

Report of Challenger Cruise 76/90

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Dates of the cruise

The cruise ran from March 6 (Troon, Scotland) to April 2 (Barry, S.Wales), 1991. Loading of equipment began on the morning of March 5; the scientists boarded the ship the same day.

Scientists participating in the cruise

1. C.M.G. van den Berg (PSO)
2. M. Boussemart
3. A.C. le Gall
4. L. Campos
5. K. Yokoi
6. E. Achterberg
7. J.J.H. Brito
8. M.R. Preston
9. A.M. Harbin
10. D. Caballero
11. A. Cruzado

Aims

The aims of the cruise were to investigate the biogeochemistry and possible photochemistry of a number of trace elements (including aluminium, copper, nickel, zinc, titanium, platinum and chromium) in oceanic waters. This part of the North Atlantic was selected for this study as it can be reached comparatively easily from the UK, and as it provides waters of varied origin. Possible photochemical effects and effects related to biological activity can be compared in the cold waters from the North with the warmer waters further south. Chromium was added later to the list of elements studied as this element is particularly interesting for photochemical aspects of this study because of its occurrence in two oxidation states.

Cruise track

The cruise track for this study ran from 53° N to 35° N along 20° W, and was continued to 30° N / 25° W. A map containing the cruise track, and the station numbers and dates is shown in Fig.A1 in the appendix.

Stations

A total of 13 stations were visited and 19 CTD/rosette casts were made. A listing of these is given in Table 1 in the appendix of this report. The majority of the stations were along 20°W.

Comments concerning the RRS Challenger

Interaction officers and crew with the scientists: Very good assistance and cooperation was obtained in all cases from the Captain, and the officers and crew. No frictions occurred. Furthermore it was noted that the crew was generous with its assistance, and appeared to take good care of the ship.

Assistance from RVS personel: Very good assistance and cooperation was also obtained from the RVS technicians (Darryl Philips, Chris Rymer and Doriel Jones) which were very capable and helpful.

Technical aspects related to the functioning of the ship

Vibrations:

An important aspect of this cruise concerned the on-board measurement of trace elements using electrochemical techniques. The level of vibrations and the stability of the powersupplies were therefore important to us. Some of the equipment used on this cruise had not been to sea before, so we can not properly compare the conditions with those on other ships. However, it is my impression that the vibrations were worse than experienced four years ago on the Charles Darwin though much better than on the F. Russell which has fortunately been sold. Our electrodes (Metrohm) had frequent breakdowns which could be ascribed to vibrations affecting the distribution of mercury oxide particles in the mercury reservoirs and subsequently blocking the needle which made contact with the mercury in the capillary. This problem had not occurred in several years use in the laboratory in Liverpool, but occurred in three of the four electrodes a few times during the cruise.

It was noticed that the strength of the vibrations varied across the two laboratories (the general and the chemical laboratory) used. The vibrations appeared to be strongest in the chemical laboratory, especially on the part of the central bench away from the wall. This bench could benefit from anti-vibration mountings as it was noticed that also the floor underneath this bench vibrated comparatively strongly.

The electricity supply though stabilised was not fully stable or free of spikes. Computers were found to crash occasionally and the electrochemical equipment suffered from varying amounts of interference which could be ascribed to the mains supply. We are not absolutely certain whether these problems were always due to interference from the mains or indirectly from vibrations sensitising the electrodes. The computer crashes were due to the mains as occasionally some crashes occurred simultaneously. Nevertheless these computer crashes were infrequent, approximately 6 times in the chemical lab for the duration of the cruise. The mains supply in the cabins was much more variable. For instance, there were occasions that the computer located in the cabin of the PSO crashed several times within an hour, whereas at other times it would run for a full day without problems. For these reasons I would recommend that it is investigated whether the mains supply to the laboratories could be better stabilised, and whether the mains supply to the sockets in the cabin of the PSO could also be connected to the stabilised mains.

Go-Flo bottles, CTD cable, and clean container

Problems with the Go-Flo bottles occurred fairly frequently, usually one bottle failing at each cast of twelve bottles. I understand that this failure-rate is good compared with that obtained in North Sea waters where the bottles suffered from the high suspended particle load. Fortunately parts were on-board to repair the bottles each time, but the failures

meant that some casts were impaired as it was often only noticed during the analysis that a bottle had failed.

CTD/rosette

It was noticed that the water samples collected using the combination CTD/Go-Flo bottles were contaminated with iron. The iron data produced were rather erratic and variable, and higher for instance than surface samples collected using a plastic bottle lowered to the water surface from the ship using a plastic rope. Subsamples were taken from the Go-Flo bottles on the deck, and these were already contaminated suggesting that the samples had been contaminated during collection. It was attempted to minimize this contamination by taping the steel cable above the rosette, as well as the rather corroded clamp connecting the cable to the rosette. This helped but did not eliminate the problem. We think that the cable may be a large source of this contamination, and for trace metal work it is therefore essential if this cable would be replaced by a plastic coated cable. All clamps on the rosette should be from rust-free steel and replaced when corrosion sets in. The rosette itself can perhaps be coated with teflon or epoxy resin.

Clean container

The clean container is starting to show signs of age: rust is starting to appear at spots inside the container. The air-filtration unit in the container had not been used for a while and appeared to be full of fungus producing a strong musty smell which lasted for several days after switching it on. The air-filter had not been serviced prior to this cruise, and I recommend that its effectivity is checked. The main filter should be replaced every five years, whereas the prefilter should be replaced after 3 to 4 months use.

The Milli-Q water deionising system needs servicing: the water produced by the system, though having a resistivity of nearly 18 ohm^{-1} was not as clean as it can be, and was found to contain for instance significant levels of ammonia. The deioniser resins can be replaced readily. Probably the resins in the Reverse Osmosis system should be replaced as well. The resins should be replaced every half year, although it is possible that their life is extended somewhat by the long periods of no use.

The nutrient analyzer (owned by the NERC): this system was not found to be ready for ocean work as dilution ratios had been installed which made it suitable for high nutrient concentrations only, perhaps as occurring in polluted coastal waters or deep waters. One of us (Dr. Cruzado) worked fulltime on this analyzer to get it adjusted and got it to work for some of the nutrients only.

Stand-alone pumps (SAPs) for in-situ filtrations

Three SAPs were used for in-situ filtrations using large (280 mm) filter holders attached to the pumps. Use of these pumps and the in-situ filtrations was meant as an experiment to investigate its application in the collection of suspended particles. One of us (Boussemart) had been trained at PML by Dr. T. Fileman in the use of the pumps. Nevertheless problems caused the loss of several filters. This could largely be prevented by using two filters simultaneously. Some 5 filters were collected successfully and are to be analysed later.

SUMMARY OF NERC EQUIPMENT

The scientific equipment for general use held by NERC was not in very good condition. This comment is not a complaint but the problems related to maintaining the equipment in optimal condition indicate that perhaps scientists who use it regularly could be made responsible for its maintenance, or that a chemical technician could be hired by

NERC and be made responsible for the maintenance and occasionally for running it during cruises. Another possibility is that the Reynolds Centre takes this responsibility on.

Scientific Report

The following measurements were carried out on-board:

Basic parameters:

Conductivity, temperature, oxygen, fluorescence and transmittance using probes on the CTD, and underway using a deck based system.

In samples:

Nutrients (using the RVS nutrient analyser)

Copper complexing capacities at two detection windows

Dissolved copper and labile copper concentrations

Labile and dissolved nickel

Chromium (VI/III) speciation

Labile aluminium

Labile vanadium

Ammonium and nitrite (using voltammetry)

Platinum

Labile and dissolved titanium

Labile iron

Glutathione and folic acid (using voltammetry)

DOC

Furthermore a large number of samples were collected and stored in polyethylene bottles for later analysis in the laboratory.

On-board measurements using voltammetry

Eight polarographs were intensively used on-board ship during this cruise. This is probably a record number of polarographs used on a ship during a single cruise anywhere on the world. The following makes were used: PAR 174A (2) with PAR 303 and 303A electrodes; Autolab polarograph (3) connected to Metrohm electrode stands; Metrohm VA processor (1) connected to a Metrohm 667 electrode stand with sample changer; home-built instruments (2) from J. Brito, connected to PAR 303A electrodes. One of the Autolabs had been altered to allow connection to a sample changer and an autoburet.

Generally very good results were obtained for all voltammetric measurements producing data which could be evaluated on-board along with the nutrients. The data illustrate the advantage of on-board measurements in obtaining data quickly on samples which have not been stored. Some of the on-board measurements (those of glutathione and folic acid, the organic speciation of copper, and the redox speciation of chromium) illustrated that these could be measured successfully immediately upon sampling but not after sample storage, illustrating that on-board determinations are essential to obtaining accurate data if the analyte cannot be stored.

Generally all equipment functioned well. Unexpectedly large problems occurred with the Metrohm electrodes which normally are very reliable. It is thought that these recurrent problems (poor signal, poor reproducibility of the drop) were caused by strong vibrations which caused a small amount of mercury oxide to become dispersed in the mercury and

become attached to the needle which forms the contact with the capillary. Measurements then had to be interrupted to remove and replace the capillary or filter the mercury. This particular type of problem did not occur with the PAR electrodes.

Vibrations due to the ship's engines did not cause mercury drops to fall off the capillary as might be expected, but caused large background currents. This problem could be overcome by using fast square-wave techniques when the measurements allowed this. Unfortunately a large number of otherwise successful platinum, glutathione and folic acid measurements were lost due to this problem as fast square-wave scanning could not be used with these analyses.

The automation of one Autolab polarograph (performed as part of NERC grant GR3/7611) was very successful resulting in very reproducible complexing capacity titrations and a high throughput of samples (8 samples could be titrated every 24 hours, so a new 12-bottle cast could be made every 1.5 days). The Metrohm VA processor polarograph was also automated by transferring the data to a computer, but the sample throughput was lower as its sample changer could only hold 10 cells. Furthermore the sensitivity of this instrument was affected by the engine vibrations and could not be improved by using high frequency square wave voltammetry as this wave-form was not available in this instrument.

Specific reports on the above topics are given below.

Salinity, Oxygen, fluorescence and transmittance

The vertical profiles for the salinity, oxygen, temperature, fluorescence and the transmittance, are shown in Figs.A2-A14 in the appendix. A maximum appeared in the fluorescence at a depth of 60 to 70 m in the southerly stations (7 and 8); the fluorescence was highest at the surface at the more northerly stations, producing a secondary maximum at greater depth at station 4 (ca 350 m), and a diffuse maximum at station 3 at 500 m at station 3. This is consistent with an algal bloom having taken place in the upper water column between stations 4 and 5, ie between 42 and 36 °N; this bloom still has to take place in the more northerly waters.

Nutrients (determined using conventional spectrophotometric techniques by Antonio Cruzado)

The concentrations of silicate and nitrate are shown in Fig.A15 in the appendix. The location of each profile on the drawing corresponds with the latitude of each station. The nitrate concentration drops to near 1 μM at station 5, 6 and 8, whereas it is much higher at more northerly stations (5 μM at station 4, 10 μM at station 3, 17 μM at station 2, and 8 μM at station 10), consistent with an algal bloom having taken place at latitudes south of station 4, whereas this bloom still has to take place at the more northerly stations, in agreement with the fluorescence data.

The presence of an algal bloom in the upper water column of some of the profiles sampled provided us with an opportunity to compare the metal speciation in waters affected by this bloom with waters unaffected.

DOC analyses / Martin Preston

Objectives

To measure dissolved organic carbon concentrations in water column samples from along 20 degrees W and to relate these to trace metal concentrations and other parameters.

Additionally, it was intended to make a comparison of the results obtained after GF/F and Nuclepore filtration.

Results

Almost immediately upon collection of the first samples the TOC analyser suffered a failure of the temperature controller in the inorganic carbon oven. This led to an oven runaway with the consequent blowing of a thermal protection fuse. A temporary repair was initially made by using a piece of solder of approximately the correct melting point in place of the fuse and attempting to control the oven temperature with a manual switch. This arrangement, however, rapidly failed and for the next 10 days or so the system was operated without thermal protection and with manual temperature control. This permitted the analysis of samples from 5 profiles though, because of the difficulty of operating the system with manual control, the reproducibility of the results was not as good as it would otherwise have been.

At the end of this period the machine suffered a more serious failure of the detector system and had to be completely shut down. Samples from 9 profiles were collected and stored so that they can be analysed back in the laboratory when the machine has been repaired.

A preliminary examination of the results obtained indicates a wide variation in DOC concentrations from 75- > 750 $\mu\text{M C}$. The most northern station had the lowest concentrations. Most profiles showed a sub-surface maximum and a number also showed an elevated value in the near-bottom sample.

Conclusions

The early failure of the machine was disappointing and greatly reduced the number of analyses that it was possible to perform. Nevertheless, I hope that it will be possible to draw some useful information from the limited data set that it was possible to produce.

Analysis of nutrients using cathodic stripping voltammetry (Anne Marie Harbin)

Introduction

The purpose of this study was to test a new (voltammetric) method to determine sub-micromolar levels of ammonia and nitrite. These micronutrients play an important role in the growth of algae and in the uptake of nitrogen by the oceans and the conventional spectrophotometric procedure is not sufficiently sensitive to detect the low levels occurring in areas of high productivity.

Analysis was done using a PAR 174A polarograph and a PAR 303 hanging mercury dropping electrode. Initially, noise due to ship motion was high. This was minimized by placing the equipment on foam pads. The voltammetric method used had a limit of detection of 5 nM ammonia and below 1 nM nitrite.

