pH 2 or at the natural pH of the sample.

The suspended matter samples were prepared by filtering 10 l of sea water, collected in 5 l Niskin bottles, through membrane filters with 0.45 μm pore size under reduced pressure. These filters were then stored in plastic Petri dishes until analysed in the shore lab.

ANALYTICAL PROCEDURES

Dissolved Vanadium

Because of its low concentration (ca. 1.5 μg/l; Riley and Chester, 1971), the methods employed for determining vanadium in sea water have usually used some form of preconcentration such as coprecipitation with $Fe(OH)_3$ (Chan and Riley, 1966), coprecipitation with chitosan (Muzzarelli, 1971), solvent extraction (Chau and Chan, 1970; Crump-Wiesner and Purdy, 1966), and ion exchange (Chan and Riley, 1966; Kiriyama and Kuroda, 1972). The analysis may then be completed by colorimetric methods or by atomic absorption spectrophotometry.

In the present study, vanadium was determined by a sensitive catalytic technique which did not require a pre-concentration step. However, because of the interfering elements present in raw sea water, it was necessary to first isolate the vanadium, a step which was accomplished using a chelating ion exchange resin as described by Riley and Taylor (1968). The Chelex-100 resin (Bio-Rad Laboratories) employed for this purpose contains iminodiacetate groups on a styrene-divinyl benzene copolymer matrix.

The catalytic technique employed is a modification of that developed by Fishman and Skougstad (1964), in which vanadium is determined on the basis of its ability to increase the oxidation rate of gallic acid by acid persulfate. The extent of oxidation, which was measured colorimetrically after a reaction time of one hour, is proportional to the concentration of vanadium present.

Reagents

Ammonium Nitrate Buffer: Dilute 200 ml of 4 N ammonium hydroxide plus 100 ml of 4 N nitric acid to 2 l. Adjust the pH to 9.4.

Acid Persulfate: Dissolve 3.0 g of ammonium persulfate in 25 ml deionised water, heat to boiling, add 25 ml concentrated reagent grade phosphoric acid and let stand one day before use.

Gallic Acid: Dissolve 1.0 g of gallic acid in 50 ml deionised water, heat to boiling, filter through Whatman No. 1 filter paper and let stand 30 minutes in a 30°C water bath before using. Prepare fresh daily.

Mercuric Nitrate: Dissolve 0.035 g mercurous nitrate in 100 ml deionised water.

Stock Vanadium Solution: Prepare a 100 ppm solution using vanadium pentoxide that was ignited, dissolved in sodium hydroxide and then made slightly acidic in the manner described by Sandell (1965).

Working Vanadium Solution: Prepare a 0.10 ppm solution each week by diluting the stock vanadium solution with deionised water.

Procedure

The Chelex-100 resin (50-100 mesh) was soaked in 2 N nitric acid for 24 hours, rinsed with deionised water, poured into 1 cm diameter glass columns fitted with fritted glass discs to give a bed depth of 3 cm, and washed with deionised water until the pH of the eluate was 6. Then the pH of the sea water samples

was adjusted to 6 with dilute sodium hydroxide, and a 25 ml aliquot passed through the column at a rate not exceeding 5 ml/min. The column was then washed with 100 ml of deionised water and, finally, the vanadium eluted into a covered 100 ml beaker with 30 ml of 4 N ammonium hydroxide followed by 10 ml of deionised water.

After evaporating the eluate to dryness overnight at low heat on a hot plate, the residue in the beaker was brought back into solution by allowing it to sit for two hours in contact with 30 ml of the pH 9.4 ammonium nitrate buffer. This solution was then transferred to a measuring cylinder, made up to 35 ml with more buffer, transferred to a 60 ml polyethylene bottle and placed in a water bath at 30°C. After one hour, 1 ml of the mercuric nitrate and 1 ml of the acid persulfate solutions were added to each bottle, and the sample was mixed and returned to the water bath. Then, 1 ml of the gallic acid solution was added to successive bottles at three minute intervals, and the bottles were again mixed and returned to the water bath. Sixty minutes after the addition of the gallic acid, each of the samples was removed from the bath, filtered through a Whatman No. 42 filter paper, and its absorbance measured at 415 nm in a 10 cm cuvet with a Beckman Model DU spectrophotometer.

Six solutions containing known amounts of vanadium were also prepared each day and treated as above. These standards were prepared by first passing sea water through a resin column to remove any vanadium, and then adding from 0.00 to 0.08 µg of vanadium to 25 ml aliquots. The vanadium concentration of the

sea water samples being analysed was then determined by reference to the calibration curve derived from processing these standards.

Discussion

The calibration curves were linear up to a vanadium content of 0.08 µg in a final solution volume of about 30 ml. However, because the slope of the calibration curve and the absorbance of the reagent blank increased markedly with the strength of the ammonium nitrate buffer, a new calibration curve was made for each batch of samples analysed. Due to the non-catalysed oxidation of gallic acid, the absorbance of the standard containing no added vanadium (i.e. the reagent blank) was always appreciable (Figure 3).

Eight replicates of a sea water sample were analysed to determine the precision of the method. The results are shown in Table III.

Table III

Sample Number	ppb V found
1	0.64
2	1.60
3	0.64
4	0.64
5	0.64
6	0.80
7	0.80
8	0.80

Rejecting the result for sample number 2 (Laitinen, 1960; pp. 574), the relative standard deviation of the analyses at a mean concentration level of 0.71 µg/l is 7.9%.

The recovery of V from sea water, using the chelex 100 resin, as recommended by Riley and Taylor (1968), was found to be slightly low. The per cent recovery was determined by taking sea water that had previously been stripped by passage through the resin and then, after spiking it with varying amounts of vanadium (as in the case of the calibration series), analysing the samples by the standard procedure. The slope of the resulting absorbance vs concentration curve was then compared to that obtained using samples of ammonium nitrate that had been spiked with identical amounts of vanadium, but which were not passed through the resin.

When the vanadium was eluted from the resin with 20 ml of 2 N ammonium hydroxide, as recommended by Riley and Taylor (1968), the ratio of the slopes of the curves obtained using spiked sea water to those obtained using the spiked ammonium nitrate solutions ranged from 0.5 to 0.6, indicating 50 to 60% recoveries. Increasing the depth of the resin bed to 6 cm did not significantly improve the recovery, although doing so increased the time required for the separation step by about 50% because of the decreased flow rate. The bulk of the vanadium was recovered in the first 10 ml of eluate, suggesting that the remainder was being retained by the column, a supposition consistent with the fact that the recovery was improved by eluting with 30 ml of the 4 N ammonium hydroxide and then rinsing with 10 ml of deionised water. Using this latter procedure, the recoveries averaged over 90%.

To determine the stage at which the remaining recovery losses were occurring, three standard calibration series were

run. In the first, sea water that had been passed through the resin column was spiked with vanadium, and then the samples were analysed as described in the standard procedure. In the second, 4 N ammonium hydroxide that had been passed through the resin column was spiked with vanadium and then the analyses were completed as described in the standard procedure following the elution step. In the third, ammonium nitrate buffer was spiked with vanadium and then the samples were analysed applying only those steps pertaining to the colorimetric test.

The results (Figure 3) showed that the slopes of the absorbance vs concentration curves of the first and second series were essentially the same; the slope derived from the third series, however, was somewhat higher, implying that the incomplete recoveries were due either to interferents leached from the resin column, evaporation losses, or incomplete re-solution of the vanadium by the ammonium nitrate buffer.

Attempts to destroy interfering organic substances by boiling the column eluate with concentrated nitric acid had little apparent effect on the recovery. Moreover, as standards made up in ammonium hydroxide which had been passed through the resin gave calibration slopes essentially the same as those using ammonium hydroxide solutions which had not been passed through the resin, the loss does not appear to be due to any organic interferent leached from the resin. Since the solutions were evaporated on low heat over approximately an eighteen hour period, and were all well covered, any loss due to spattering during evaporation should have been minimal. Increasing the re-solution time of the evaporation residue to two hours, however,
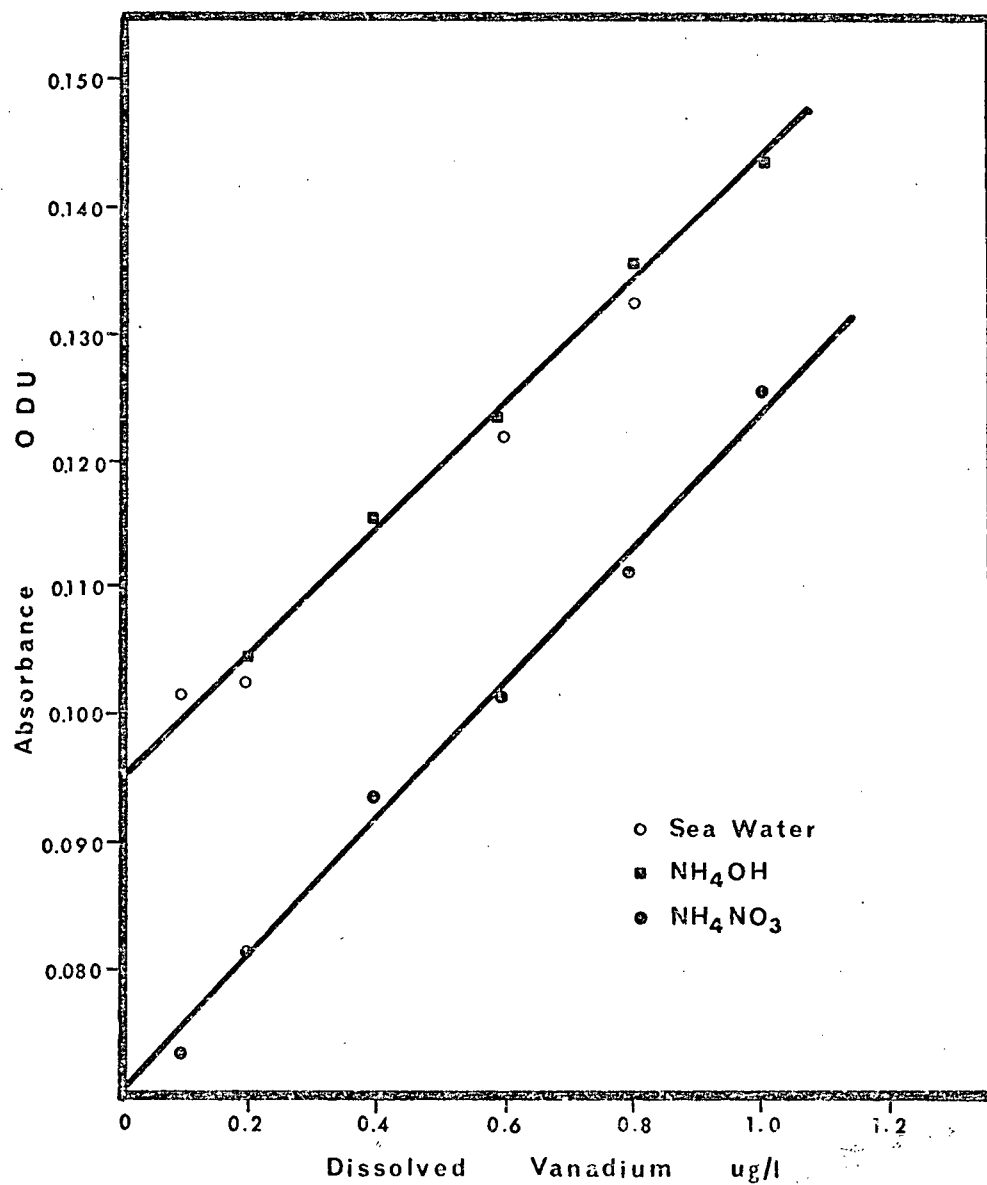
Figure 3.   Recovery curves for dissolved vanadium.
Concentrations based on 35 ml sample
size.

increased the recoveries somewhat. Thus it appears that there
are small losses due to incomplete elution and re-solution.

In addition, there may be apparent losses due to ionic
interferents present in the sample. The various ions which
interfere with the catalytic procedure, and their limiting con-
centrations, as given by Fishman and Skougstad (1964), are
listed in Table IV.

Table IV

Element	Limiting conc. (ppb)	Conc. in sea water (ppb)[1]
Ag	2,000	0.04
U(VI)	3,000	3.00
Co(II)	1,000	0.10
Ni(II)	3,000	2.00
Cu(II)	50	3.00
Mo(VI)	100	10.00
Fe(II)	300	) 10.00
Fe(III)	500	)
Cr(VI)	1,000	0.05
Cl	100,000	19,000,000.00
Br	100	65,000.00
I	1	60.00

(1) Riley and Chester (1971)

It is evident that, with the exception of the halides, few
of these ions are present in sea water in high enough concentra-
tion to interfere. Riley and Taylor (1968a) report that most
metal ions, except for V(V), Mo(VI), Re(VII) and W(VI), will be
retained on the resin and will not be eluted with ammonium
hydroxide.

The halides, since they are not adsorbed by the resin, are
for the most part, washed off with the 100 ml water rinse.
Moreover, some halides can be tolerated in the final reaction
mixture where they are complexed by adding the mercuric nitrate

solution, which itself does not interfere at the concentrations employed. The mercuric nitrate reportedly allows determinations of vanadium in the presence of 100 ppm of chloride and 0.25 ppm of bromide and iodide (Fishman and Skougstad, 1964). Welch and Allaway (1972) found a slight positive error in the determination of vanadium in the presence of molybdenum; however, in sea water, where the concentration of Mo is about 10 $\mu g/l$, this error should not be greater than about 1.5%.

The major cations in sea water (Na^+, K^+, Ca^{2+} and Mg^{2+}) do not interfere even at concentrations above 500 $\mu g/l$. And, as these are largely washed off the resin with the chloride, only trace amounts should be eluted with the 4N ammonium hydroxide.

Dissolved vanadium in oxygenated natural waters should occur mainly in the penta-valent state (Chau and Chan, 1970). However, under reducing conditions, such as those which sometimes exist in Saanich Inlet, the tetra- and tri-valent states may also be present. In order to test the retention efficiency of the resin for these lower oxidation states, 25 ml aliquots of a 3% NaCl solution, which was used to simulate sea water, were spiked with 0.05 μg of vanadium and boiled for one hour with 1 ml of a 6% sodium sulfite solution made up in 2% sulfuric acid. The samples were then adjusted to a volume of 25 ml and a pH of 6, passed through the resin and then analysed in the normal manner. A group of four samples was tested along with solutions which had not been treated with the reducing solution. The results showed that the recovery from the reduced solutions, on average, was 12% lower than that from the untreated solutions. Thus, the vanadium recovery from Saanich Inlet waters

exposed to reducing conditions might be somewhat low, although re-oxidation during storage may have reduced this error.

Because of the sensitivity of the analytical technique, only 25 ml samples of sea water need be used. This contrasts greatly with the large volumes (3 to 7 l) employed by Riley and Taylor (1968b, 1972) or Riley and Chan (1965). This smaller sample size reduces the amount of space required for storage and the time required for the filtration and ion exchange steps.

Suspended Matter Samples

The suspended matter samples were prepared for analysis by transferring the filters to 100 ml beakers and boiling for ten minutes with 10 ml of 2 N HCl. After cooling, the resulting solutions were transferred to 25 ml measuring cylinders and diluted to 20 ml with deionised water. According to Müller (1967) such treatment should dissolve any amorphous or crystal-line manganese or iron oxides but have relatively little effect on silicate minerals.

Suspended Vanadium

A 10 ml aliquot of the acid leach of the suspended matter was adjusted to pH 6 with dilute NaOH, filtered through Whatman No. 42 filter paper, and then analysed by the same procedure as that given for dissolved vanadium.

Suspended Iron

A 2 ml aliquot of the acid leach was treated in a manner similar to that described by Sandell (1965) by adding 2 ml of a

10% hydroxylammine-hydrochloride solution, 6 ml of a sodium
acetate - HCl buffer (prepared from 50 ml of 75% sodium acetate
plus 10 ml of concentrated HCl), and 1 ml of a 0.3% solution of
ortho-phenanthroline in 4% HCl. The pH of the solution was
adjusted to a value between 3 and 6 and the volume made up to
50 ml with deionised water. After allowing 24 hours for colour
development, the absorbance was measured at 513 nm using a
Beckman Model DU Spectrophotometer and a 10 cm cuvet. Calibra-
tion curves were prepared by adding known amounts of a standard
iron solution to deionised water, adding the reagents and diluting
to 50 ml. The curves were linear and had a slope whose mean
value was 24.93 μg Fe per unit absorbance.

Suspended Manganese

The suspended manganese concentration was measured on the
remaining sample volume by aspirating it directly into an air-
acetylene flame of a Techtron Model IV Atomic Absorption Spec-
trophotometer and measuring the absorbance at 2795 Å. Calibra-
tion curves were prepared by using HCl solutions containing 0.0
to 4.0 ppm manganese.

Dissolved Oxygen

The dissolved oxygen content was determined on ship by the
standard Winkler Titration (Strickland and Parsons, 1968), using
the modified reagents of Carrit and Carpenter (1966).

RESULTS

All experimental results are listed in the data tables in the appendix. The dissolved vanadium concentrations observed in Saanich Inlet ranged between 0.53 and 3.25 μg/l. The changes in the vertical distribution of dissolved vanadium observed at station 3 between September 1973 and July 1974 are shown in Figure 4.

At the surface, the concentrations were greater than 2.3 μg/l except in July when they dropped below 1.0 μg/l. Then, below the surface, they tended to increase with depth towards a concentration maximum which was located between the depths of 50 and 80 m throughout the entire study period. From November to April, the values at this maximum were above 2.6 μg/l, but in July they fell below 2.4 μg/l. Below this maximum, the concentrations in November decreased continuously with depth; however, from January to July, after passing through a minimum between 80 and 120 m, they again increased to a secondary maximum located at about 140 m. Values at this deeper maximum ranged above 2.5 μg/l in January and May to 2.23 μg/l in July.

Below 160 m concentrations were invariably below 2.0 μg/l except in January. Moreover, in November and April, they decreased in value continuously with depth. In July, after passing through a minimum of 1.0 μg/l at 175 m, they again increased to about 1.5 μg/l at the bottom.

Although the pattern was irregular, the dissolved vanadium concentration maximum observed at station 3 between 50 and 80 m seemed, as shown in Figures 5, 6 and 7, to extend the length of

Figure 4.   Distribution of dissolved vanadium (µg/l)
             at Station 3. Dots represent sampling
             points.

Figure 5.   Distribution of dissolved vanadium (µg/l)
             during January 1974. Dots represent
             sampling points.

Figure 6.   Distribution of dissolved vanadium (µg/l) during April 1974. Dots represent sampling points.
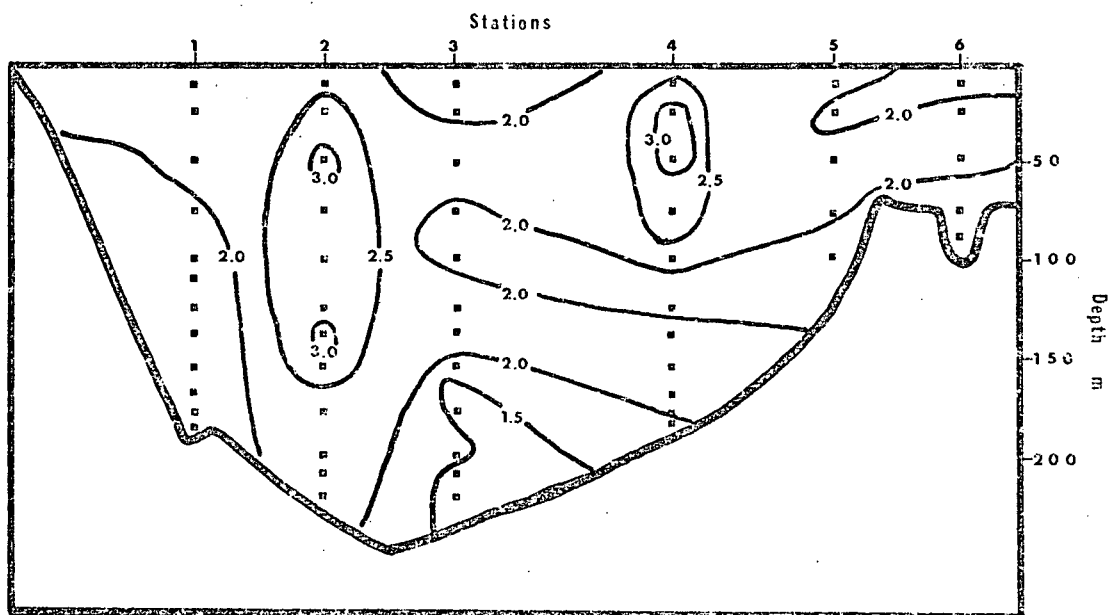
Figure 7.   Distribution of dissolved vanadium (µg/l) during July 1974. Dots represent sampling points

the inlet in January, April, and July. Furthermore, the

deeper maximum, found between 140 and 160 m at station 3 seemed

to also occur at stations 1 to 4 during these three cruises.

In January (Figure 5) and April (Figure 6) the highest values

at this deeper maximum were found at station 3, while in July

they were found at station 2 (Figure 7).

The increase in the vanadium content observed in the deep

waters below 160 m at station 3 in January was largely restric-

ted to that single station, with values decreasing towards both

the head and the entrance. By contrast, in April, the concen-

trations decreased from the head to the entrance, while in July,

the highest values were found at stations 2 and 4. In July, the

general concentration level in the deep waters was much higher

than in April.

Suspended vanadium concentrations ranged from below

detection limits up to 500 ng/l. Figure 8 shows how the values

below 75 m varied throughout the study period at station 3. In

September, between 140 and 155 m, and in November, below 140 m,

suspended vanadium values were above 100 ng/l. However, these

values were short lived, as they had given way to ones less than

30 ng/l by January. Since values at station 1 in September were

less than 20 ng/l, it appears that these high values were

characteristic mainly of station 3, although a value of 84 ng/l

was observed in a sample taken from the bottom waters at

station 2.

From January to July the vertical distribution at station

3 exhibited a distinct layering. In the uppermost layer, which

was found above 90 m, values exceeded 20 ng/l. Then, below this,

there were successive layers in which the concentrations first
dropped to values less than 20 ng/l and then rose to greater
than 25 ng/l. Finally, in the bottom waters the concentrations
again decreased to values less than 20 ng/l.

Figure 9, which shows the longitudinal distribution of
suspended vanadium in January, indicates that the layering
evident in the temporal distribution at station 3 tended, with
various modifications, to extend throughout the length of the
inlet. That is, the concentration minimum observed at about
175 m at station 3, although rising to shallower depths at
stations 1 and 4, appears to be a continuous feature, and the
underlying concentration maximum, although located at or just
above the bottom, at station 2, appears to also extend from
head to entrance.

In April and July (Figures 10 and 11), when concentrations
generally decreased towards the entrance, a similar layering
pattern was again evident. In April, there was a layer with
values below 10 ng/l stretching between stations 2 and 4 above
125 m, and below this, a layer with values exceeding 20 ng/l
centred roughly between 120 m at station 1 and 195 m at station
4. Then, in July, there was a distinct layer in which concentra-
tions exceeded 40 ng/l centred between 120 m at staion 1 and
140 m at station 4.

The suspended manganese values ranged from 0.5 µg to
50 µg/l. The temporal variations at station 3 are shown in
Figure 12. While the concentrations above 140 m remained fairly
constant with time, below 140 m they at first decreased, and
then following January, began to increase. From September to
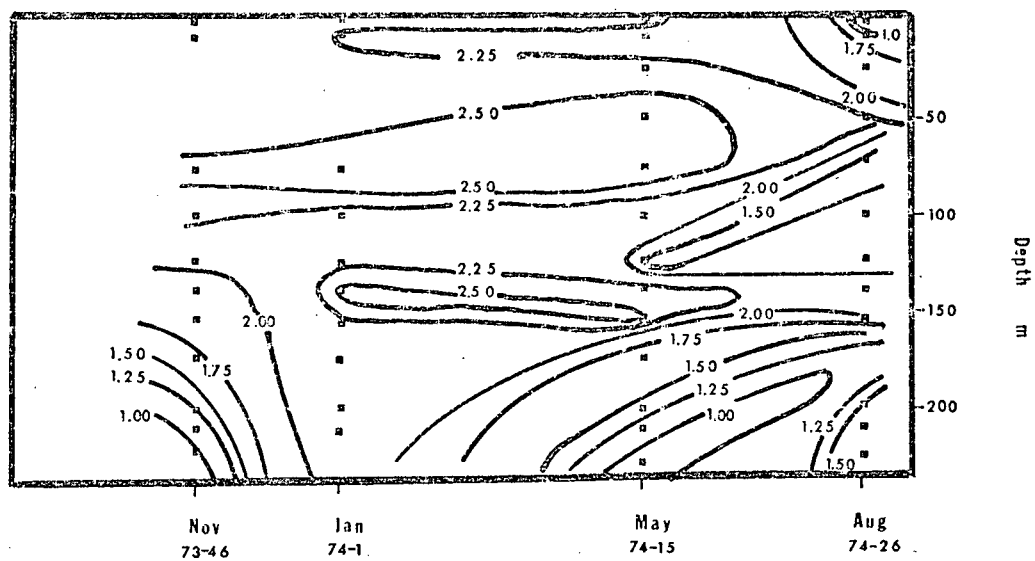
Figure 8.   Distribution of suspended vanadium (ng/l)
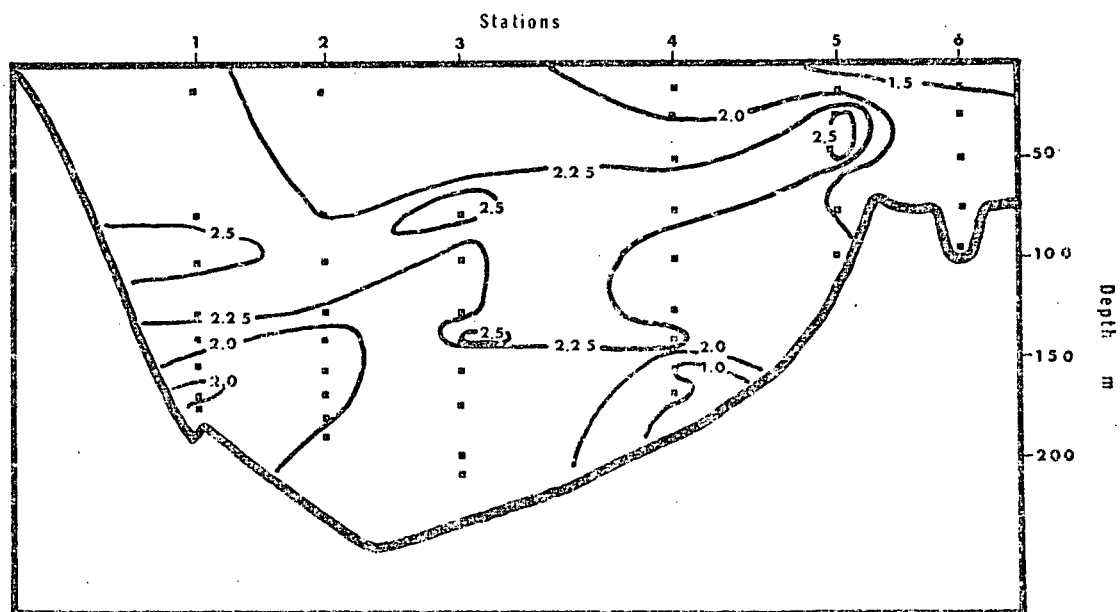at Station 3. Dots represent sampling
points.