Nitrite analysis

Two profiles were acquired and the profiles made oceanographic sense. Nitrite maxima were found below the fluorescence maxima (see Fig.1). Experimental difficulties were related to contaminated or old reagents as shoulders were seen on the peaks.

Ammonia analysis

Several casts of varying depths were studied. In general, ammonia concentrations were higher in the samples from the upper water column (up to 500m) with maxima of ammonia below the fluorescence maxima. In the samples from greater depth (below 2000m) the concentrations tended to be lower. The contribution of contamination from

reagents was 5nM and this increased during the cruise to 10nM. In general sea water concentrations were found to be greater than 100nM and the effect of reagent contamination on the detected levels of ammonia was therefore negligible.

CONCLUSION

Both ammonia and nitrite could be readily detected in all samples using the voltammetric procedure. The nitrite was generally below the limit of detection of the spectrophotometric analyzer illustrating the usefulness of the voltammetric approach although it could be argued that the spectrophotometric analyzer was not fully optimized. Unfortunately, for this and other practical reasons data from the autoanalyser were not available to compare the nitrite and ammonia concentrations from this instrument with the results obtained using the voltammetric procedure. In the future, it will be interesting to compare the two techniques. Samples from several stations were frozen and it is hoped to determine nitrite concentrations using the conventional spectrophotometric technique in the laboratory.

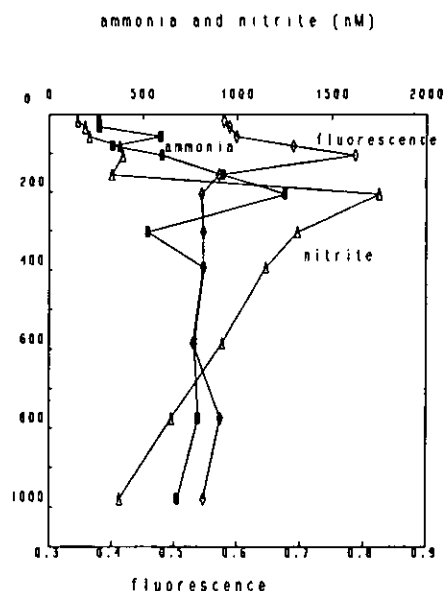


Figure 1 Ammonia and nitrite determined using voltammetry at cast 9

Trace organics (glutathione and folic acid) by voltammetry (Anne Christine le Gall).

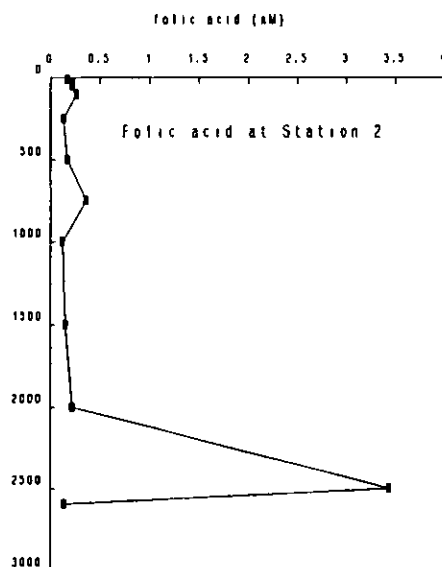


Figure 2 Folic acid (nM) versus depth (m)

ca. 100 m depth, and a second near the sediments. The DOC data are not yet fully evaluated so a good comparison can not yet be made with this parameter. Preliminary data suggest that there is some similarity in the DOC profile with that for folic acid, but

The purpose of this work was to evaluate, in oceanic waters, the concentrations of two compounds of biological origin, glutathione and folic acid. The measurements were done using cathodic stripping voltammetry with a computerised polarograph (Autolab from Ecochemie) and a hanging mercury drop electrode (663 Metrohm). The concentrations were calculated after standard addition of the compound studied.

The concentration of folic acid was successfully determined in samples from five stations at depths varying between 10 and 2500 m. The preliminary data for one (deep) station are shown in Figure 2. The data reveal two maxima, one near the surface at

the deep water maximum in the folic acid concentration was not apparent in the DOC concentration.

The glutathione data appeared to co-vary with the fluorescence, both showing a clear maximum at 50 m depth

(figure 3). A maximum in the glutathione concentration at this depth is in line with the expectation as one would expect the primary productivity to peak at this depth too.

Instrumental problems related to excessive vibrations of the laboratory bench in addition to ship's motion prevented measurements during rough weather.

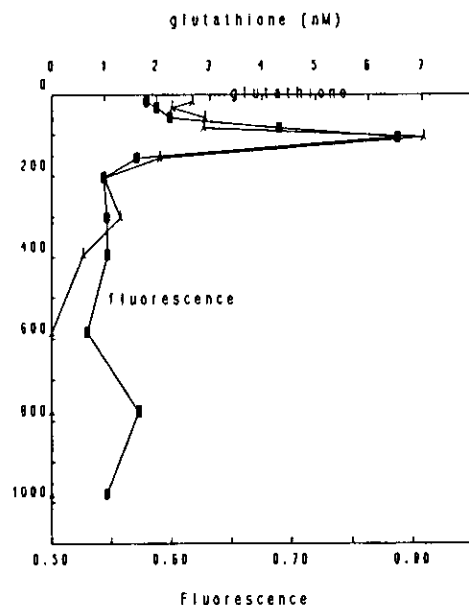


Figure 3 Glutathione at station 8.

The determination of copper and its complexing ligand concentration (Lucia Campos and Eric Achterberg).

The concentration of copper was determined using cathodic stripping voltammetry of filtered samples. The total dissolved copper concentration was determined after UV-irradiation of the samples, whereas the labile fraction was obtained in the untreated samples. The concentration of organic complexing material in the sea water was determined by titration with copper whilst monitoring the labile copper concentration at two detection windows in order to detect both strong and weak complexing material. The complexing ligand titrations are quite time consuming taking approximately 4 hours to perform each, and a waiting time of 8 hours was maintained after the metal additions to ensure equilibration between the added metal and the natural complexing material. It was necessary to carry out these titrations on board as the organic complexing ligands cannot be stored for an extended period.

Two polarographs were used for this work, a Metrohm VA 646 with a Metrohm VA 675 sample changer, and an Autolab connected to a Metrohm electrode stand and a computer. Instrumental problems related to vibrations were minimized by siting the electrodes on thick foam pads and by using a faster scan rate and the square wave modulation (for the Autolab only).

Results

Labile and total dissolved copper concentrations were obtained in some of the vertical profiles, whereas the samples from the other profiles will be analysed later in the laboratory. Most equipment time was consumed in the complexing ligand determinations. The results for labile and total dissolved copper for station 4 are shown in Figure 4. It can be seen that the labile copper concentration is much lower than the total dissolved copper concentration indicating that this metal occurs complexed strongly throughout the water column. It can be seen that the total dissolved copper concentration did not diminish in the upper water column; in fact at several stations its concentration actually increased perhaps as a result of atmospheric inputs. The labile copper

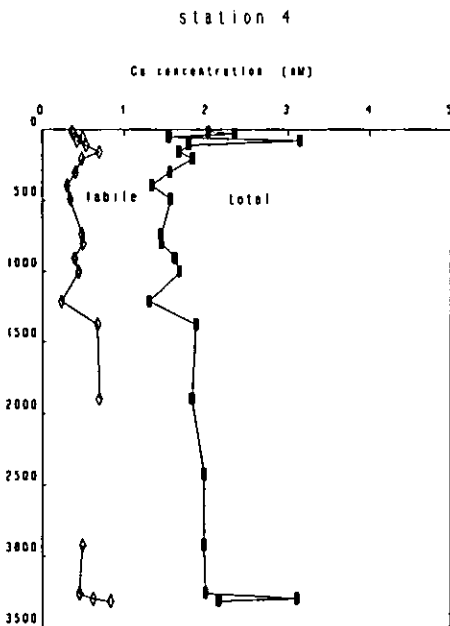


Figure 4 Labile and total dissolved copper.

complexes formed is very high with values for $\log K'$ around 13 (sea water is thought to contain more than one organic complexing ligand with large differences in the stability of the complexes; which ligand is detected depends on the detection window of the technique [1]). A lower detection window was used at later stations as a result of which higher concentrations of weaker ligands were detected (not shown in this report).

The ligand concentrations were always higher than the copper concentrations indicating that this element occurs fully complexed in deep waters as well as the upper water column. The ligand concentration was found to be greatest in the upper water column and was found to covary with the fluorescence which in its turn is a measure of recent primary production. The ligands are therefore produced during primary productivity, and part of the ligands is broken down rapidly whereas another part is very stable and persists in the deep water column.

The speciation of iron and titanium (Kunihiko Yokoi and Stan van den Berg)

Very little is known about the distribution and organic complexation of titanium in open ocean [2]. One of the reasons of this is the lack of a sensitive method to determine Ti. Recently we developed a sensitive voltammetric method for Ti [3], and we used this to

concentration showed less increases and occasionally decreased in the upper water column probably as a result of increased organic complexation in the waters where primary production took place.

The concentration of complexing ligands in the water column of the same station (Station 4) is shown in Fig.5. These ligand concentrations were determined using salicylaldoxime as competing ligand, at a rather high detection window. The ligand concentrations detected are therefore rather low, although the stability of the

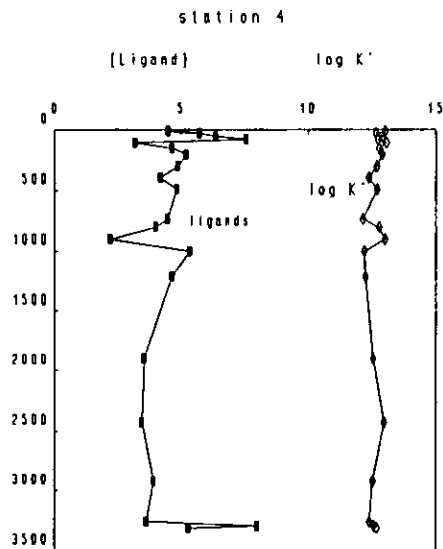


Figure 5 Complexing ligand concentration and values for $\log K'$ at station 4.

determine the concentration of labile and total Ti in the North Atlantic Ocean on board during the Challenger cruise.

Only little more is known about iron in the North Atlantic Ocean. We used a catalytic CSV method [4] to determine the concentration of labile and total dissolved iron in some of the profiles collected during the cruise. A PAR174 polarograph was used with a PAR303 electrode and a Houston Omnigraphic recorder.

Ti measurements were carried out at pH 3-3.5 whereas the iron measurements were carried out at pH 7 with PIPES buffer. Filtered sea water was analyzed without further treatment for labile metal and after UV-irradiation for total metal.

Results

Ti:

The titanium concentration was found to increase generally with depth reaching a maximum near the sea bottom in agreement with data recently produced by Oriens et al.[2], and suggesting that the titanium is transported downward and released in deeper (older) waters, although it should be noted that the profile does not resemble that of a nutrient. The titanium concentrations in the upper water column were low (0.06-0.1 nM and ca.0.02-0.05 nM for total and labile respectively) and increased with depth to a maximum near the bottom of 0.3-0.6 nM. A large difference was observed between labile and total dissolved titanium concentrations even though the measurements were carried out at a rather low pH of 3. These data indicate that a large fraction of of the titanium occurs in a non-labile form which could be of inorganic colloidal nature or an organic complex the sea water. An interesting feature was the occurrence of low titanium concentrations in the bottom waters of the most northerly stations; this finding is in agreement with the low age of North Atlantic deep waters. Further measurements are necessary to investigate this phenomenon in detail. A profile for titanium in the N. Atlantic at station 4 is shown in Fig.6.

Fe:

We had great difficulties collecting uncontaminated water samples using the standard rosette Go-Flo bottle holder attached to the steel cable and many casts had to be discarded for the purpose of determining iron. The steel cable was taped with electric insulation tape for a length of ca. 10 m above the rosette which seemed to help somewhat in minimizing the release of iron. In some casts therefore the iron concentrations

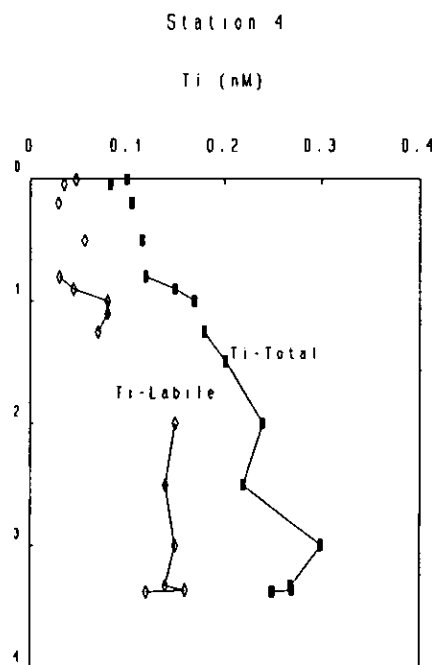


Figure 6 Labile and total dissolved titanium at Station 4 in the N. Atlantic.

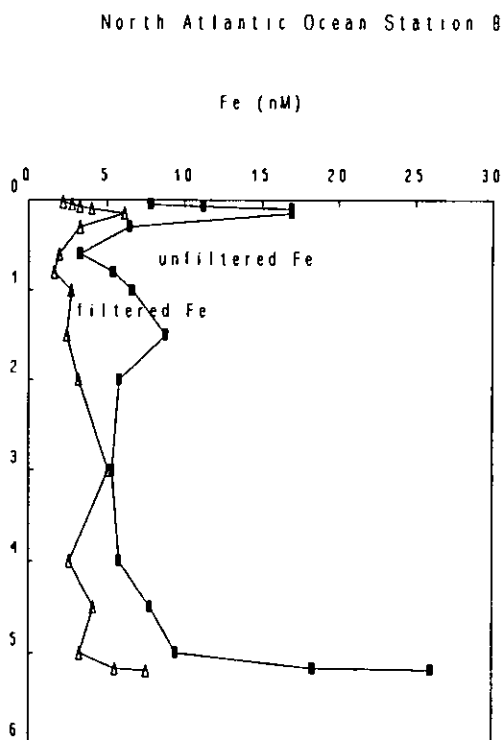


Figure 7 Total (unfiltered) and dissolved iron at Station 8 in the N. Atlantic.

shows that a large fraction of the unfiltered iron is non-labile. The iron is soluble at these low concentrations so it likely that the non-labile fraction is organically complexed although an inorganic colloidal component cannot be excluded.

Chromium and nickel (Boussemart and van den Berg)

Chromium(VI) and Chromium(III) were determined on board using a recently developed voltammetric procedure [7]. Samples were transferred to silica tubes immediately upon filtration and UV-irradiated for total dissolved chromium. Labile chromium(VI) was determined without UV-treatment. Reactive Cr(III) was determined separately after preconcentration on silica particles and was determined later in the laboratory. The results obtained on-board ship for chromium(VI) for one of the stations is shown in Fig.8. It can be seen that the chromium concentration (between 2

appeared to make sense oceanographically and these data are likely to be okay. In order to eliminate sample contamination during filtration we determined iron in unfiltered and in filtered samples. Occasionally the filtered levels were higher than the unfiltered levels indicating problems with the sample handling.

In summary, we found that the total dissolved iron concentration (measured after filtration, acidification and UV-irradiation) showed an almost linear increase with depth but the concentrations were higher than those expected especially in the upper water column [5,6]. It is possible that these high levels were caused by atmospheric inputs considering the proximity of N. Africa to the study area. Sometimes the labile iron concentration did not vary much with depth whilst in other cases an increase in the bottom waters was apparent. Unfortunately not many data could be obtained for iron and further measurements on unfiltered and filtered samples (both for labile and total) are required to clarify the oceanographically consistent behaviour of Fe. Data for total (unfiltered) and dissolved (filtered) iron at Station are shown in Fig.7. The figure

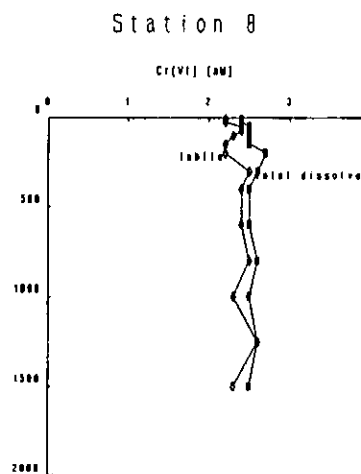


Figure 8 Labile and total dissolved chromium(VI) at Station 8 in the N. Atlantic.

and 3 nM) in the N. Atlantic is quite low, lower for instance than in the Mediterranean where we found levels between 5 and 6 nM during an EROS cruise in 1990 (unpublished data). There was a significant difference between the labile chromium(VI) and total dissolved chromium concentrations probably due to the presence of chromium(III). The difference was largest in the upper water column indicating that algae may be a contributor to the formation of chromium(III) but a further enhancement in the surface waters (top 50 m) as seen in the Mediterranean during the cruise with M. Dufresne (April, 1990) and an indication of photochemical effects, was not observed during this cruise, perhaps because the Challenger cruise was held earlier in the year.

The speciation of nickel (not shown here) was also determined successfully in samples from several profiles. A large fraction of dissolved nickel was found to be strongly but reversibly bound by organic complexing material, and several experiments were carried out to investigate the kinetics of complex formation and complex dissociation. Some of this work, including the determination of total dissolved nickel concentrations, is to be continued later in the laboratory.

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SUMMARY OF CRUISE REPORT

Overall the cruise was scientifically very successful. The voltammetric equipment worked very well during the cruise and a large number of casts were made and samples collected. Several trace metals were determined in samples from the oceanic water column and the speciation of copper, chromium, titanium, iron and nickel were determined on-board. Tests indicated that it is essential to carry out these speciation determinations, and the determinations of glutathione and folic acid, on board ship as soon as possible, in the case of folic acid and glutathione within 10 hours of sample collection. The successful studies have shown that these determinations can indeed be carried out in the field.

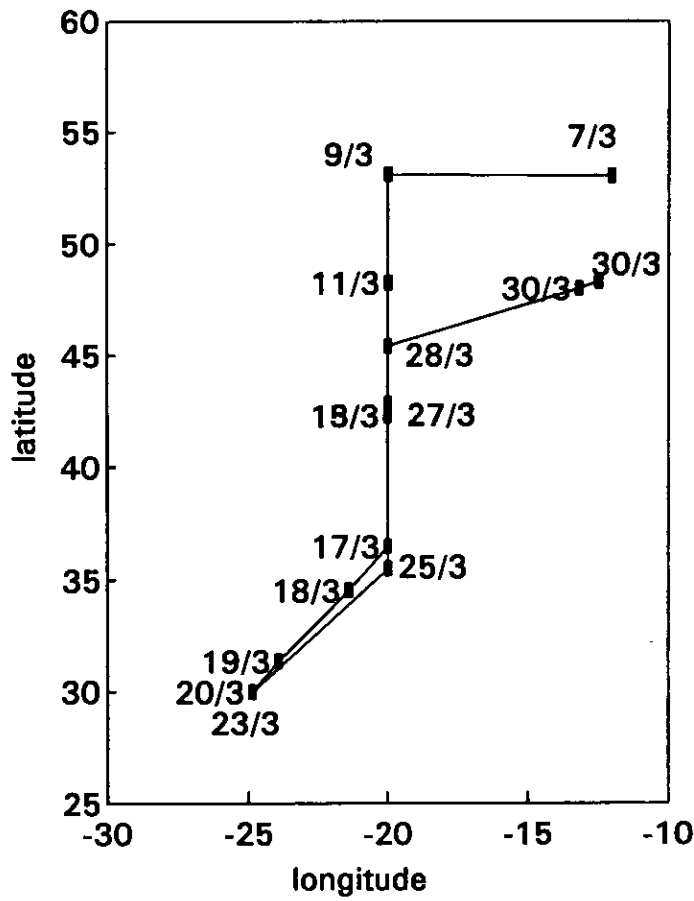
ACKNOWLEDGEMENTS

On behalf of the participating scientist I wish to thank the captain, officers and crew of the RRS Challenger, and the RVS technicians, for their generous assistance which greatly helped in making this cruise a successful one. This assistance extended to quite personal aspects such as support for one of scientists who was severely seasick; the good interactions made the cruise enjoyable and allowed us to work as well as we could.

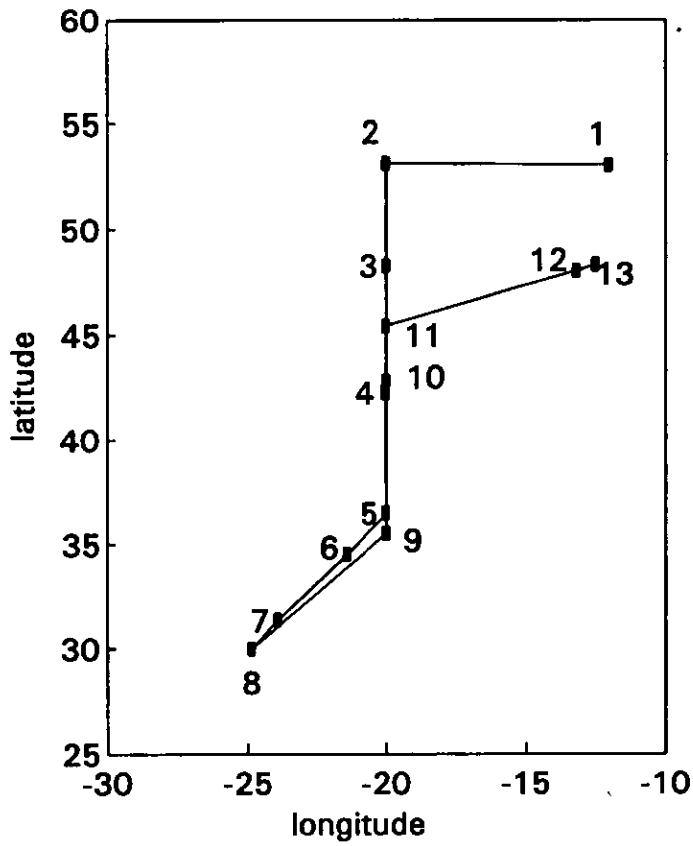
Table 1 These are the station locations and cast numbers of Challenger cruise 76/90. Please note that only one large sample (not a full profile) was collected at 1000m depth of cast 11.

Station locations						
Station#	Cast#	time	date	latitude/longitude	depth	cast-depth
1	1	15:25	7/3	53:01:40/-12:00:40	2800	0-2500
2	2	8:22	9/3	53:7:20/-19:59:35	2605	0-2595
3	3	11:06	11/3	48:15:50/-19:59:40	4410	0-4365
4	4	9:08	13/3	42:16:28/-20:1:9	3345	0-1000
	5	13:06	15/3	42:16/-20:2	3350	1000-3350
5	6	14:25	17/3	36:29/-20:0	5120	0-200
6	7	9:03	18/3	34:31/-21:25	5140	0-1200
7	8	16:20	19/3	31:22/-23:55	5365	0-70
8	9	8:55	20/3	29:59:39/-24:50:24	5370	0-1000
	10	8:16	22/3			0-150
	11	16:13	22/3			1000
	12	17:38	22/3			0-150
	13	8:27	23/3			1000-5370
9	14	12:33	25/3	35:29:54/-19:59:45	5235	300-5220
	15	16:57	25/3			0-150
10	16	15:28	27/3	42:49:54/-19:59:36	2700	0-200
11	17	11:04	28/3	45:24:54/-20:0:24	4630	0-4595
12	18	10:43	30/3	48:0:42/-13:10:0	4588	0-4573
13	19	16:42	30/3	48:18:0/-12:28:42	2765	0-2000

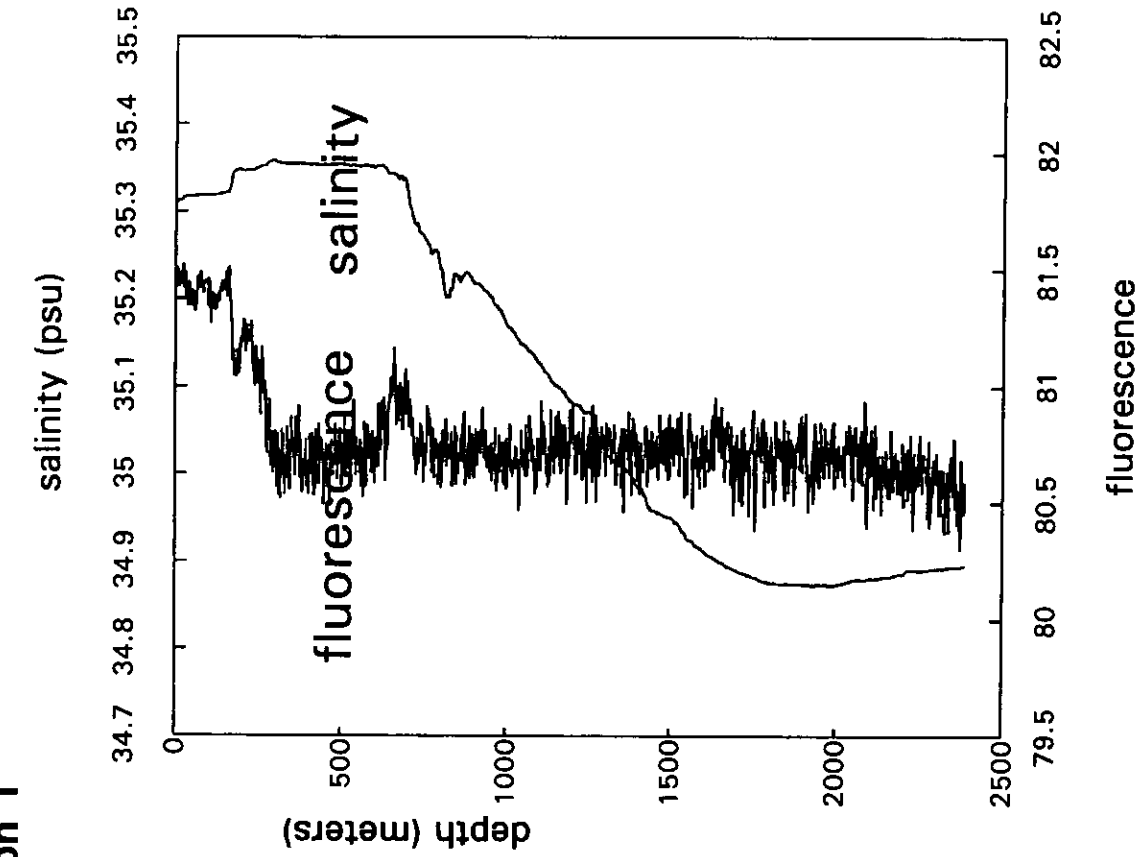
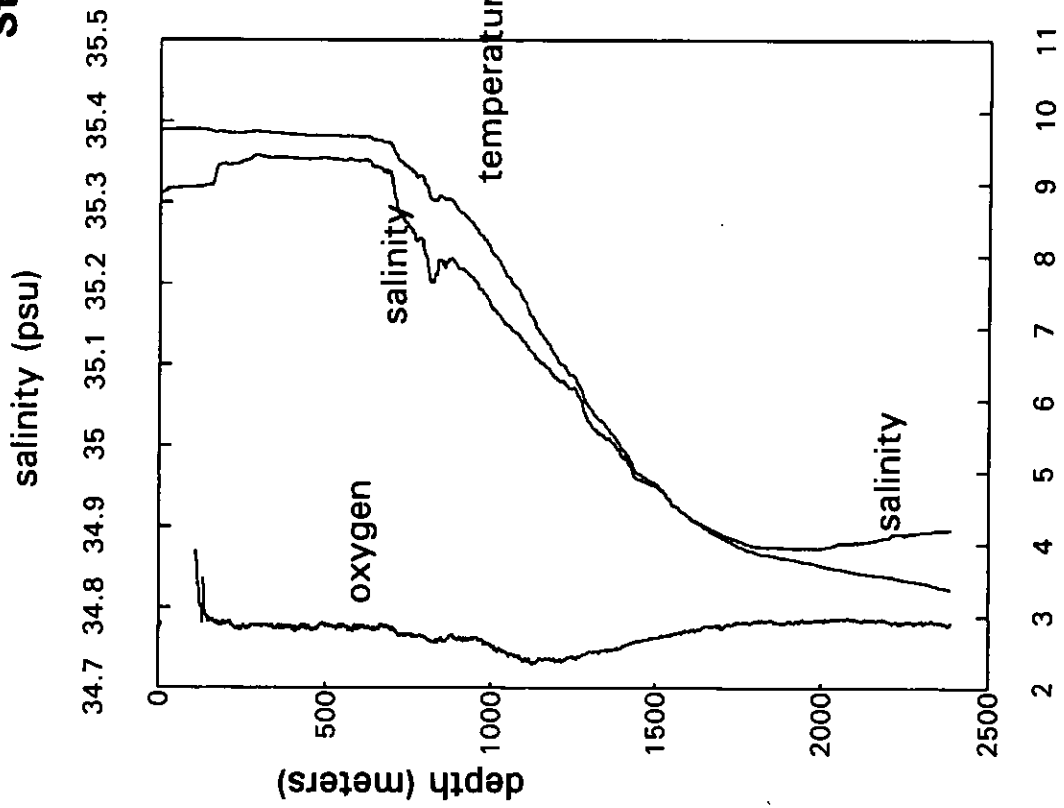
Map of station locations and dates of CH76/90