Figure 9.   Distribution of suspended vanadium (ng/l)
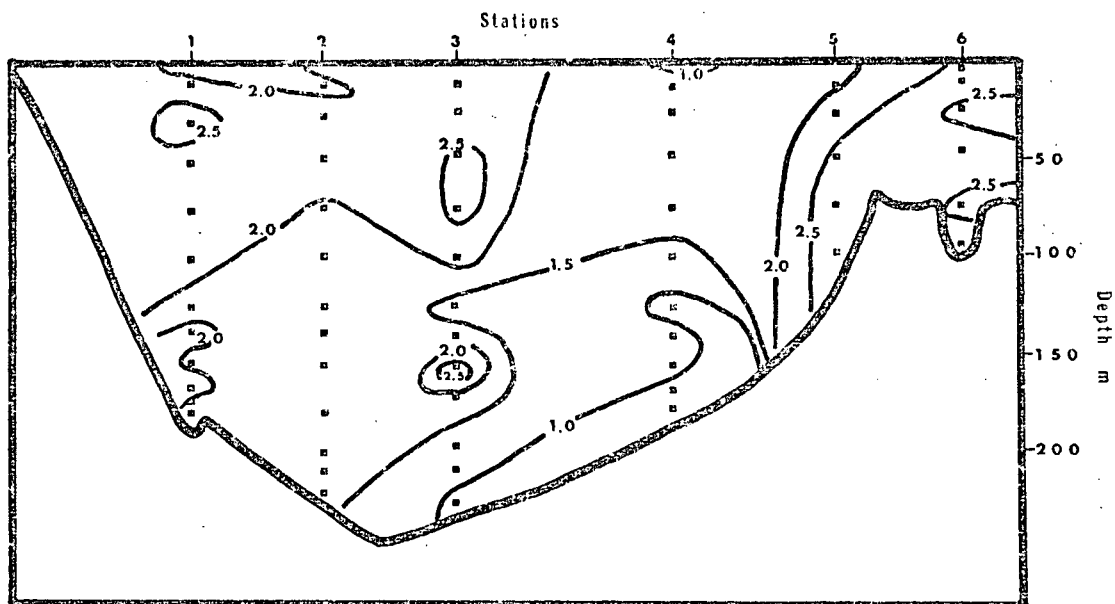during January 1974. Dots represent
sampling points.

Figure 10.   Distribution of suspended vanadium (ng/l)
during April 1974. Dots represent sampling
points.

Figure 11.   Distribution of suspended vanadium (ng/l)
during July 1974. Dots represent sampling
points.

January, when the deep water values were decreasing with time, they also increased continuously with depth. By contrast, in April and July, as the concentration levels increased with time, there was an inversion below which values were less than 2 μg/l.

In January (Figure 13) the suspended manganese concentrations increased with depth at all four stations. However, in April there was a mid-depth layer with values above 10 μg/l stretching between 160 m at station 1 and 180 m at station 4 (Figure 14). A similar mid-depth maximum was again evident in July as a layer containing values greater than 10 μg/l stretching from about 120 m at station 1 to about 150 m at station 4 (Figure 15). In April, the highest values at this mid-depth maximum were found at station 3, while in July, the highest values were found at the head.

Suspended iron values ranged between 2.9 and 29.4 μg/l. As illustrated by Figure 16, the highest concentrations at station 3, except in September, occurred between 75 and 100 m, and then, below this, the values generally decreased with increasing depth. Concentrations exceeding 20 μg/l were found only in November and January, the same time period when the values observed in the bottom waters reached their lowest levels. The longitudinal distribution observed in January (Figure 17) illustrates the fact that suspended iron values normally not only decreased with increasing depth, at least below 75 m, but that they also tended to decrease with increasing distance from the entrance of the inlet.

The temporal changes in the distributions of temperature,
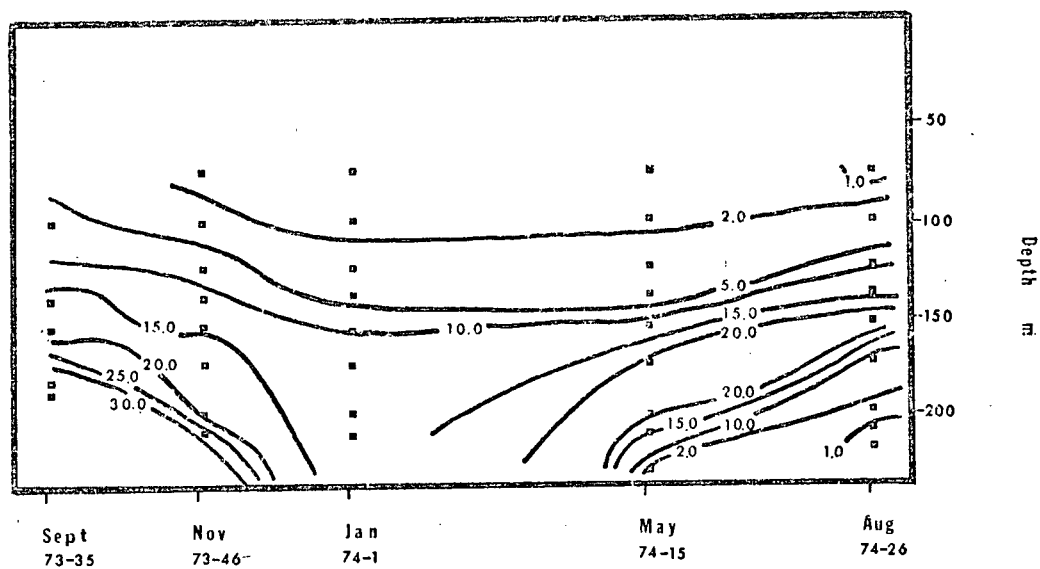
Figure 12.   Distribution of suspended manganese (µg/l)
at Station 3.   Dots represent sampling
points.
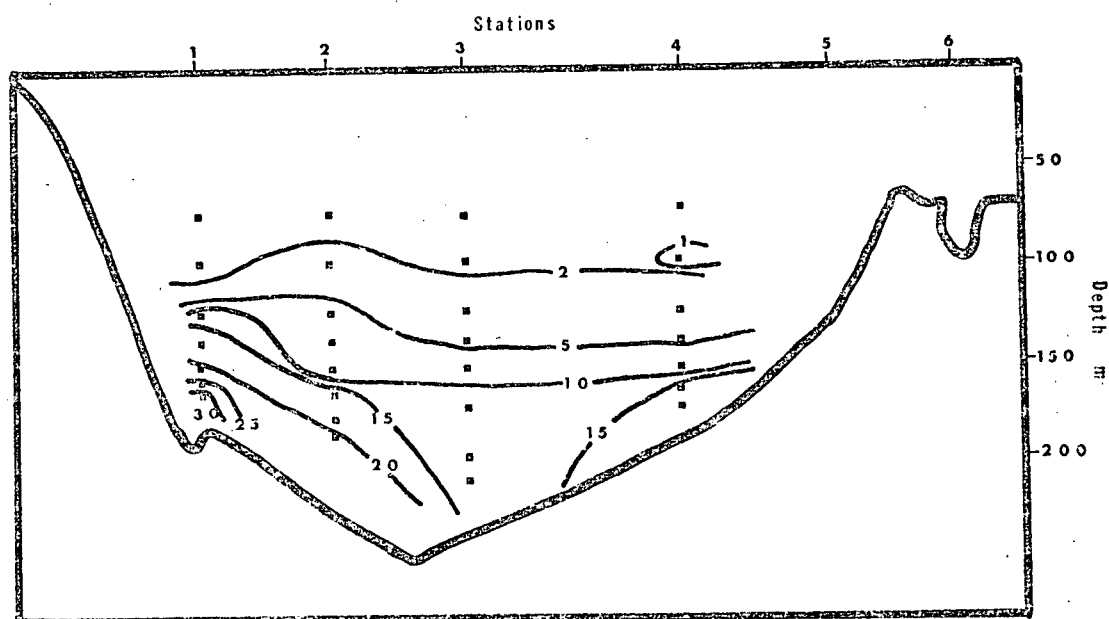
Figure 13.   Distribution of suspended manganese (µg/l)
during January 1974.   Dots represent
sampling points.
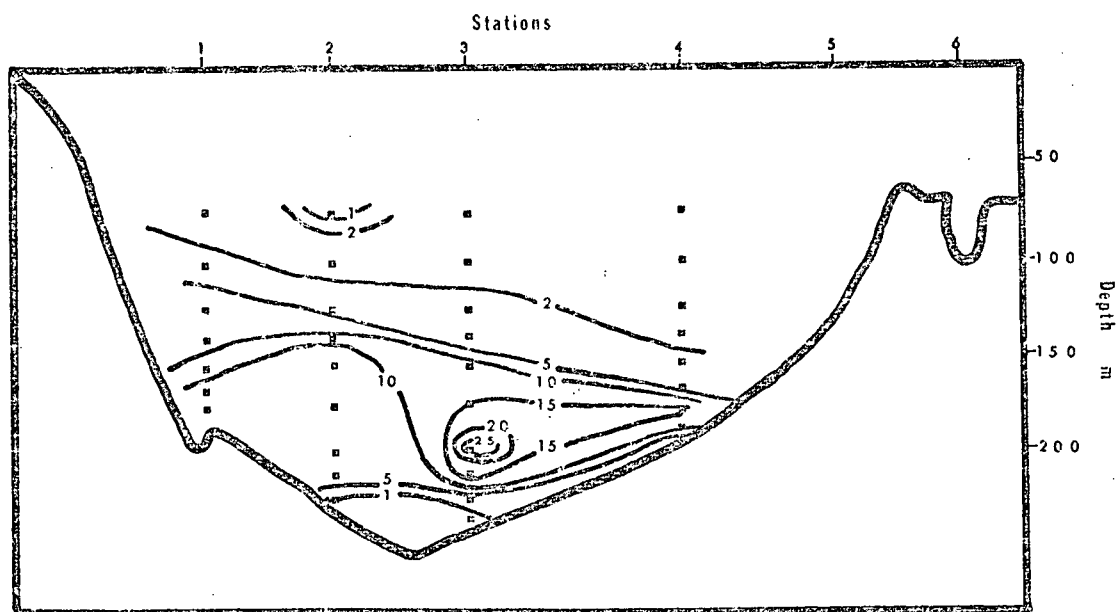
Figure 14.   Distribution of suspended manganese (μg/l)
              during April 1974. Dots represent sampling
              points.
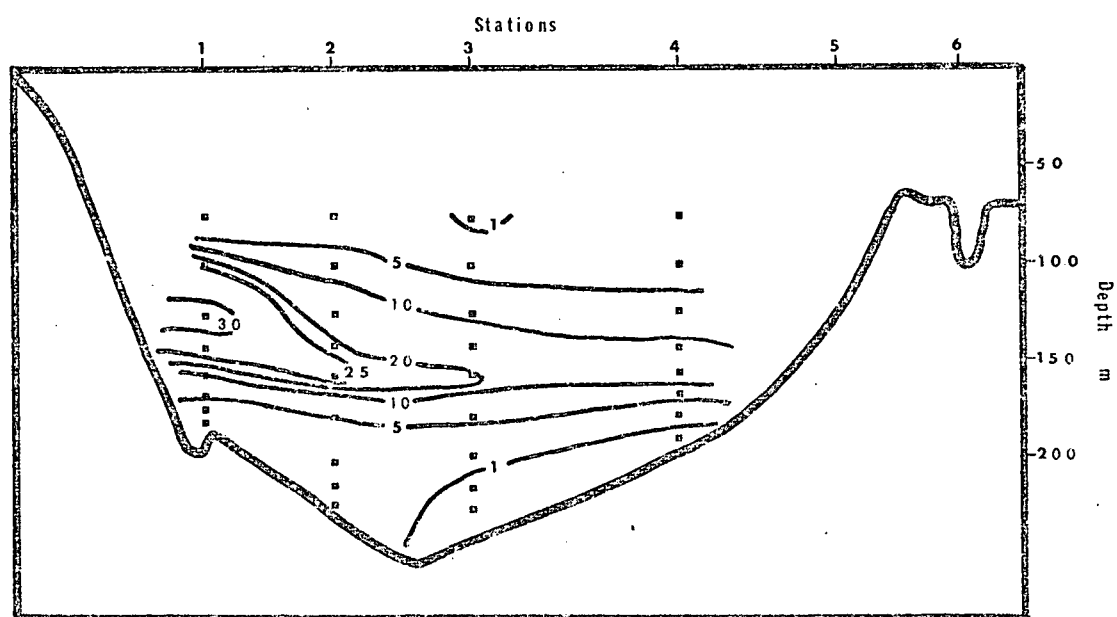
Figure 15.   Distribution of suspended manganese (μg/l)
              during July 1974. Dots represent sampling
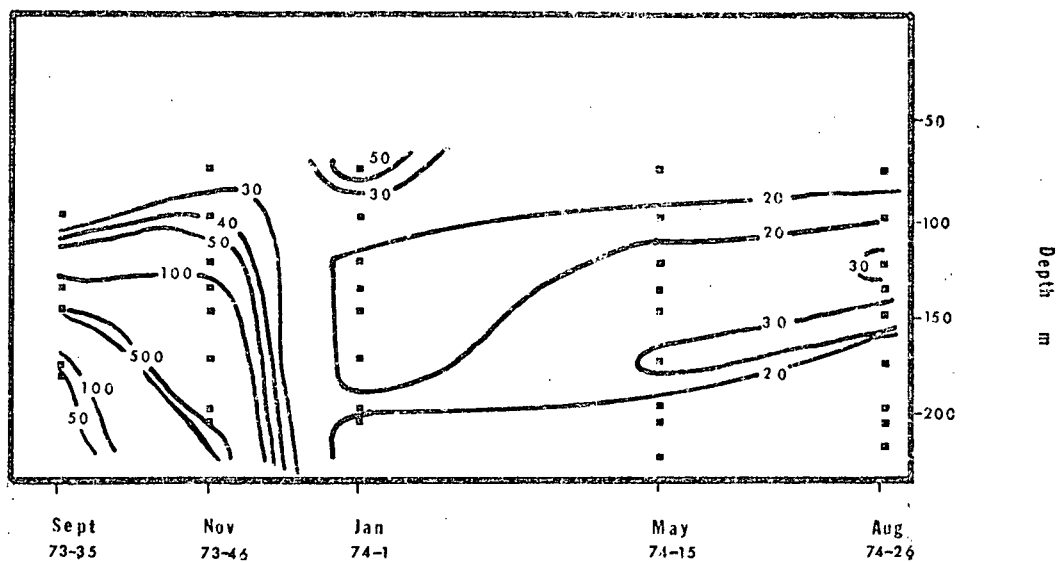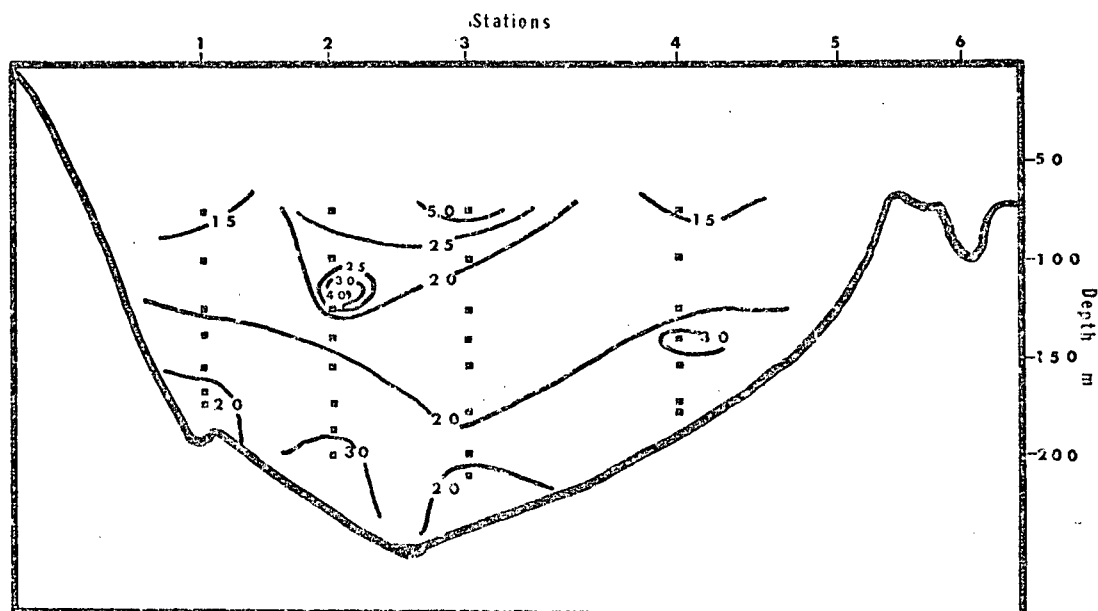   points.
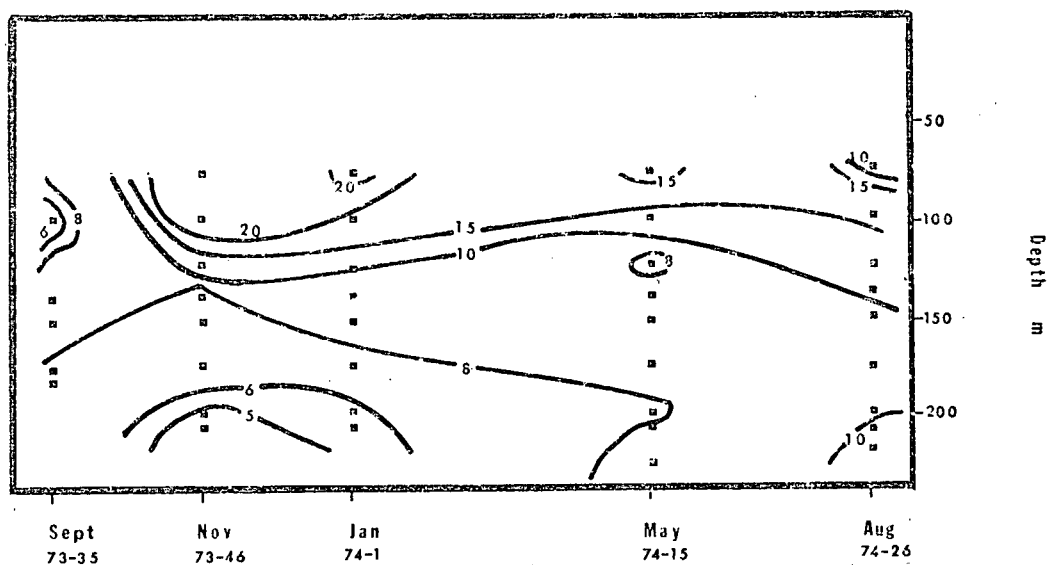
Figure 16.   Distribution of suspended iron (µg/l) at
              Station 3.   Dots represent sampling points.
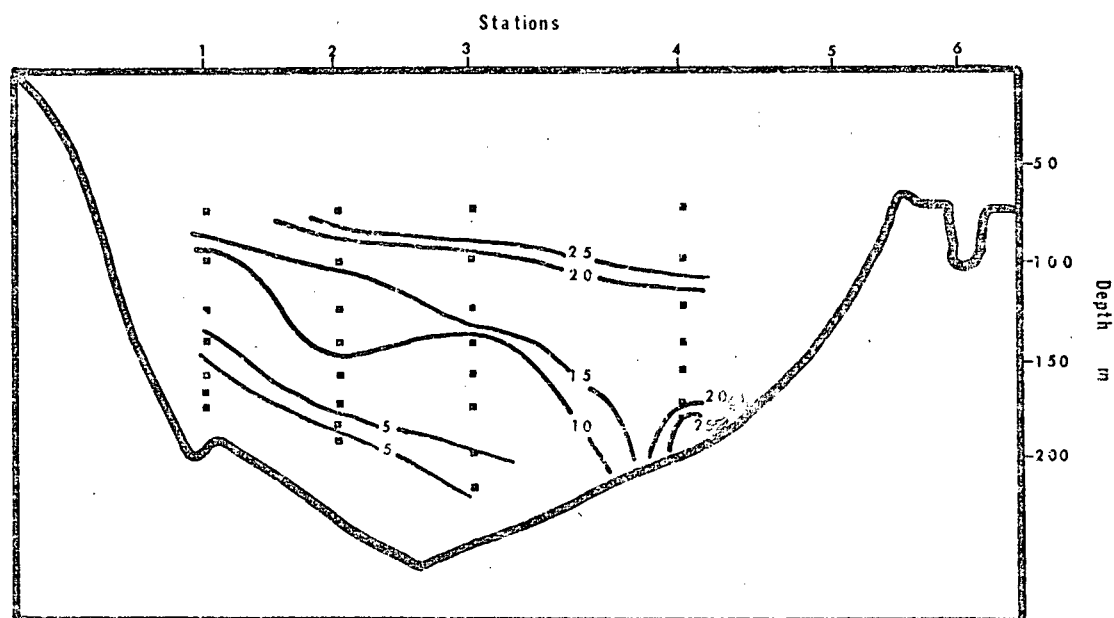
Figure 17.   Distribution of suspended iron (µg/l)
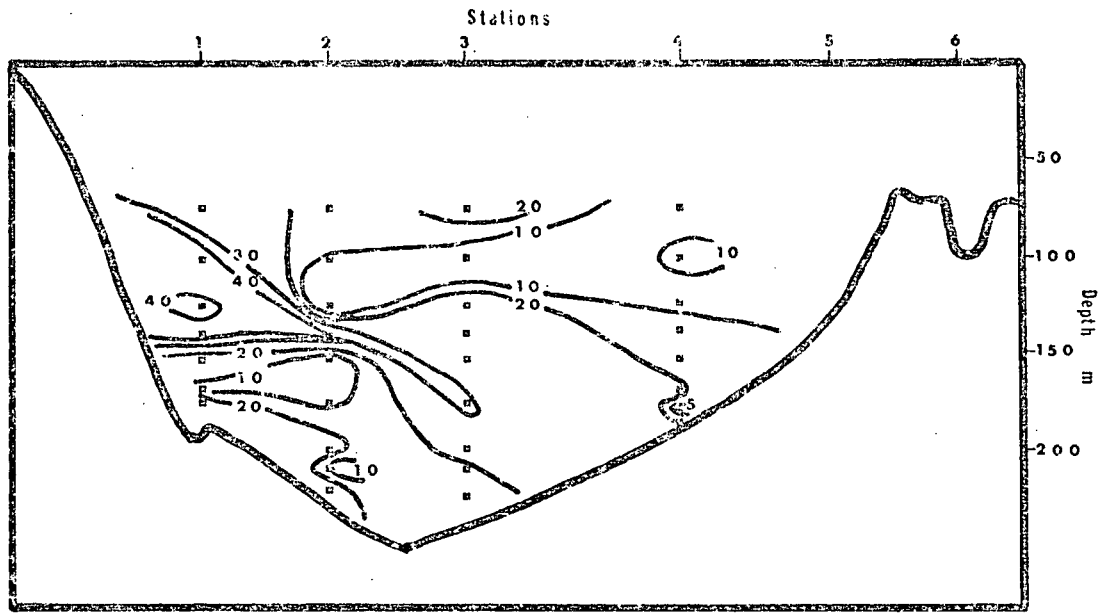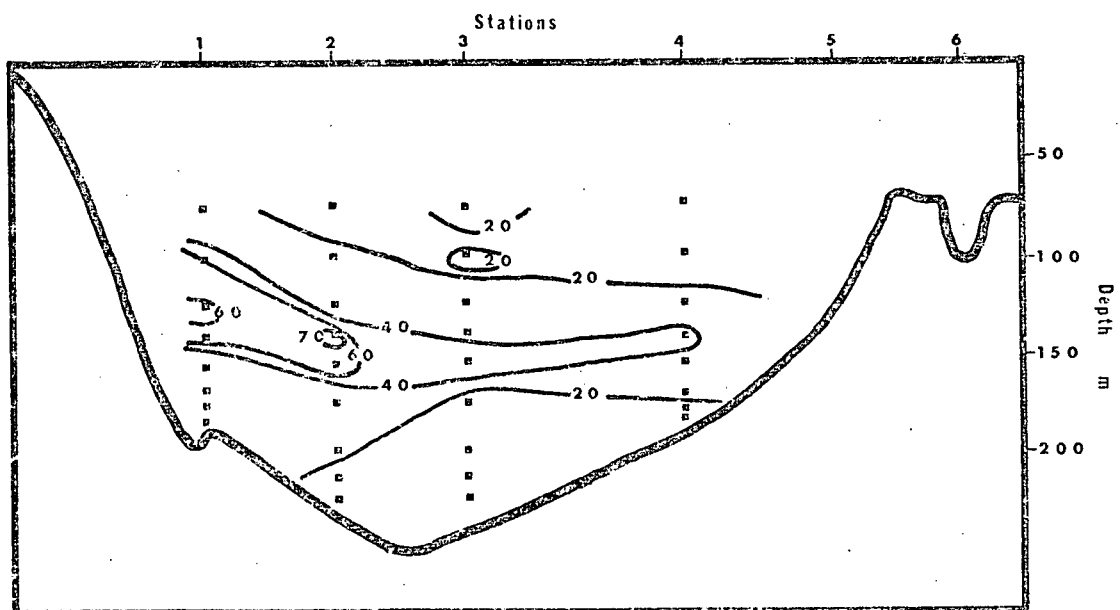   during January 1974.   Dots represent
              sampling points.

salinity and density observed at station 3 are shown in Figures 18, 19 and 20. At the surface, the density increased as the temperature decreased between September and January, and then it decreased as the temperature subsequently increased between January and July. In the deep waters, the temperature remained relatively constant at about 9°C. The density, however, increased with increasing salinity, between September and November, and then decreased when the salinity subsequently decreased from November to July, except in the bottom water sample in July when there was a marked drop in temperature and a corresponding rise in density.