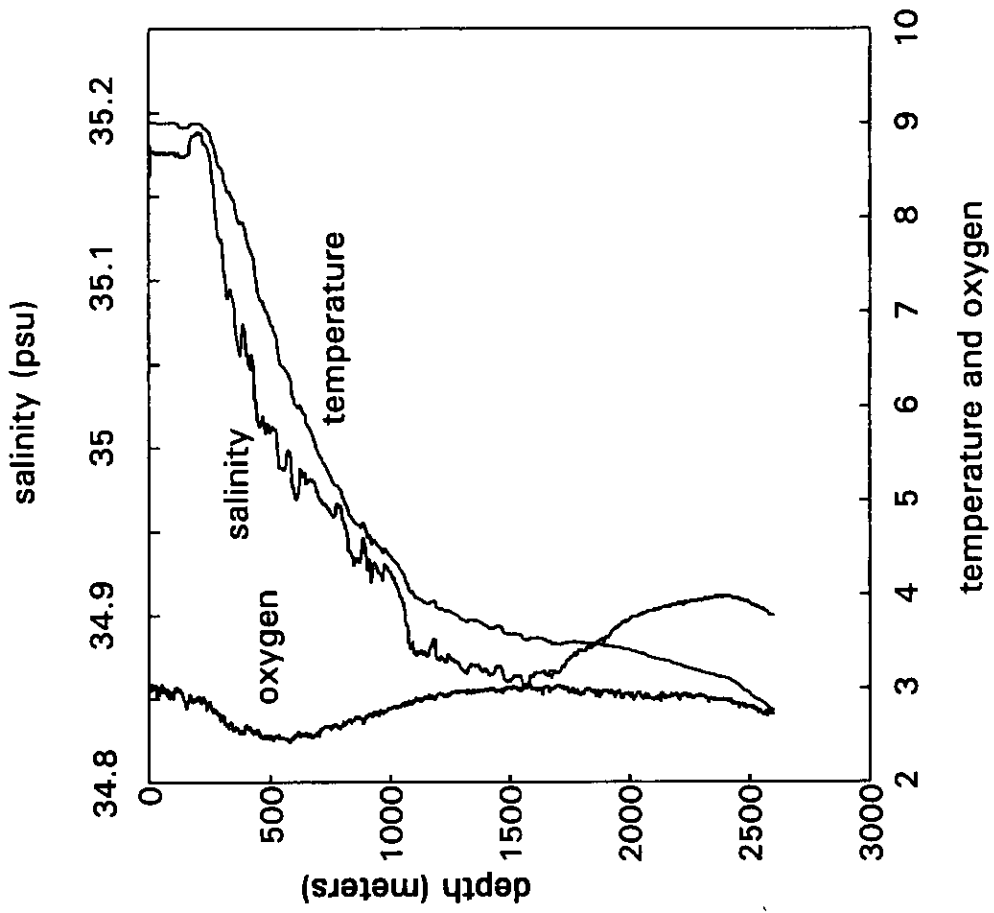
Map of station locations and numbers of CH76/90



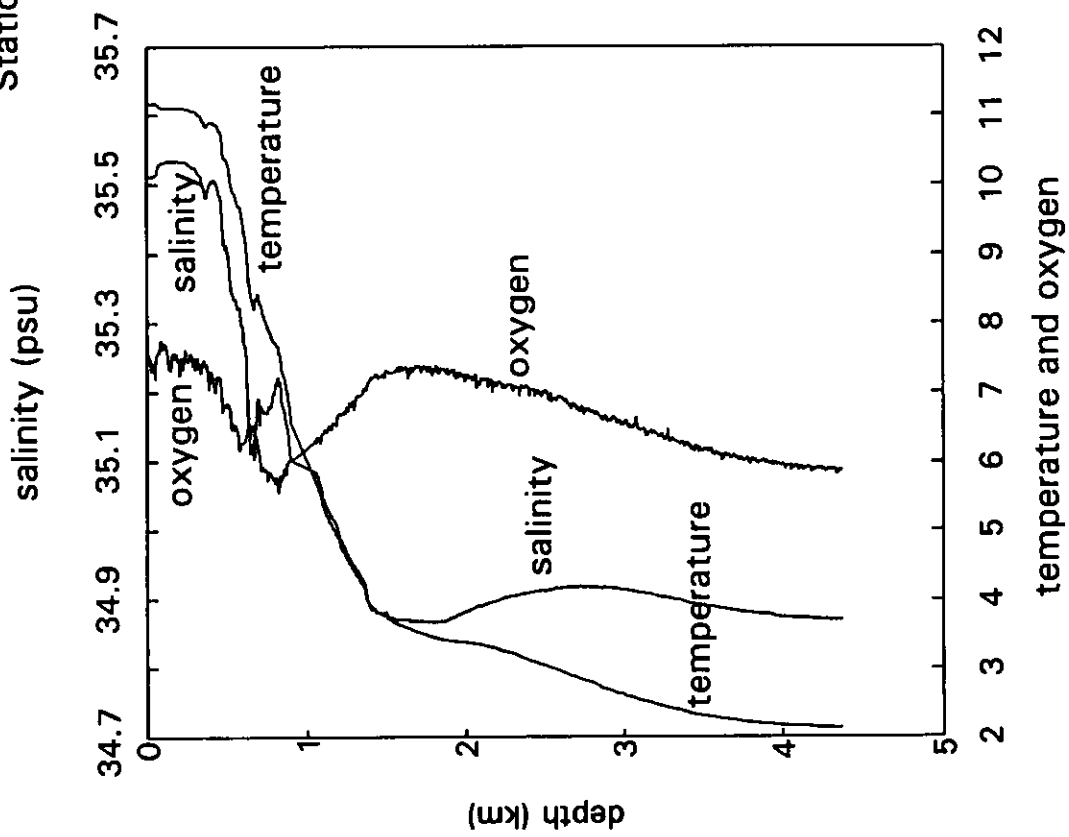
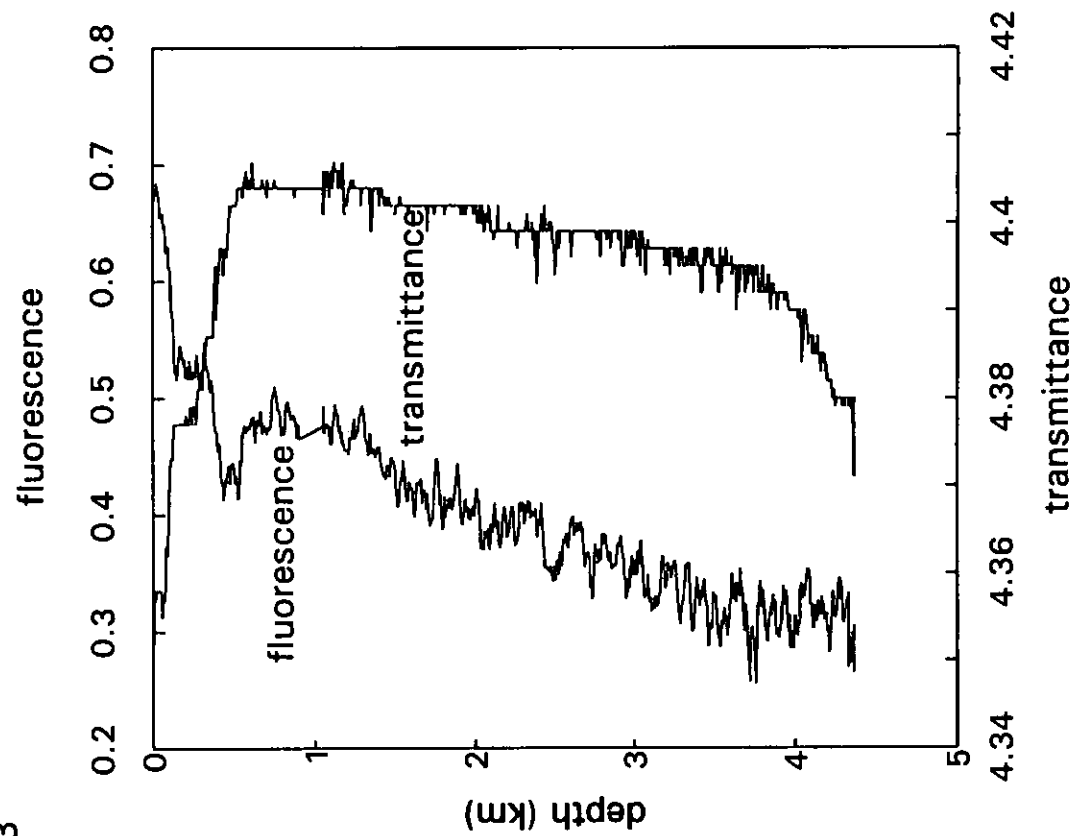
Station 1