The dissolved oxygen values generally decreased with increasing depth, ranging from 11.2 ml/l at the surface in November to 0.02 ml/l in the bottom waters in April. As illustrated by the temporal changes observed at station 3 (Figure 21), below 120 m the values were generally less than 0.5 ml/l. However, between November and January, when there were also increases in the salinity and density in the bottom waters, values greater than 0.5 ml/l were observed between 170 and 190 m. Above sill depth, the concentrations, excluding the surface samples, tended to increase from November to April and then decrease to July. However, from 125 to 175 m the opposite trend was observed. Between 175 and 200 m the concentrations decreased continuously from November to July, but below 200 m there was a slight increase from April to July.

The odour of hydrogen sulfide was detectable in a few samples taken near the sediment surface. The most noticeable was the sample taken from 220 m at station 2 in July.
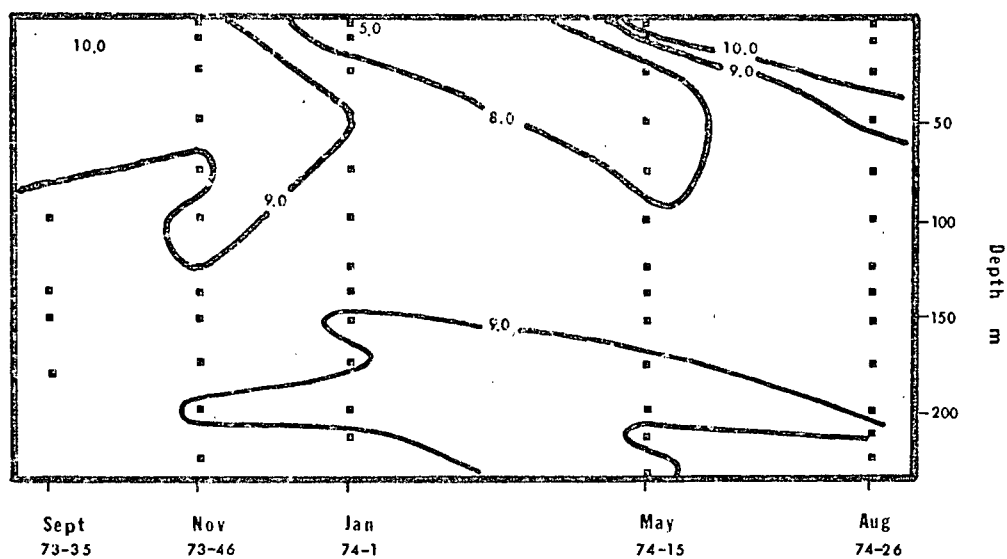
Figure 18.   Distribution of temperature (°C) at
Station 3. Dots represent sampling
points.
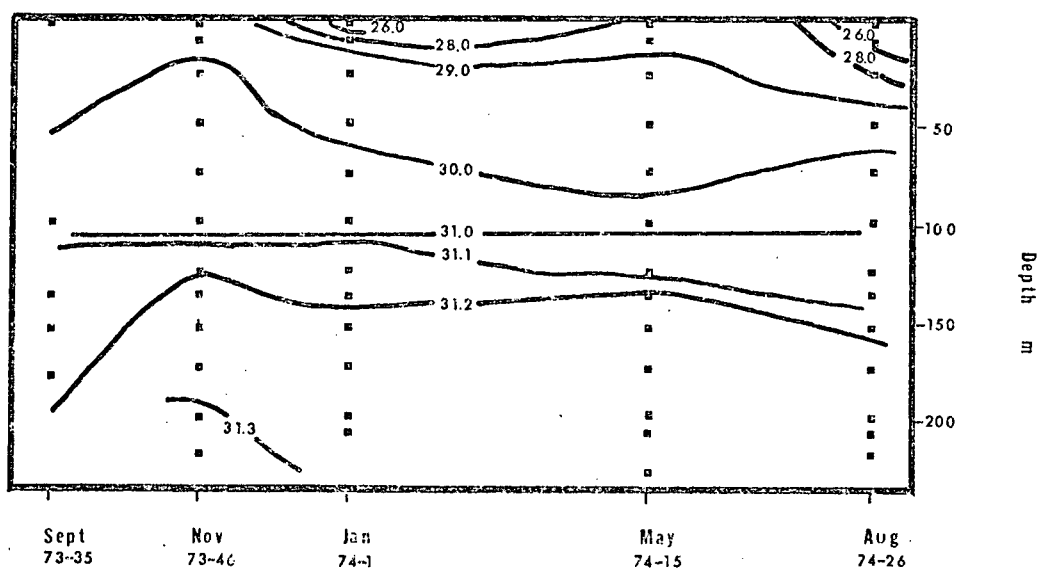
Figure 19.   Distribution of salinity (S‰) at
Station 3. Dots represent sampling
points.
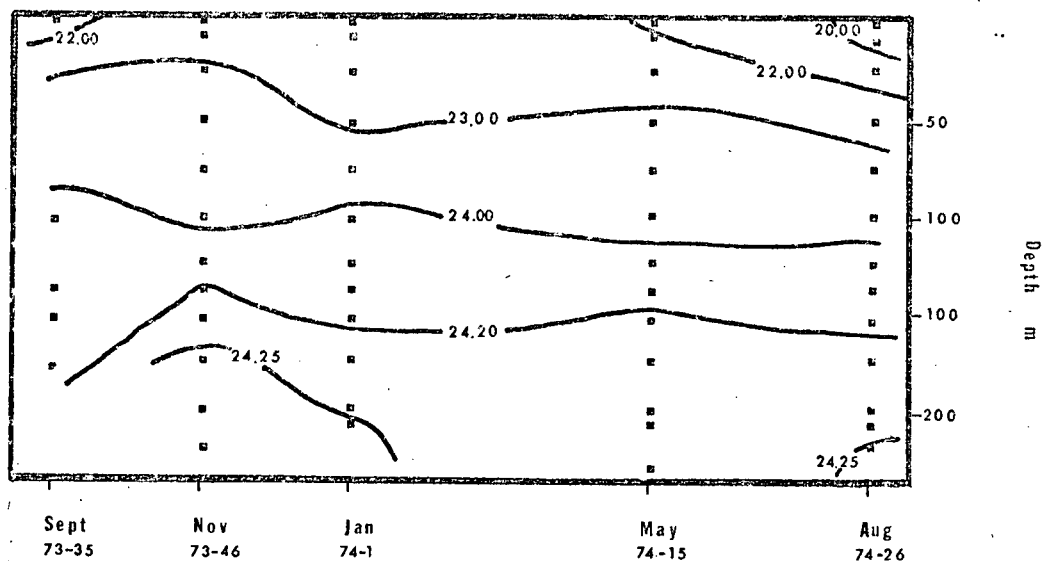
Figure 20. Distribution of density (σ_t) at Station 3. Dots represent sampling points.
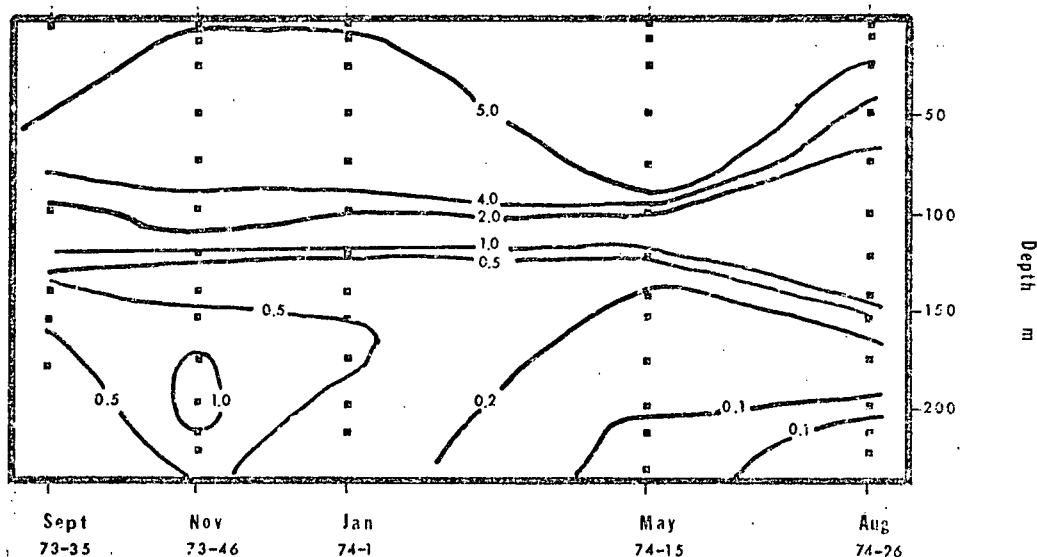
Figure 21. Distribution of dissolved oxygen (ml/l) at Station 3. Dots represent sampling points.

The data tables in the appendix indicate that in January the oxygen content decreased continuously with depth to about 155 m throughout the inlet. Below this, the concentrations increased slightly at stations 2, 3 and 4. However, at station 1, the values remained constant below 125 m. In April and July, they again tended to decrease with depth at all stations except for slight increases observed in the deep waters at stations 1 and 4 in April and at station 3 in July.

DISCUSSION

Table V compares the dissolved vanadium values observed in
Saanich Inlet with those reported in other recent studies on
sea water. It would appear that the values found in Saanich
Inlet are typical of normal sea water.

Table V

Dissolved Vanadium Concentration µg/l	Location	Authors
0.53 - 3.25	Saanich Inlet	This study
0.05 - 6.4	North-east Atlantic	Riley and Taylor (1972)
1.67	East China Sea	Kiriyama and Kuroda (1974)
0.83 - 1.57	North-east Atlantic	Morris (1975)
1.5 - 2.5	Eastern Indian Ocean	Sugawara and Okabe (1970)
0.95 - 2.36	Western Pacific	Okabe and Morinaga (1970)

Krauskopf (1956) lists the enrichment factor of vanadium
for brown algae, as determined by Black and Mitchell (1952), as
between 10 and 300, and the average enrichment factor for nine
marine mammals, as determined by Noddack and Noddack (1939), as
being 280,000. However, as these values were calculated using a
vanadium concentration which is about ten times lower than that
currently reported as the average concentration in sea water,
these values evidently should be reduced by roughly a factor of
ten. Brooks and Rumsby (1965) report the enrichment factors for
scallops, oysters, and mussels as 4,500, 1,500 and 2,500 res-
pectively. Hence, uptake by living organisms is a potential
factor removing vanadium from the surface and the weakly oxy-

genated waters found below sill depth.

As the organisms die and their remains sink towards the bottom, some of the vanadium consumed may be released as a result of decay, but some may be removed permanently if this detrital material becomes part of the sediment. In studies of Black Sea sediments, Ostroumov and Volkov (1957) found the highest vanadium concentrations in the ancient sediments which have a very high organic carbon content, while Volkov and Fomina (1974) found that vanadium co-varied directly with organic carbon. The highest values of organic carbon in Saanich Inlet are in the fine grained black sediment of the deep central basin (Gucluer and Gross, 1964); however, Gross (1967), in a study of minor elements in Saanich Inlet, found higher vanadium values near the sill than in the central basin. Thus, lithogenous rather than biogenous matter appears to be the primary source of vanadium in Saanich Inlet sediment.

Figure 5 indicates that the dissolved vanadium concentrations generally decreased both above and below the sill depth. On plotting the dissolved vanadium values, $[V]^d$, for samples taken, in this case, between 10 and 75 m in January against the corresponding salinity values, S^o/oo, it becomes evident (Fig. 22) that the changes in dissolved vanadium are roughly linearly correlated to the changes in salinity. The equation of the regression curve is:

$$[V]^d = 0.664 \ S^o/oo - 17.48$$

Similar correlations existed throughout most of the year in the waters above sill depth, suggesting that the main factor controlling the dissolved vanadium values was not biological
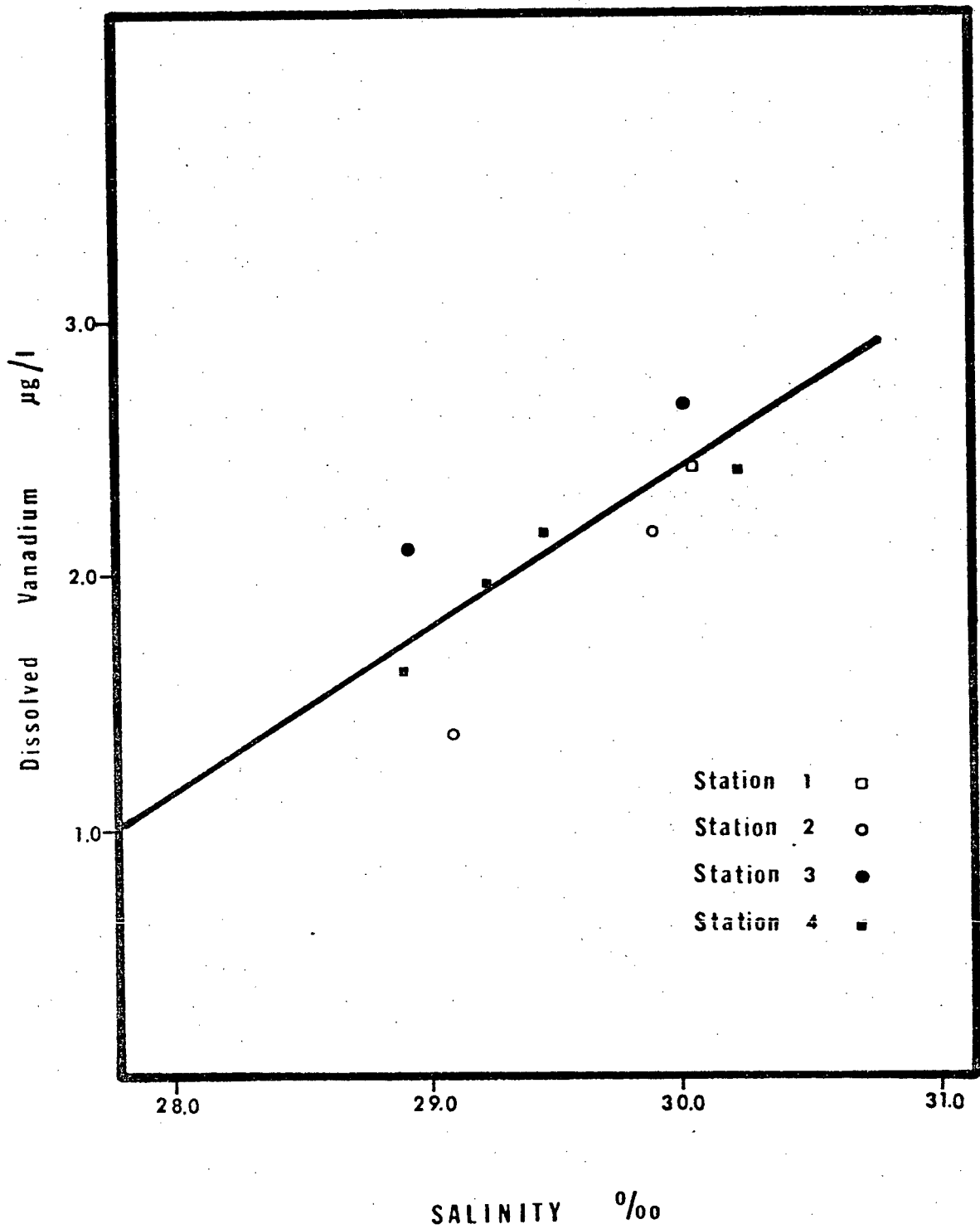
Figure 22. Plot of dissolved vanadium (μg/l) against salinity (S%oo) during January 1974, for depths between 10 and 75 m.

activity but the mixing of low salinity, low vanadium surface water with higher salinity, higher vanadium sea water found at depth. This was clearly not the case in July (Fig. 7), however, when there appears to have been an intrusion of low vanadium water at about sill depth.

Below sill depth, the dissolved vanadium values normally showed marked negative deviations from the trend observed above sill depth (Fig. 23). Moreover, although dissolved vanadium values generally increased from September to November in parallel with salinity and dissolved oxygen values (Figs. 4, 19 and 21), from November to January, they increased as salinity and dissolved oxygen values decreased (Figs. 4, 19 and 21). Then from January to May, the dissolved vanadium values below 160 m decreased in parallel with the salinity and dissolved oxygen values, but between May and late July, below 200 m, they increased as the salinity decreased and the dissolved oxygen increased. Thus, there appears to be no simple relationship between salinity and dissolved vanadium values below sill depth.

The dissolved vanadium increases observed in the bottom waters in November 1973 and July 1974 may have been due to the intrusions of new bottom water evidenced by the simultaneous increases in density and dissolved oxygen values. The low dissolved vanadium concentrations observed prior to these intrusions may thus have been the result of its precipitation or co-precipitation from anoxic or sulphide containing waters. Although vanadium would not be expected to form insoluble sulphide phases under the conditions that occur in sea water, co-precipitation with ferrous sulphide is evidently possible
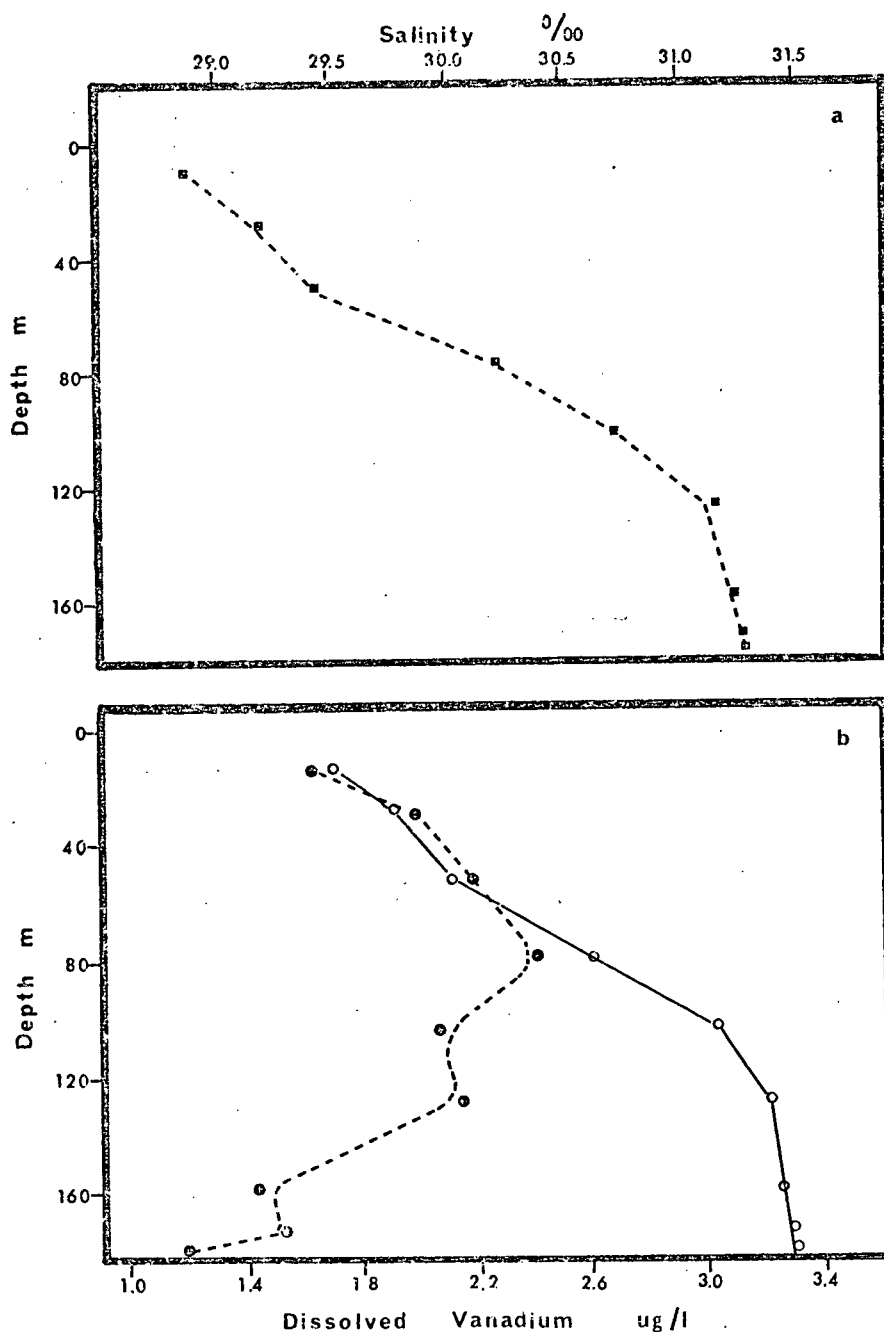
Figure 23. Vertical profile of (a) salinity (S%oo) and (b) dissolved vanadium (μg/l) at Station 4 during Jan. 1974. Solid and dashed curves in Fig. 23(b) represent predicted and observed dissolved vanadium values respectively. Dots represent sampling points.

(Krauskopf, 1956). Furthermore, under anoxic conditions quin-
quevalent vanadium may be reduced to a quadri- or tervalent
state in which it may precipitate or be adsorbed more readily
than in the quinquevalent state. The data of Evans and Garrels
(1958) show that pentavalent vanadium, which should predominantly
exist as the $V_4O_{12}^{4-}$ ion in the pH range of sea water, would be
reduced to at least the quadrivalent state in sulphide bearing
waters at pH 7.5 upon equilibration with the redox half-reaction
$HS^- + 4H_2O = SO_4^{2-} + 9H^+ + 8e^-$ where $[SO_4^{2-}]/[HS^-] = 10^3$
The calculations of Krauskopf (1956) indicate that, at the vana-
dium concentrations present in sea water, the reduced species
which result would be unable to precipitate as the hydroxides
$VO(OH)_2$ or $V(OH)_3$; however, he demonstrated experimentally that
V(IV) was readily adsorbed from sea water by both hydrous iron
oxides and plankton.
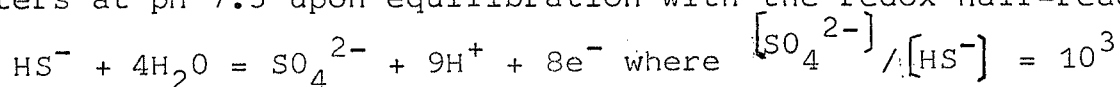
The fact that dissolved vanadium values continued to
increase between November and January, after the intrusion of
new bottom waters had apparently ceased, might be related to its
release in the newly oxygenated bottom waters from decomposing
biogenous material, or some reduced or sulphide phase formed
under anoxic conditions. However, such an increase could have
also been in part due, as was apparently found in the case of
molybdenum in Saanich Inlet (Berrang and Grill, 1974), to a co-
precipitation of vanadium with manganese oxides, and its subse-
quent release at the sediment-water interface following settle-
ment and reductive dissolution of the manganese oxide carrier.
Such a mechanism is suggested by the fact that, from September
to January, very high suspended manganese concentrations were

found throughout the deep water (Fig. 12). As shown elsewhere (Berrang and Grill, 1974), this suspended manganese apparently resulted from the oxygenation of the deep waters and the oxidative precipitation of the large amounts of dissolved Mn(II) which accumulate there during anoxic periods.

By the end of January, after the dissolved oxygen content had decreased to about 0.27 ml/l, suspended manganese values also decreased, either due to the exhaustion of the supply of dissolved manganese or the decrease in the dissolved oxygen concentration. Whatever the case, due to solution of the manganese oxides that settled onto the sediment surface, dissolved manganese values eventually would have to increase again throughout the deep and bottom waters.

In April, a layer with high suspended manganese concentrations (above 15 μg/l) appeared between 170 and 210 m at station 3 and 175 and 185 m at station 4 (Fig. 14). Spencer and Brewer (1971) and Berrang and Grill (1974) noted similar accumulations of suspended manganese just above the interface between oxygenated and anoxic waters in, respectively, the Black Sea and Saanich Inlet, and attributed these concentration maxima to oxidative precipitation of the dissolved manganese that is being mixed upwards from the oxygen deficient bottom waters. Then, as these oxide particles sink back into the oxygen deficient waters, they undergo reductive solution, thus restricting the high suspended manganese values to a thin mid-depth layer. By the end of July, this thin layer of high suspended manganese water stretched continuously from stations 1 to 4 between 100 and 150 m (Fig. 15).

Laboratory studies (Krauskopf, 1956) show that hydrous manganese oxides will adsorb vanadium from sea water. If the manganese oxides precipitated in Saanich Inlet are in fact scavenging significant amounts of vanadium from sea water, then it would be expected that where there are high suspended manganese values, there should also be high suspended vanadium values.

Figures 8 and 12 indicate that from September to December, when suspended Mn values were at their highest, suspended vanadium concentrations were also maximal. Moreover, the thin mid-depth layers of high suspended manganese water found in April and July (Figures 14 and 15) also tended to have high suspended vanadium values (Figures 11 and 12). Thus, where there is an accumulation of suspended manganese, there tends to be a corresponding accumulation of suspended vanadium. Figure 24, which shows the vertical profiles of the two suspended metals at stations 1 and 2 in July, better illustrates the close parallel between their distributions.