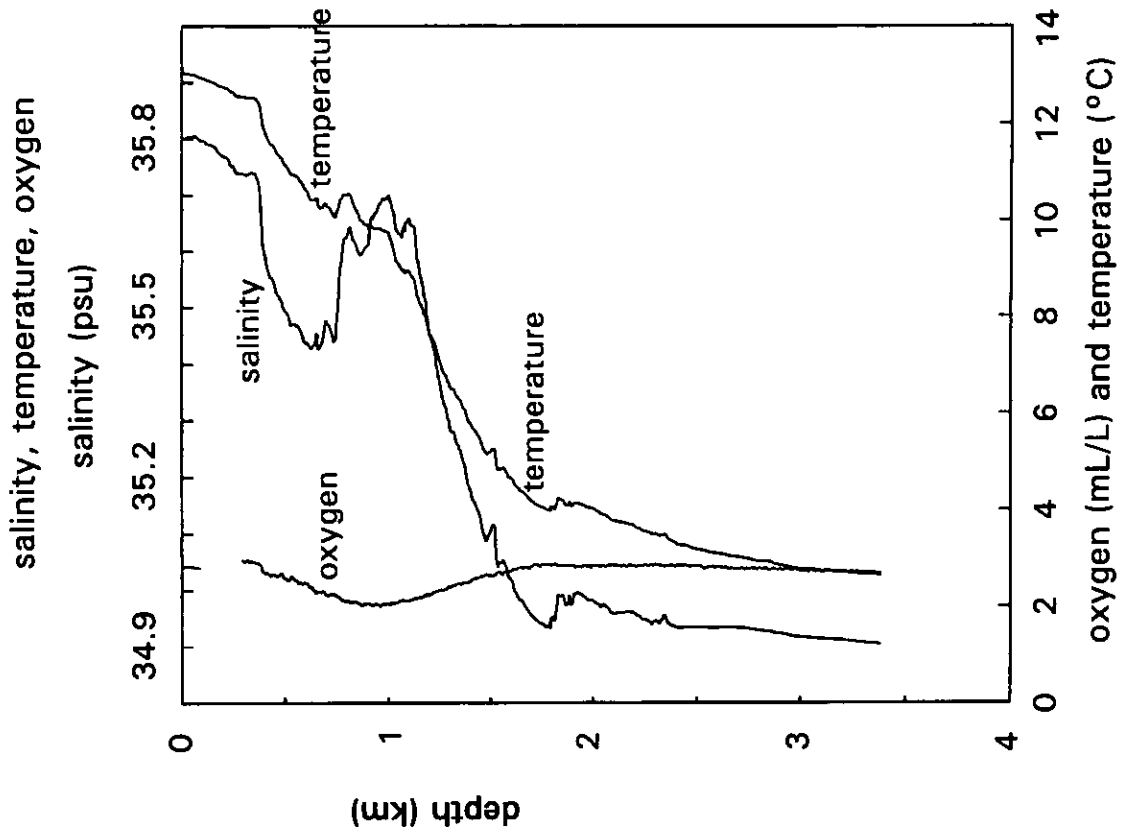
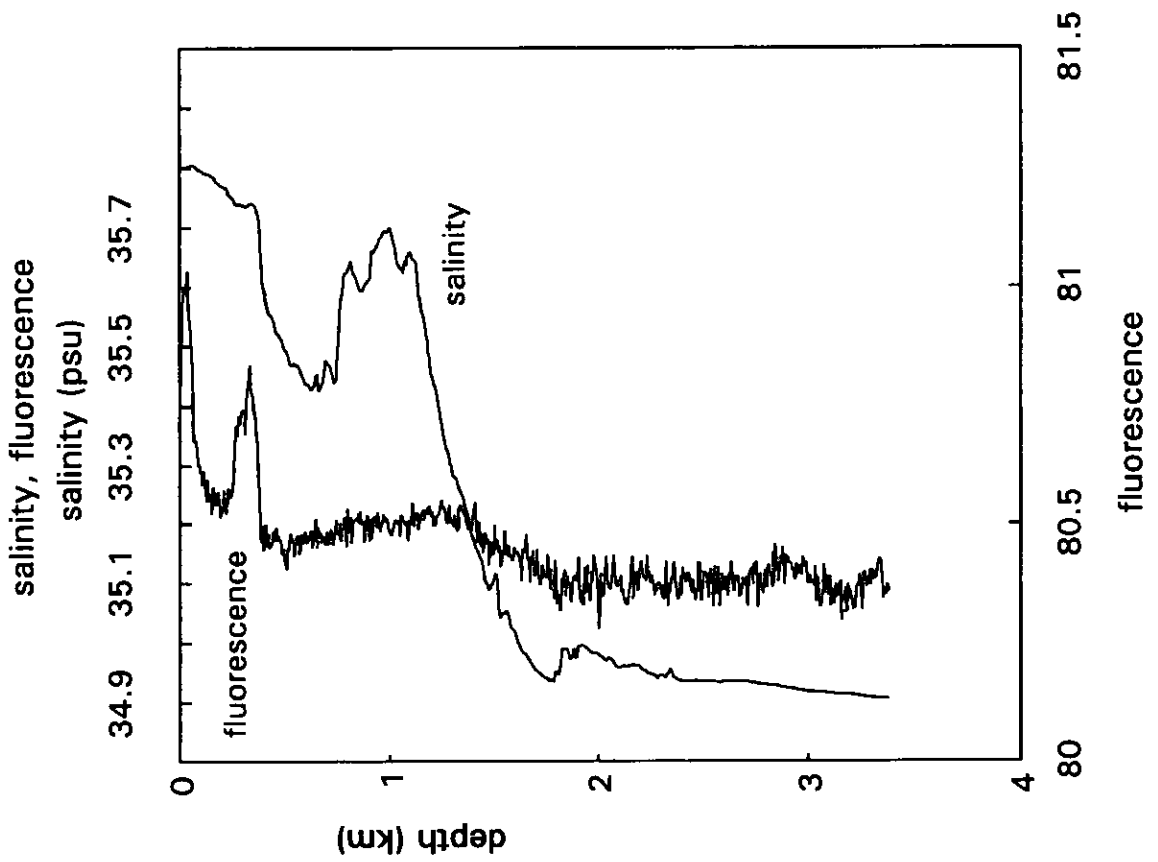
Station 2



Station 3



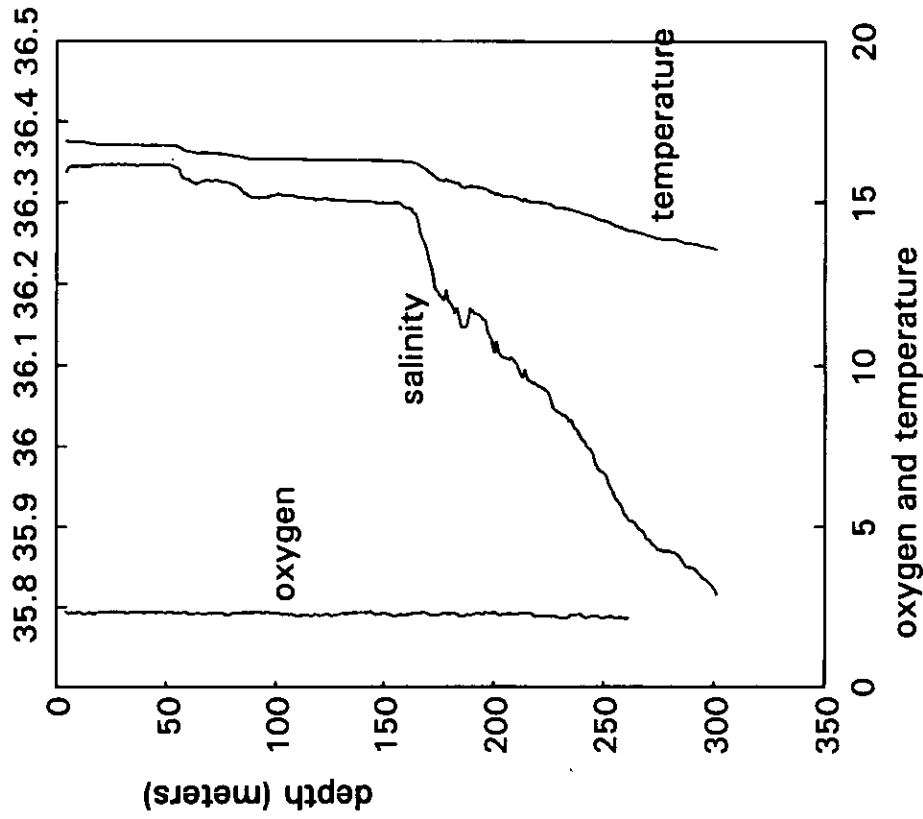
Station 4



Station 5

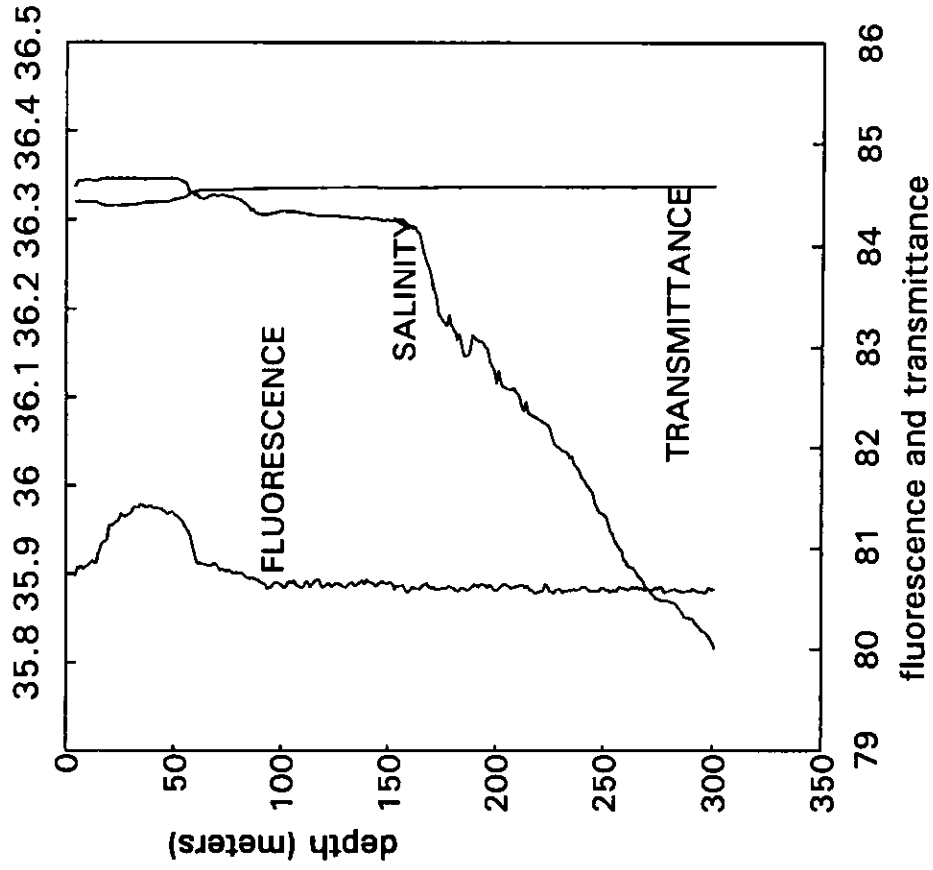
salinity, temperature and oxygen

salinity (psu)



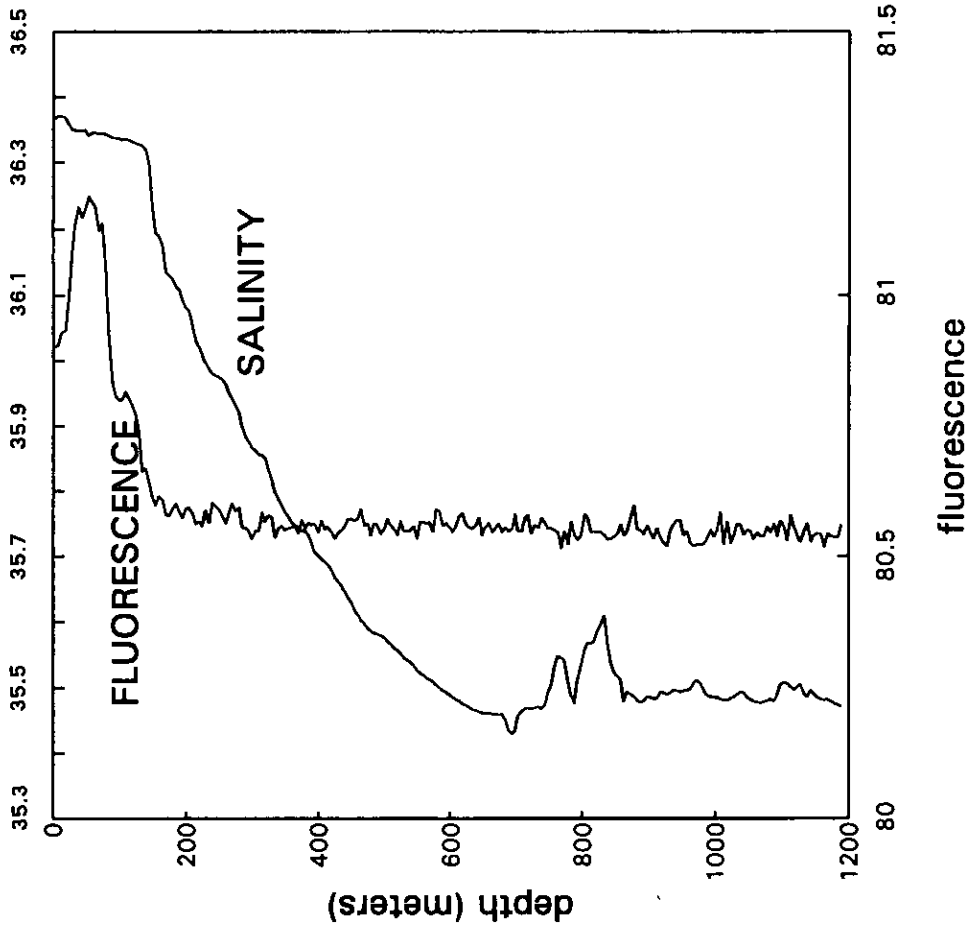
salinity, fluorescence and transmittance

salinity (psu)

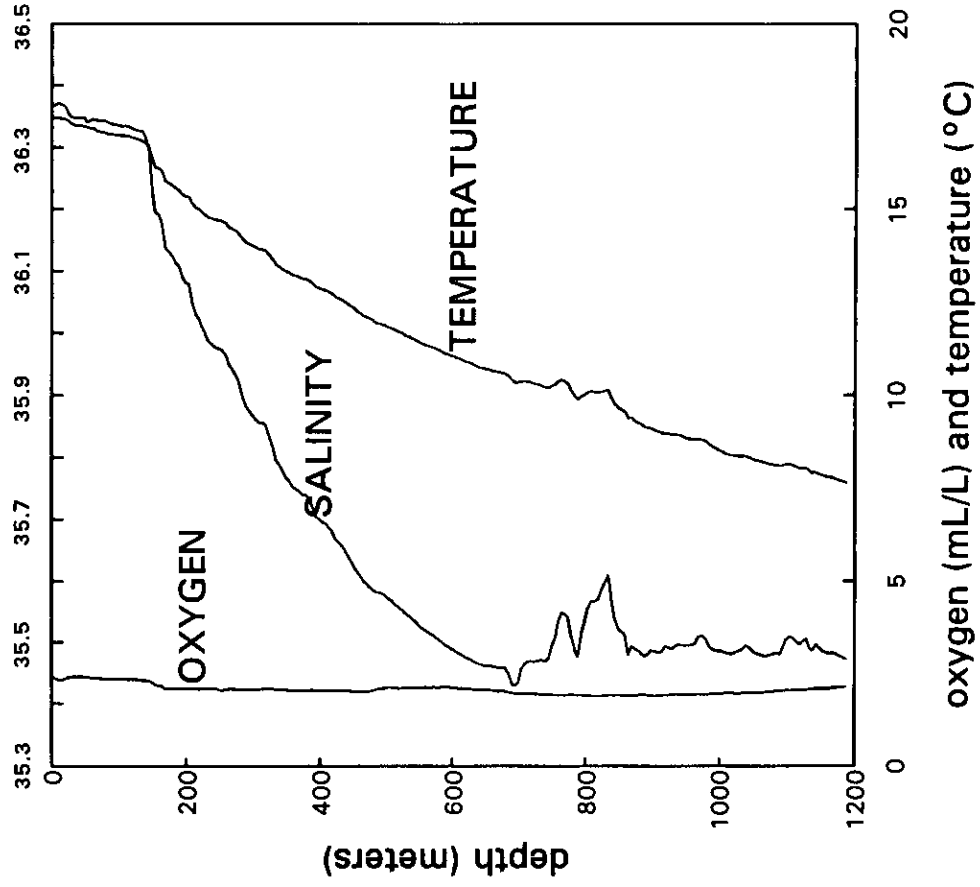


Station 6, cast 7

Salinity and fluorescence

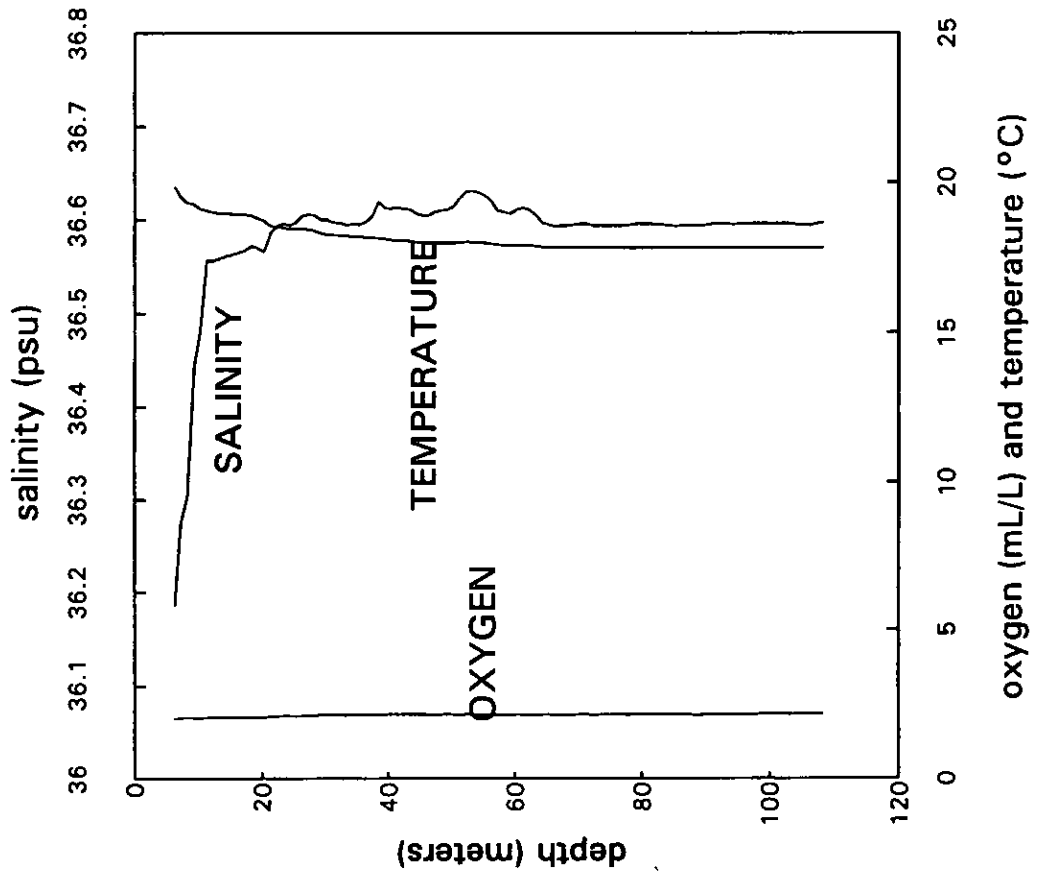


Salinity, temperature and oxygen

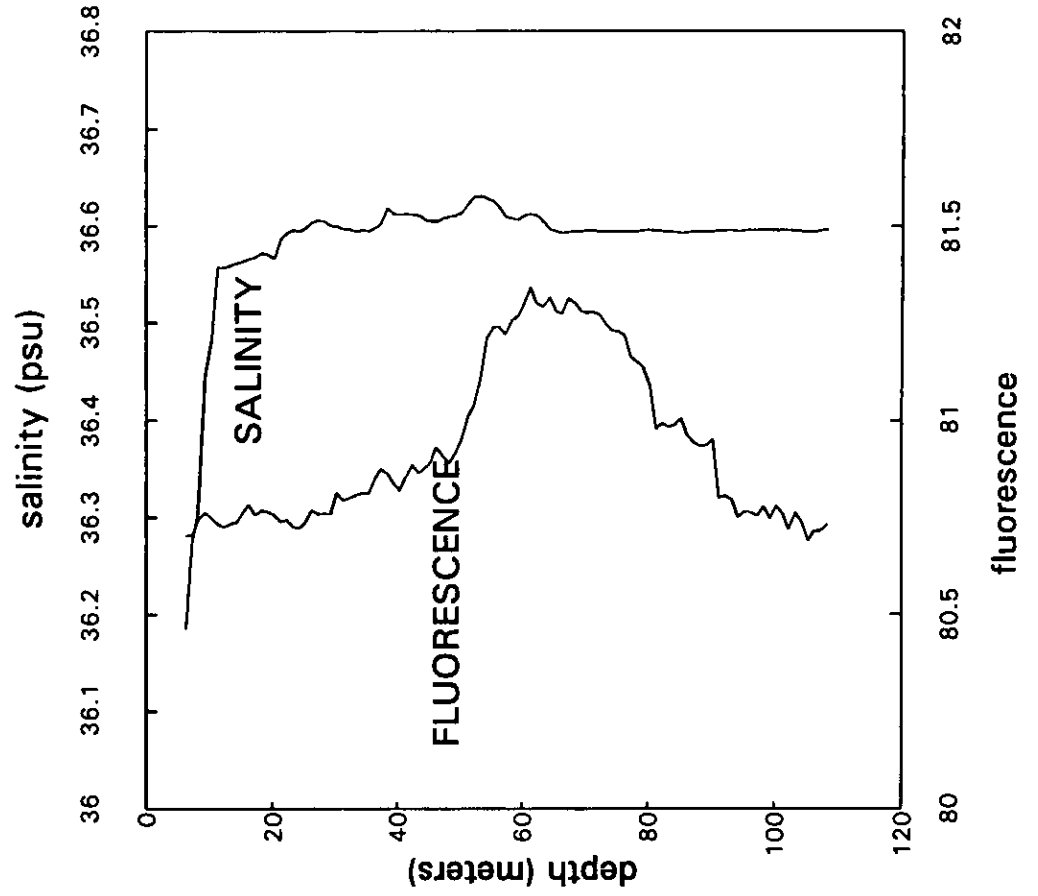


Station 7, cast 8

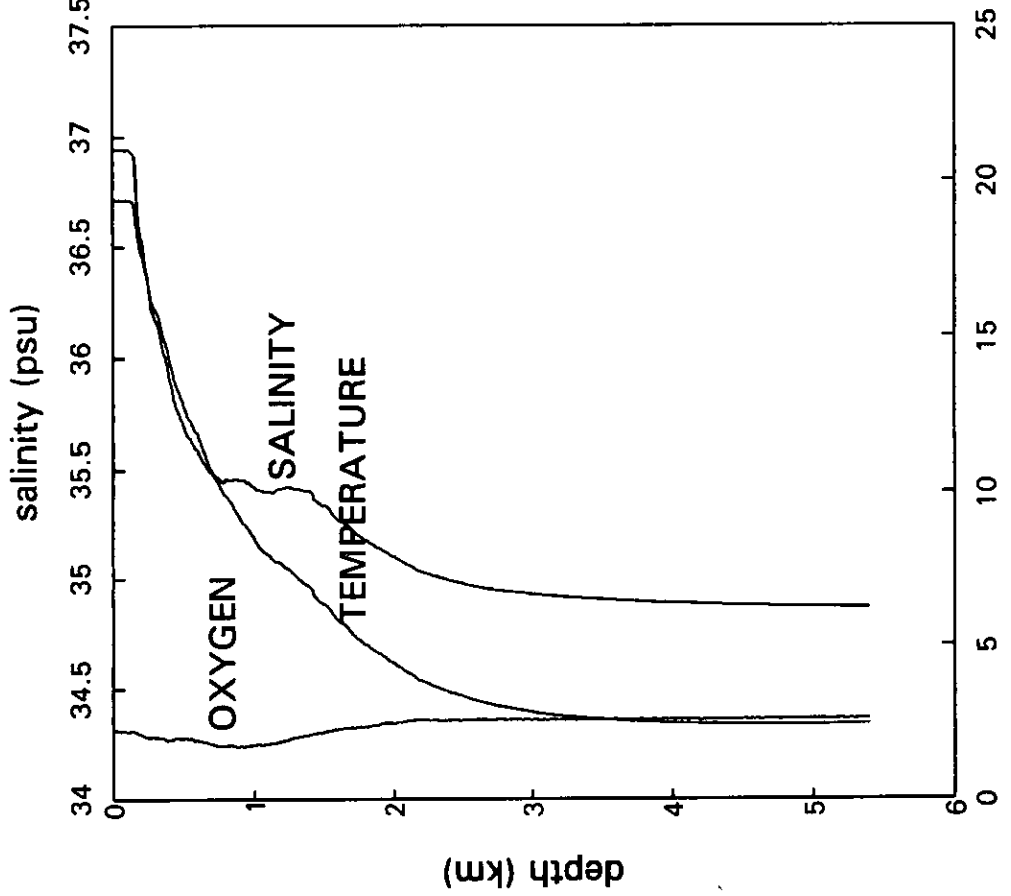
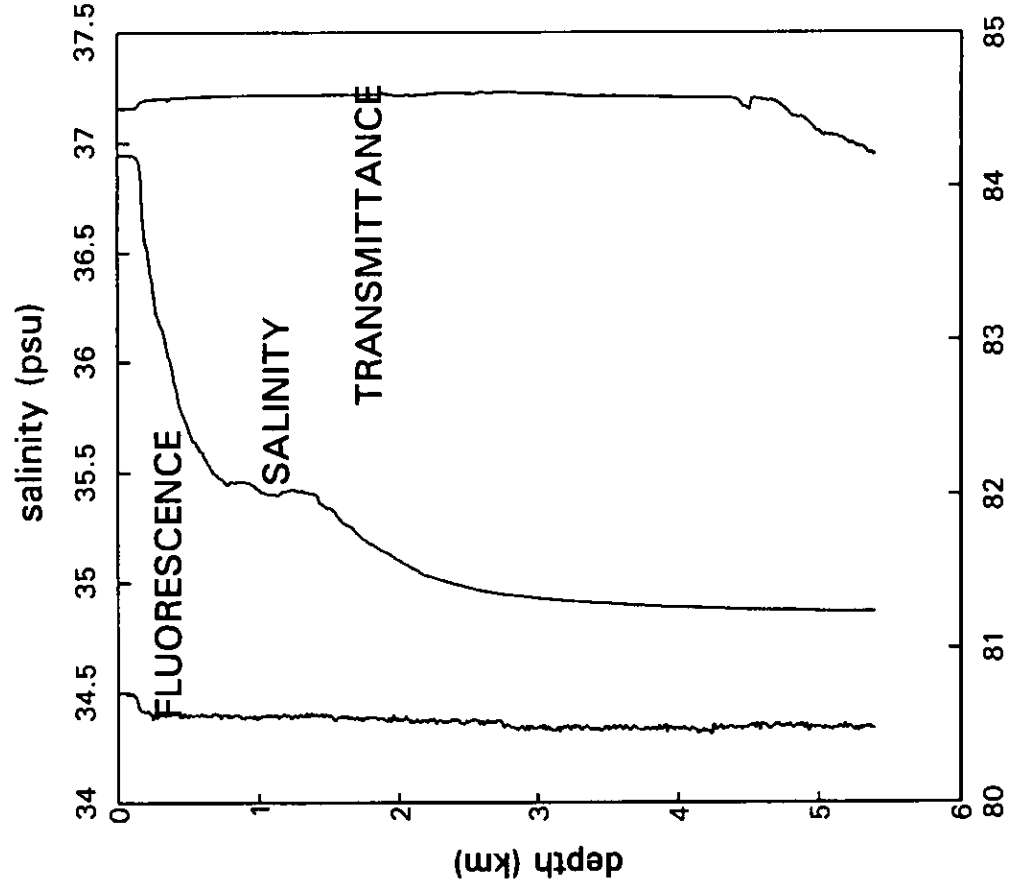
Salinity, oxygen and temperature