If the July suspended vanadium values are plotted against the corresponding suspended manganese values (Fig. 25) the points may be fitted roughly with a straight line indicating a vanadium to manganese weight ratio averaging 2.1×10^{-3}. Grill et al., (1968) found V to Mn weight ratios of 4×10^{-4} and 6×10^{-4} in manganese nodules from Jervis Inlet. Riley and Sinhaseni (1958) found V to Mn weight ratios in Pacific Ocean nodules to be 6.5×10^{-4}, while Pachadzhanov (et al., 1963) found the ratio in Indian Ocean nodules to be 4.7×10^{-3}. Thus, vanadium is apparently associated with suspended manganese oxide
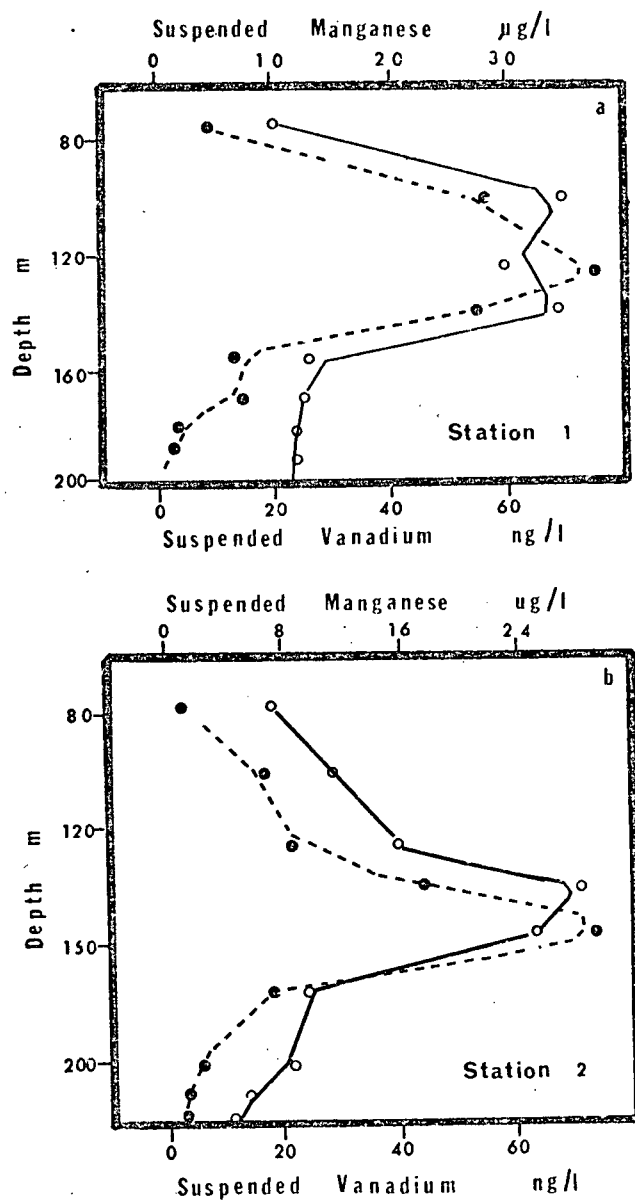
Figure 24.   Vertical profiles of suspended vanadium
(ng/l) and suspended manganese (µg/l)
at (a) Station 1 and (b) Station 2 in
July 1974. Solid and dashed curves
indicate suspended vanadium and suspended
manganese respectively.
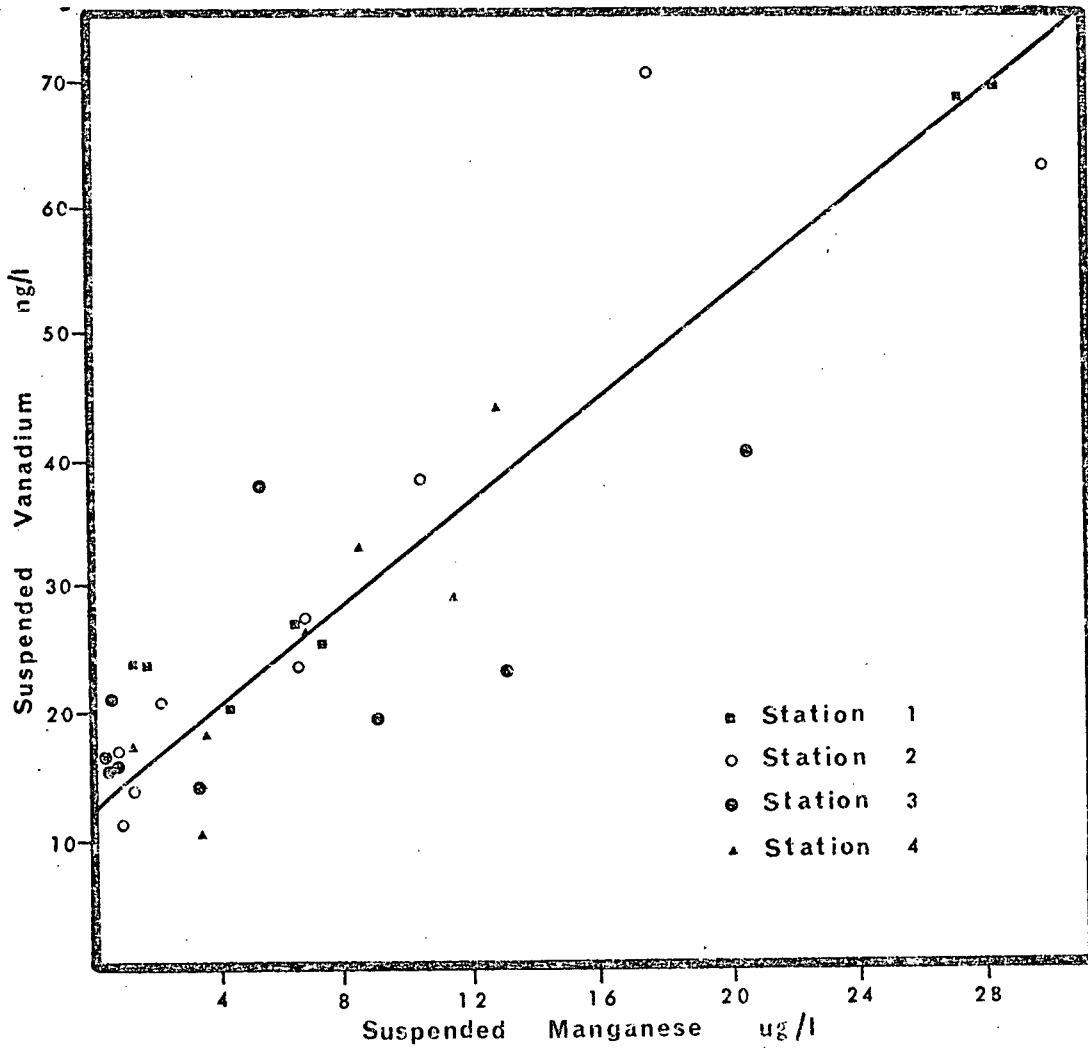
Figure 25.   Plot of suspended vanadium (ng/l) against sus-
              pended manganese (μg/l) during July 1974.

particles in Saanich Inlet to roughly the same extent that it
is presumably adsorbed by manganese oxides in marine manganese
nodules.

The slope, intercept and correlation coefficient of the
suspended vanadium and manganese regression curve for each
cruise is listed in Table VI.

Table VI

Cruise	Date	Slope x 10^{-3}	Inter-cept	Corr. Coeff.	No. of Samples
73/35	Sept. 1973	5.79	15.3	+0.45	7
73/46	Nov. 1973	11.80	0.8	+0.94	8
74/1-A	Jan. 1974	− 0.11	23.9	−0.10	30
74/15	April 1974	0.20	16.9	+0.10	33
74/26-A	July 1974	2.10	15.3	+0.89	34

These data indicate that the strongest correlations between
suspended vanadium and manganese values occurred in the autumn
of 1973 and July 1974. There appears, however, to be no cor-
relation between the two suspended metals in January or April,
with the exception of the thin layer of high suspended manga-
nese water found in April between 175 and 185 m at station 3
and 170 and 210 m at station 4 (Fig. 14).

The V:Mn weight ratios, as derived from the slopes of the
regression lines (Table VI), exhibit a much greater spread than
those reported by Willis and Ahrens (1962) for oceanic manga-
nese nodules. Moreover, the regression lines exhibit a positive
intercept, implying that there is some form of suspended vana-
dium which is not associated with the suspended manganese
oxides. Variation in this non-manganese associated vanadium
may account for some of the scatter about the regression lines.

Krauskopf (1956) found that vanadium was adsorbed onto iron oxides even more strongly than onto manganese oxides. However, his experimental conditions differed from natural conditions and, in particular, from those found in this study. This might explain the fact that no relationship was found between the suspended iron and suspended vanadium values found in Saanich Inlet. It should be noted, however, that iron oxides may not have been the only form of iron extracted from the samples by the HCl leaching procedure.

As the dissolved vanadium is adsorbed onto the manganese oxides, it might be expected that this would result in a negative anomaly in its vertical profile. In agreement with this, below the sill depth, dissolved vanadium values are generally lower than the values indicated by the salinity correlations observed above sill depth (Fig. 23). While adsorption of dissolved vanadium by manganese oxides may account for the negative anomaly at mid-depths, since the manganese oxides must ultimately dissolve releasing vanadium, other processes, such as intrusion of low dissolved vanadium water, anoxic processes or adsorption by silicate minerals or organic matter must be operative for this anomaly to persist throughout the deep waters.

In summary, the dissolved vanadium distribution in Saanich Inlet may be influenced by several factors. Living organisms may take up vanadium in the surface waters or the weakly oxygenated waters found at mid-depth (Brooks and Rumsby, 1965; Noddack and Noddack, 1939) and after death, may release it to the water through decay or carry it to the sediment. Manganese oxide particles appear to adsorb vanadium at mid-depths, and on

sinking, carry the vanadium to the deeper waters where it presumably is released by reductive dissolution of the manganese oxide carrier. However, correlations between dissolved vanadium and salinity observed in the waters above sill depth suggest that there is a net loss of vanadium from the waters below sill depth. Such losses may be due to its adsorption by and co-precipitation with detrital silicate or organic particles, or ferrous sulphide, either as pentavalent vanadium or, following reduction under anoxic conditions, in some lower oxidation state.

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APPENDIX

CRUISE DATA

DEPTH m	TEMP $^\circ$C	SALINITY $^o/_{oo}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
1	15.03	29.170	21.51	6.75	1.86	–	–	–
100	8.63	30.994	24.07	0.16	1.46	19.0	24.6	4.13
140	8.79	31.140	24.16	0.07	1.68	–	–	–
155	8.80	31.147	24.16	0.06	1.34	13.6	1.82	4.37
180	8.88	31.182	24.18	0.02	1.10	18.4	0.63	3.84

CRUISE DATA

Cruise 73/35   Station Saa-3   Date Collected Sept. 5, 1973

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
1	14.80	29.372	21.71	11.23	–	–	–	–
100	8.71	30.992	24.06	0.47	1.10	18.0	6.65	5.71
140	8.92	–	–	0.79	1.98	145	15.2	8.62
155	8.92	31.162	24.16	0.52	1.56	537	28.5	8.03
180	8.92	31.191	24.18	0.36	1.29	–	36.2	7.21
185	–	–	–	–	–	40.0	36.5	6.92

CRUISE DATA

DEPTH m	TEMP $^{\circ}C$	SALINITY $^{\circ}/_{oo}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
1	9.09	29.622	22.93	5.13	2.34	–	–	–
10	9.25	29.659	22.94	4.72	2.45	–	–	–
25	9.44	30.111	23.26	4.29	–	–	–	–
50	9.10	30.292	23.45	4.22	–	–	–	–
75	8.90	30.552	23.68	4.19	2.64	26.4	1.91	20.3
100	9.09	30.908	23.93	2.24	2.26	36.0	4.03	24.0
125	9.00	31.181	24.16	0.40	2.19	66.0	9.20	14.6
140	8.95	31.223	24.20	0.42	1.77	179	10.6	6.47
155	8.93	31.242	24.22	0.66	1.77	221	10.4	6.87
175	8.97	31.287	24.25	1.11	1.74	173	15.2	6.30
200	9.00	31.312	24.26	1.03	1.24	120	19.6	2.98
220	8.93	31.327	24.28	0.73	0.64	604	48.8	3.55

CRUISE DATA

Cruise 74/1   **Station** Saa-1   **Date Collected** Jan. 9, 1974

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	2.80	23.084	–	7.55	2.39	–	–	–
10	8.15	29.168	22.71	4.93	–	–	–	–
25	8.39	29.463	22.91	4.87	–	–	–	–
50	8.99	29.725	23.03	4.33	–	–	–	–
75	9.05	30.027	23.25	3.73	2.45	9.90	1.04	17.8
100	9.01	30.805	23.86	1.15	2.67	15.6	1.96	6.16
125	8.91	31.242	24.22	0.26	2.40	17.2	14.4	6.26
140	8.90	31.207	24.19	0.26	2.09	21.5	20.6	5.76
155	8.97	31.221	24.19	0.26	1.83	21.9	22.9	6.85
170	8.99	31.253	24.22	0.25	2.08	15.7	27.3	7.50
175	8.89	31.280	24.25	0.26	1.83	13.1	38.2	7.74

Cruise 74/1   Station Saa-2   Date Collected Jan. 9, 1975

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	3.50	24.185	19.28	7.55	2.04	–	–	–
10	7.97	29.093	22.68	5.09	1.38	–	–	–
25	8.26	29.473	22.94	4.91	–	–	–	–
50	8.99	29.698	23.00	5.07	–	–	–	–
75	–	29.875	–	5.18	2.18	25.6	1.58	29.4
100	4.04	30.860	24.52	1.19	2.46	23.2	2.34	16.4
125	8.97	31.145	24.13	0.28	2.26	43.0	5.30	12.1
140	8.96	31.217	24.19	0.37	1.92	17.9	6.13	12.1
155	8.97	31.237	24.21	0.36	1.92	21.1	8.32	7.87
170	8.95	31.252	24.22	0.35	1.98	24.7	15.5	7.83
180	8.98	31.275	24.23	0.58	1.78	27.7	18.2	5.10
190	8.90	31.279	24.25	0.52	2.06	36.5	20.2	7.17

CRUISE DATA

Cruise 74/1   **Station** Saa-3   **Date Collected** Jan. 10, 1974

DEPTH m	TEMP $^{\circ}C$	SALINITY %oo	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	2.70	24,435	–	8.07	2.34	–	–	–
10	7.65	28.933	22.60	5.72	2.10	–	–	–
25	8.24	29.423	22.90	4.91	–	–	–	–
50	9.00	29.660	22.97	4.96	–	–	–	–
75	8.49	30.013	23.32	4.76	2.69	59.5	1.76	27.8
100	DNB	30.767	–	1.73	2.24	24.5	1.51	17.3
125	8.99	31.139	24.13	0.38	1.32	17.1	4.54	15.1
140	8.98	31.194	24.17	0.38	2.72	19.7	4.23	8.93
155	9.01	31.236	24.20	0.50	1.66	18.0	7.08	8.87
175	8.98	31.264	24.23	0.67	1.34	15.8	10.2	6.83
200	9.01	31.286	24.24	0.27	1.06	27.7	13.8	5.43
210	8.92	31.296	24.26	0.27	0.99	12.8	14.6	5.51

DNB = Did not break.