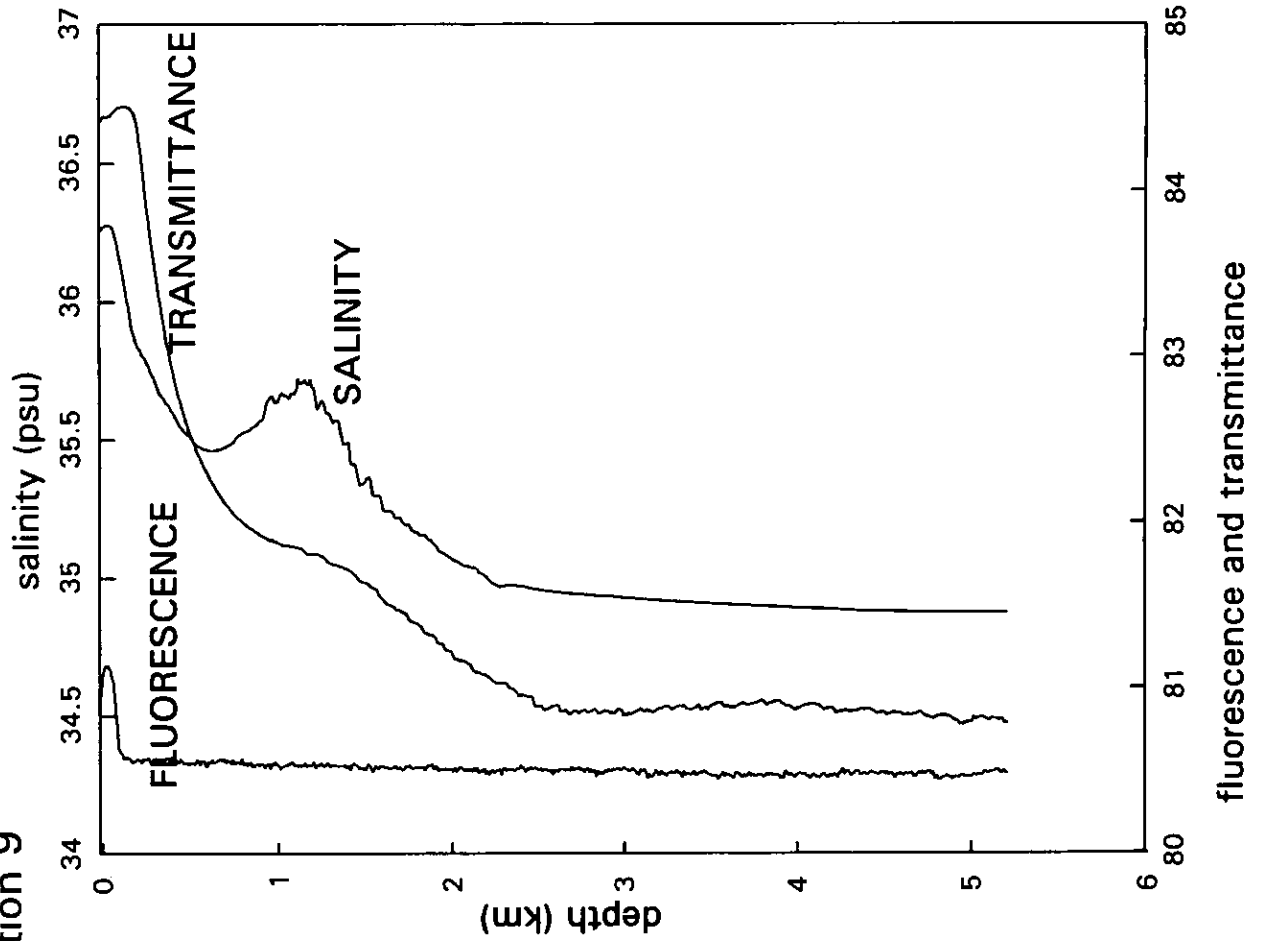
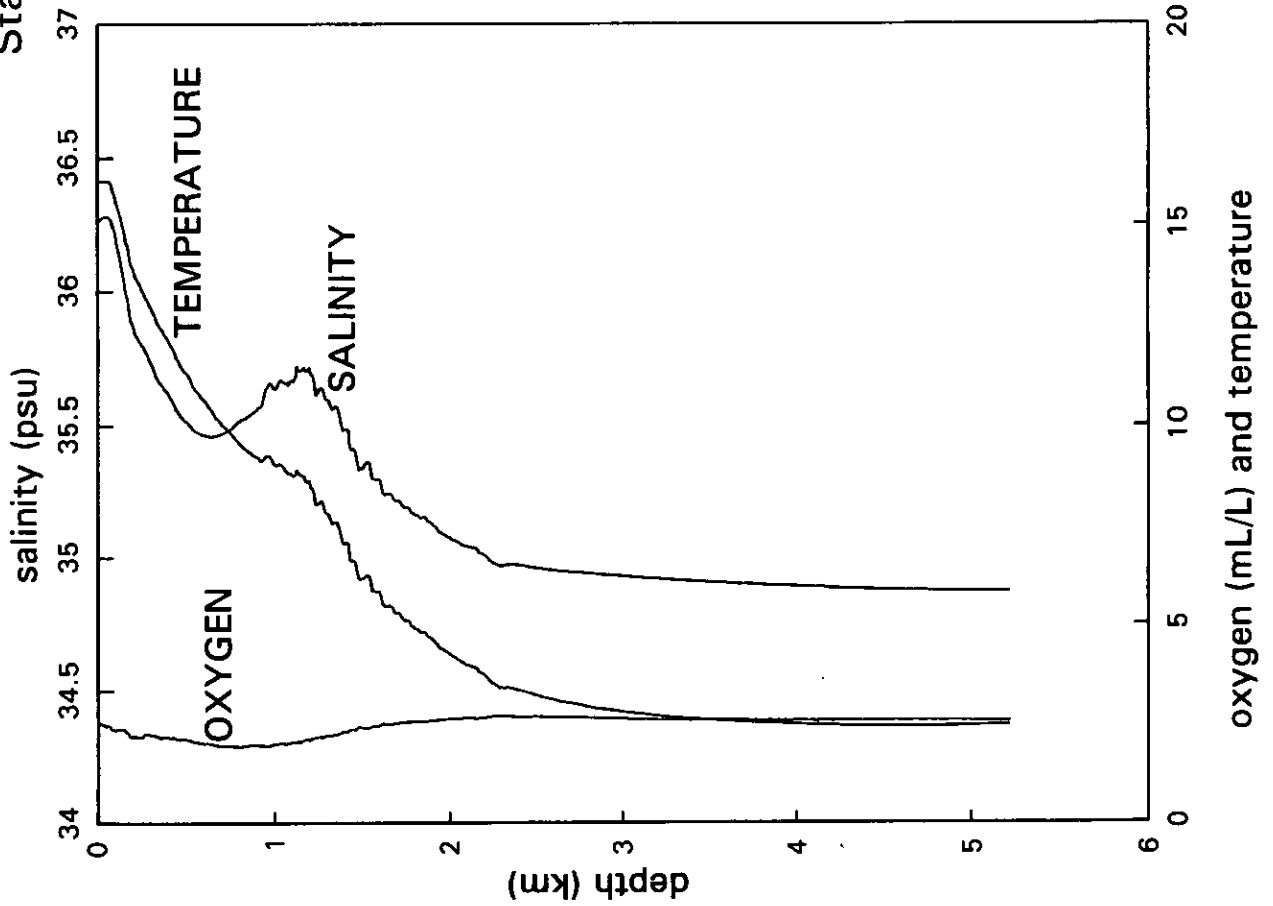
Salinity and fluorescence



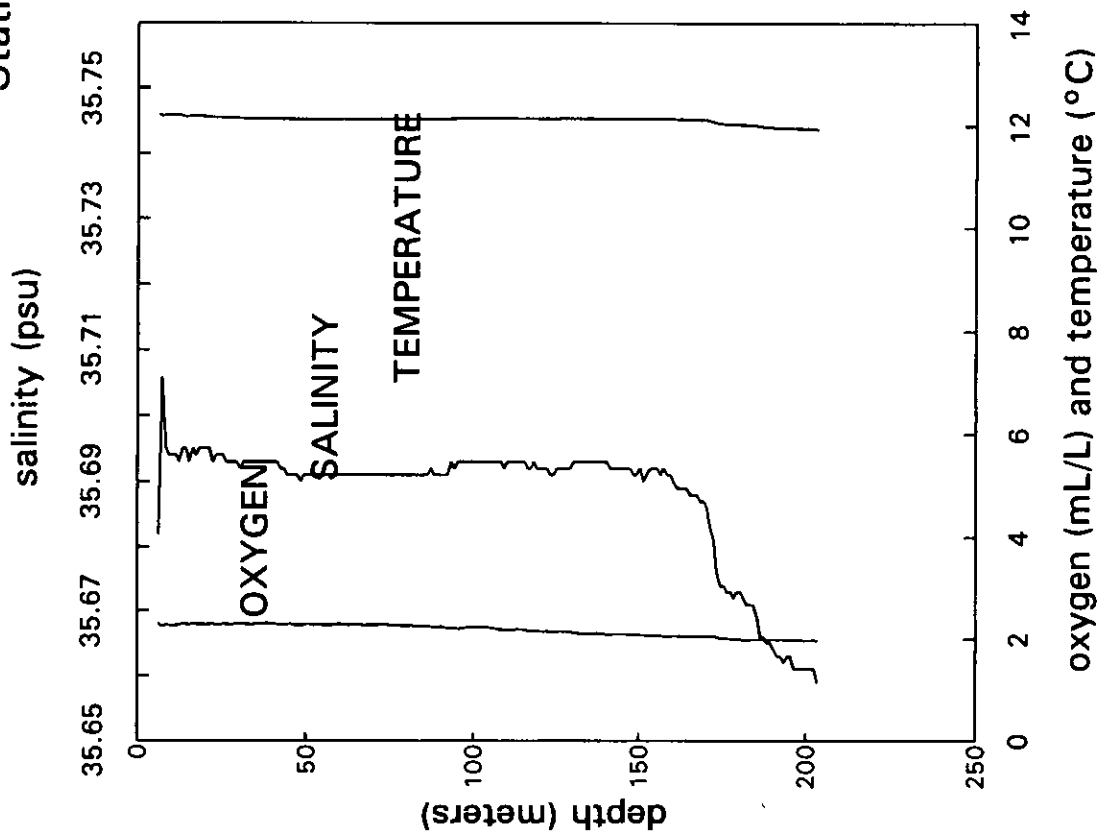
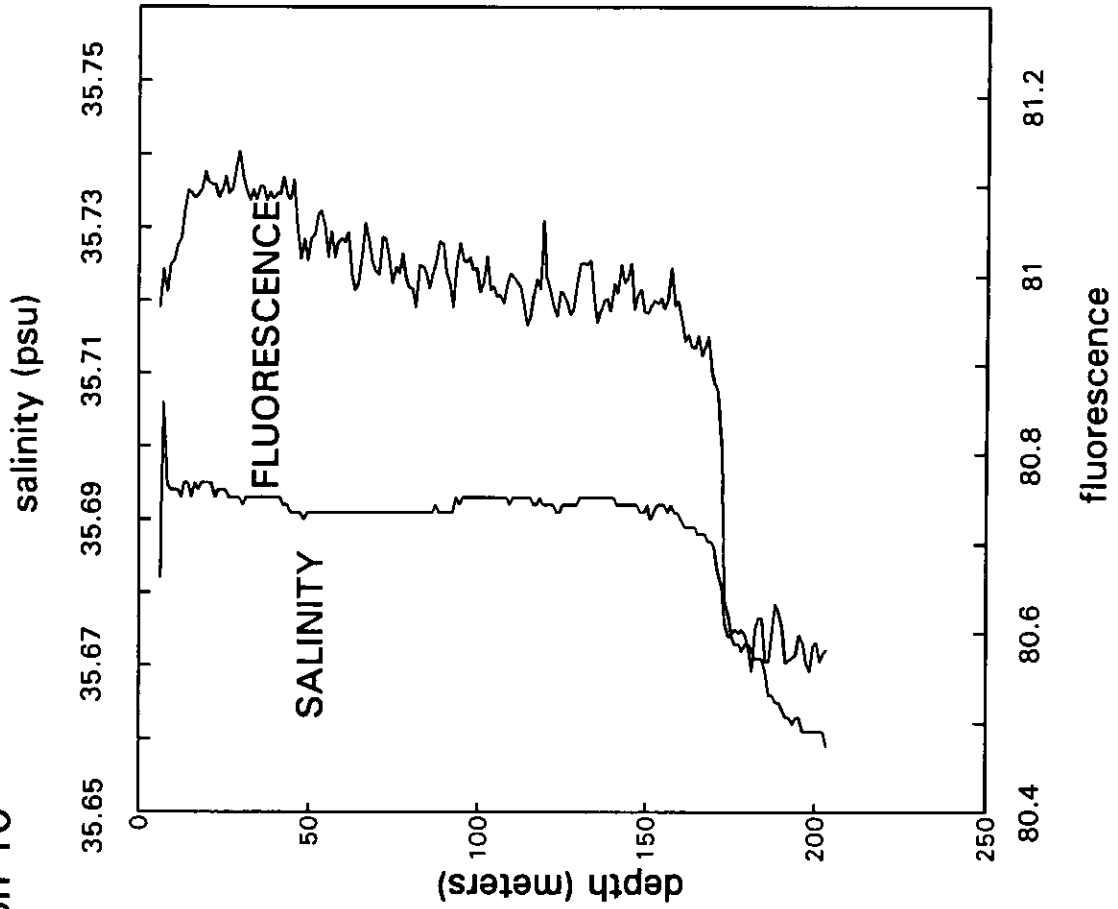
Station 8