CRUISE DATA

Cruise 74/1   **Station** Saa-4   **Date Collected** Jan. 8, 1974

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	3.40	24.706	–	7.57	1.60	–	–	–
10	7.55	28.907	22.59	5.78	1.63	–	–	–
25	7.96	29.236	22.79	5.23	1.97	–	–	–
50	9.00	29.458	22.82	5.09	2.17	–	–	–
75	8.87	30.229	23.44	3.67	2.42	13.3	1.04	28.8
100	DNB	30.871	–	1.29	2.06	16.6	0.97	26.4
125	9.01	31.156	24.14	0.27	2.14	15.5	3.02	17.7
140	9.00	NST	–	NST	–	31.6	4.25	16.6
155	9.03	31.229	24.19	0.42	1.44	25.3	8.15	15.4
170	9.05	31.254	24.21	0.49	1.55	23.7	16.5	15.6
175	8.97	31.269	24.23	0.55	1.21	27.4	19.3	26.4

DNB = Did not break.

NST = No sample taken.

CRUISE DATA

Station Saa-5 Date Collected Jan. 9, 1974

DEPTH m	TEMP $^{\circ}C$	SALINITY $^{\circ}/_{oo}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	5.30	27.163	21.48	6.22	1.42	–	–	–
5	7.69	29.061	22.69	5.49	1.97	–	–	–
20	9.00	29.162	22.59	5.48	3.17	–	–	–
25	8.24	33.409?	26.01?	4.83	2.64	–	–	–
70	DNB	30.187	–	3.78	1.97	–	–	–
95	9.01	30.825	23.88	1.49	2.11	–	–	–

DNB = Did not break.

CRUISE DATA

DEPTH m	TEMP $^\circ$C	SALINITY $^0/_{00}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	6.90	29.414	–	5.72	1.08	–	–	–
10	7.32	29.443	23.04	5.72	1.17	–	–	–
25	7.35	29.652	23.20	5.76	1.82	–	–	–
50	8.99	29.745	23.04	5.76	1.61	–	–	–
75	7.46	29.876	23.36	5.69	1.89	–	–	–
80	9.01	29.880	23.14	5.72	1.33	–	–	–

Cruise 74/15   **Station** Saa-1   **Date Collected** April 30, 1974

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	11.20	25.598	19.48	6.81	1.77	–	–	–
10	8.74	28.616	22.20	6.51	2.34	–	–	–
25	7.79	29.025	22.65	5.95	2.54	–	–	–
50	7.50	29.378	22.96	5.22	2.34	–	–	–
75	7.59	29.732	23.23	4.68	2.46	25.4	1.43	11.5
100	8.14	30.297	23.59	2.63	2.22	44.0	3.33	7.68
125	8.92	31.136	24.14	0.18	1.76	39.8	7.50	7.58
140	8.96	31.214	24.19	0.26	2.07	51.6	6.74	8.75
155	8.99	31.226	24.20	0.11	1.95	19.4	12.1	7.80
170	8.99	31.258	24.22	0.24	2.20	5.5	9.04	7.73
180	8.96	31.268	24.23	0.22	1.95	23.5	9.60	8.25
185	8.98	31.264	24.23	0.28	1.66	–	–	–

Cruise 74/15   **Station** Saa-2   **Date Collected** April 30, 1974

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	11.20	26.985	20.55	6.90	2.22	–	–	–
10	8.56	28.708	22.30	6.48	1.94	–	–	–
25	7.75	29.097	22.71	5.91	2.20	–	–	–
50	7.58	33.314?	26.03?	5.48	2.18	–	–	–
75	7.53	29.828	23.31	5.00	2.00	16.7	13.3	8.69
100	7.97	30.252	23.58	3.41	1.83	ND	1.22	7.07
125	8.91	31.047	24.07	0.36	1.64	ND	2.18	12.7
140	8.96	31.136	24.13	0.25	1.76	46.8	10.5	10.7
155	8.96	31.227	24.20	0.19	1.62	0.5	6.66	8.42
175	9.00	31.256	24.22	0.18	1.64	5.4	6.53	8.69
200	9.00	31.267	24.22	0.12	1.55	24.2	5.55	5.75
210	8.95	31.264	24.23	0.21	1.55	ND	5.28	8.19
220	9.00	31.270	24.23	0.18	1.57	28.5	1.00	9.84

ND = Not detected.

Cruise 74/15 **Station** Saa-3 **Date Collected** April 30, 1974

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	10.80	28.047	21.44	6.43	2.40	–	–	–
10	8.09	28.900	22.51	6.16	2.18	–	–	–
25	7.75	29.102	22.71	5.66	2.46	–	–	–
50	7.38	29.437	23.03	5.54	2.78	–	–	–
75	7.75	29.922	23.36	5.27	2.69	22.0	1.02	13.8
100	8.15	30.458	23.72	2.34	2.24	7.0	1.30	15.8
125	8.93	31.091	24.10	0.21	1.32	25.6	4.73	6.93
140	8.98	31.210	24.18	0.20	ND	4.95?	22.2	8.06
155	8.97	31.239	24.21	0.20	2.72	28.2	10.7	8.99
175	9.01	31.260	24.22	0.20	1.66	30.4	19.8	8.18
200	9.02	31.280	24.23	0.16	1.34	25.3	29.0	7.58
210	8.96	31.281	24.24	0.08	1.06	16.3	18.2	8.26
230	9.03	31.287	24.24	0.02	0.99	13.8	1.74	9.18

CRUISE DATA

DEPTH m	TEMP $^\circ$C	SALINITY $^o/_{oo}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	8.70	28.397	22.03	6.65	0.76	–	–	–
10	8.82	28.613	22.18	6.43	1.82	–	–	–
25	7.83	29.063	22.67	5.77	1.64	–	–	–
50	7.87	29.458	22.98	5.76	1.94	–	–	–
75	7.87	30.018	23.41	5.04	1.76	7.7	1.05	21.3
100	8.37	30.543	23.75	1.86	1.09	11.3	1.53	22.2
125	8.95	31.088	24.09	0.24	0.64	6.5	1.77	13.3
140	8.99	31.198	24.17	0.13	1.44	12.7	1.06	10.3
155	9.03	31.241	24.20	0.18	1.26	14.3	2.30	13.0
170	9.02	31.260	24.22	0.18	0.76	20.3	2.02	13.4
180	8.97	31.264	24.23	0.17	ND	7.8	19.9	13.5
195	9.01	31.270	24.23	0.26	0.53	22.5	3.76	10.2

CRUISE DATA

DEPTH m	TEMP $^{\circ}$C	SALINITY $^{0}/_{00}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	10.00	26.811	20.61	6.67	1.85	−	−	−
10	8.06	28.902	22.52	6.11	2.17	−	−	−
25	7.95	29.053	22.65	5.81	2.52	−	−	−
50	8.05	29.295	22.83	5.77	2.96	−	−	−
75	7.88	30.037	23.43	5.40	2.70	−	−	−
95	8.48	30.715	23.87	1.65	2.61	−	−	−

CRUISE DATA

DEPTH m	TEMP $^\circ$C	SALINITY $^0/_{00}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	9.11	28.822	22.30	6.67	2.56	–	–	–
10	8.60	28.974	22.50	6.43	2.76	–	–	–
25	8.28	29.343	22.83	6.07	2.44	–	–	–
50	8.16	29.638	23.08	5.85	2.60	–	–	–
75	8.02	29.954	23.34	5.71	2.39	–	–	–
100	7.98	30.548	23.81	5.37	2.85	–	–	–

CRUISE DATA

Cruise 74/26-A   **Station** Saa-1   **Date Collected** July 29, 1974

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	16.30	24.824	17.92	10.84	2.02	–	–	–
10	16.53	26.865	19.43	8.44	2.30	–	–	–
25	11.57	28.360	21.55	5.30	2.13	–	–	–
50	8.82	29,391	22.79	3.50	2.02	–	–	–
75	8.37	30.506	23.73	0.94	1.73	20.3	4.38	5.68
100	8.64	30.906	24.00	0.46	1.48	69.5	28.0	6.34
125	8.82	31.096	24.12	0.22	1.62	59.7	37.2	5.93
140	8.90	31.154	24.15	0.11	1.59	68.7	27.0	8.38
155	8.92	31.193	24.18	0.10	1.65	26.4	6.86	9.69
170	8.94	31.220	24.20	0.08	1.78	25.3	7.17	8.98
180	8.97	31.229	24.20	0.02	1.38	23.9	1.96	9.88
190	9.00	30.777	23.84	0.02	1.54	23.8	1.54	12.2

Cruise 74/26-A   Station Saa-2   Date Collected July 29, 1974

DEPTH m	TEMP °C	SALINITY %oo	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	17.20	24.862	17.76	11.69	2.48	–	–	–
10	–	26.457	–	10.71	2.60	–	–	–
25	11.07	28.334	21.62	5.10	3.11	–	–	–
50	8.78	29.286	22.71	3.77	2.78	–	–	–
75	8.41	30.601	23.79	1.50	2.79	17.6	1.20	4.37
100	8.53	30.883	24.00	1.35	2.55	27.6	6.57	5.41
125	8.79	31.073	24.11	0.71	2.64	38.7	10.2	7.53
140	8.85	31.144	24.15	0.16	3.14	70.4	17.4	6.43
155	8.92	31.202	24.19	0.21	2.71	62.9	29.7	7.87
175	8.97	31.247	24.21	0.20	2.30	24.0	7.02	6.71
200	8.99	31.256	24.22	0.07	2.33	21.0	2.53	7.20
210	8.98	31.257	24.22	0.05	2.15	14.6	1.30	6.11
220	15.23?	31.269	23.08	0.01	2.83	11.3	1.05	5.85

Cruise 74/26-A   **Station** Saa-3   **Date Collected** July 29, 1974

DEPTH m	TEMP $^\circ$C	SALINITY $\%_{oo}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	–	23.982	–	9.93	0.92	–	–	–
10	13.86	25.941	19.27	9.74	1.70	–	–	–
25	12.15	28.312	21.42	4.18	2.16	–	–	–
50	9.03	29.265	22.66	3.69	2.38	–	–	–
75	8.34	30.409	23.65	1.75	1.33	21.0	0.81	7.97
100	8.52	30.814	23.94	1.75	1.72	14.6	3.77	15.9
125	8.66	31.003	24.07	1.51	2.08	38.0	5.39	12.6
140	8.75	31.087	24.12	1.49	2.23	23.1	13.2	14.7
155	8.92	31.165	24.16	0.43	1.94	40.7	21.1	8.71
175	8.98	31.252	24.22	0.19	1.04	19.4	9.02	8.08
200	8.96	31.247	24.22	0.09	1.53	15.9	1.36	9.09
210	9.01	31.250	24.21	0.11	1.48	16.2	0.78	12.5
220	8.71	31.254	24.26	0.13	1.48	17.2	0.74	12.5

DEPTH m	TEMP $^{\circ}C$	SALINITY $\%oo$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	15.80	24.417	17.72	9.79	2.08	–	–	–
10	13.70	26.150	19.46	8.65	2.92	–	–	–
25	11.15	28.239	21.53	4.79	3.14	–	–	–
50	8.34	29.252	22.75	3.89	3.25	–	–	–
75	8.35	30.389	23.64	1.57	2.78	16.1	1.50	13.2
100	8.56	30.829	23.95	1.95	2.47	10.5	3.49	20.6
125	8.66	31.013	24.08	1.73	1.84	26.5	6.82	13.7
140	8.77	31.104	24.13	0.87	2.34	44.1	12.67	9.98
155	8.94	31.203	24.18	0.12	2.22	28.9	11.4	10.9
170	8.95	31.227	24.20	0.09	2.08	33.0	8.42	9.81
180	8.99	31.233	24.20	0.01	2.10	18.1	3.64	9.50
195	9.00	31.248	24.21	0.02	1.69	13.8	0.56	10.1

CRUISE DATA

DEPTH m	TEMP ^{o}C	SALINITY $\%_{oo}$	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	14.50	24.522	18.06	9.03	2.34	–	–	–
10	12.81	–	–	7.09	–	–	–	–
25	10.83	28.378	21.69	4.56	1.95	–	–	–
50	9.74	29.280	22.56	3.74	2.18	–	–	–
75	9.08	30.626	23.71	3.39	2.34	–	–	–
85	8.66	30.777	23.89	2.60	1.38	–	–	–

CRUISE DATA

DEPTH m	TEMP °C	SALINITY ‰	DENSITY σ_t	OXYGEN ml/l	V^d ug/l	V^p ng/l	Mn^p ug/l	Fe^p ug/l
0	14.80	23.937	17.55	8.86	1.46	–	–	–
10	13.41	25.039	18.66	7.69	1.78	–	–	–
25	11.25	28.122	21.42	5.31	2.37	–	–	–
50	9.72	29.389	22.65	3.81	2.31	–	–	–
75	9.22	30.536	23.62	4.23	1.68	–	–	–
90	8.83	31.303	24.28	3.48	1.56	–	–	–