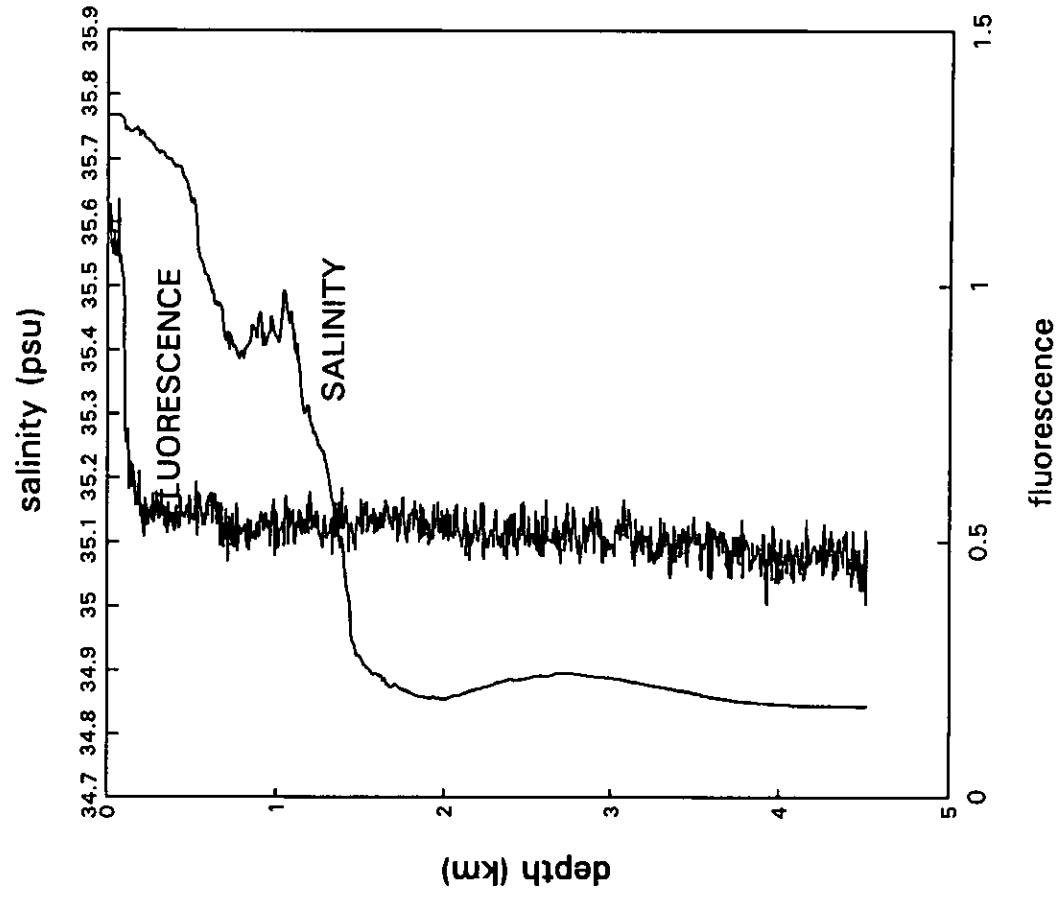
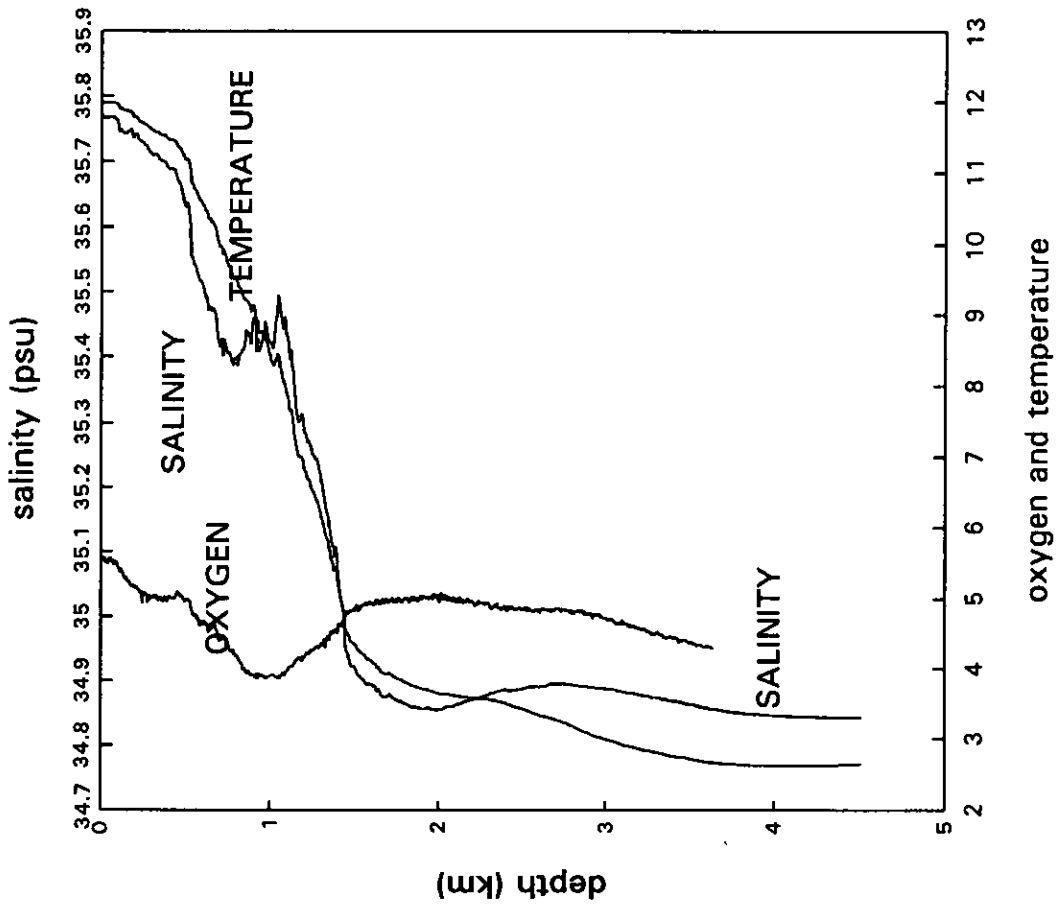
Station 9



Station 10

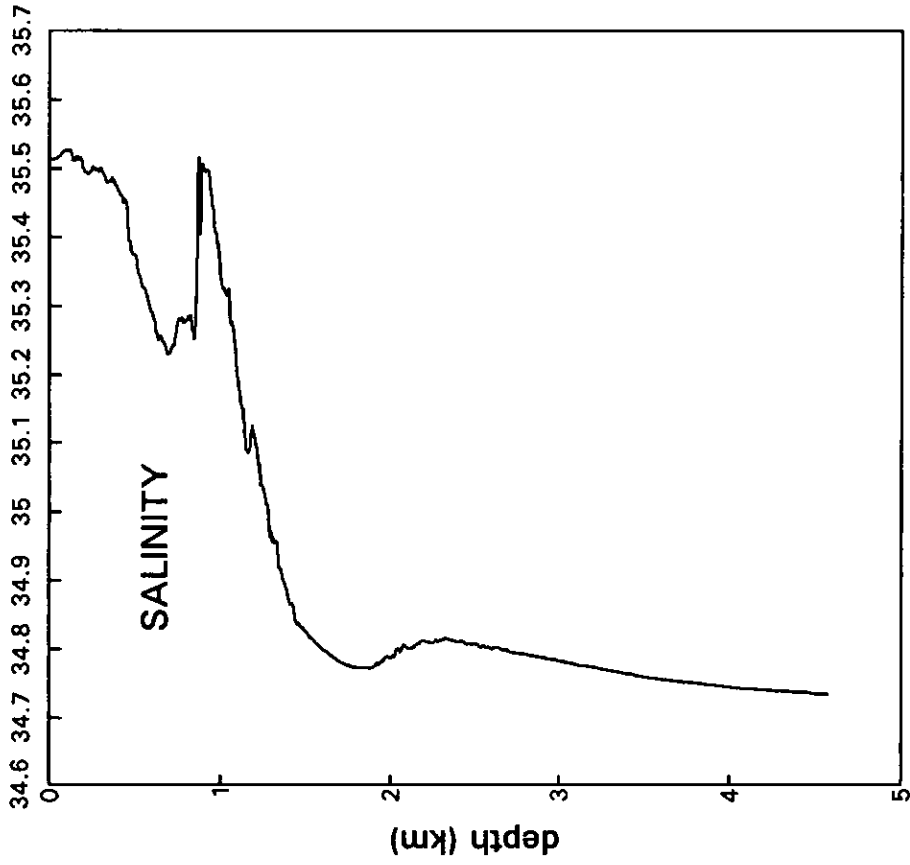


Station 11

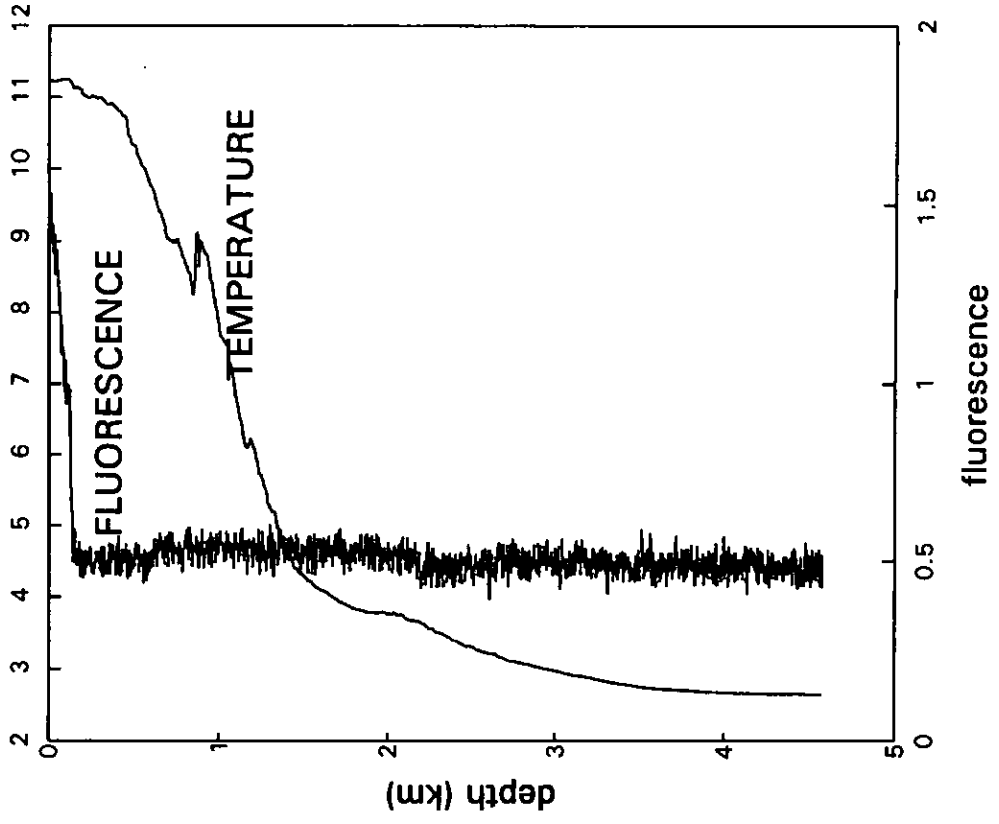


Station 12

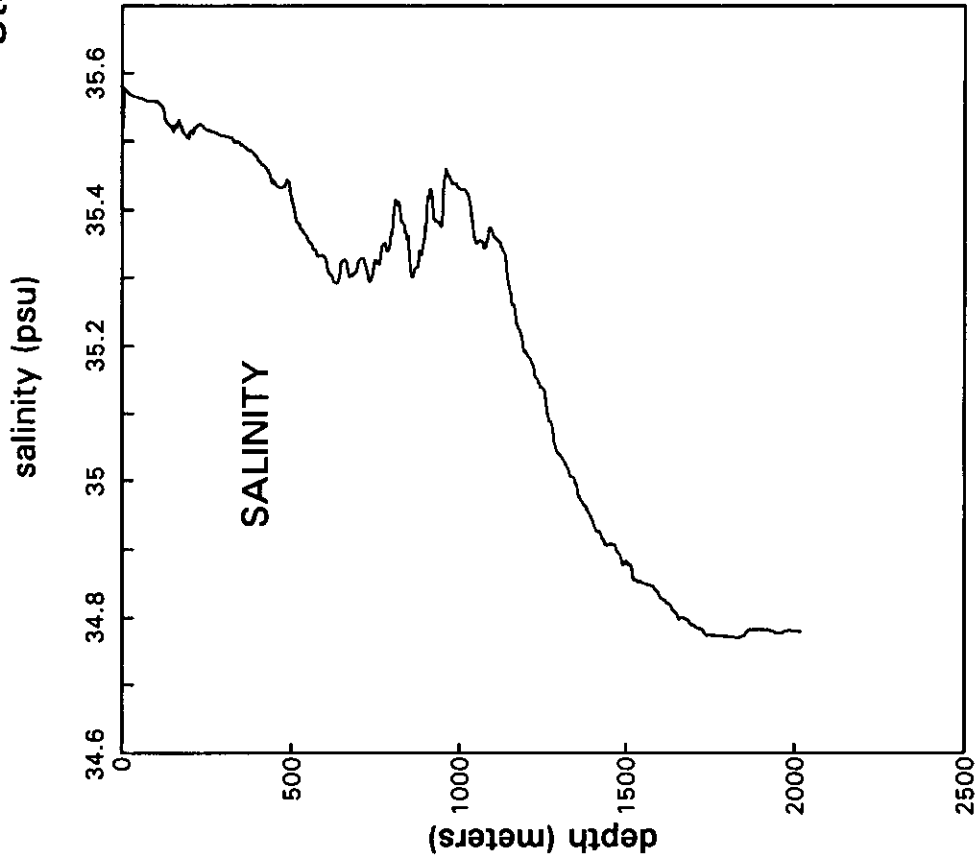
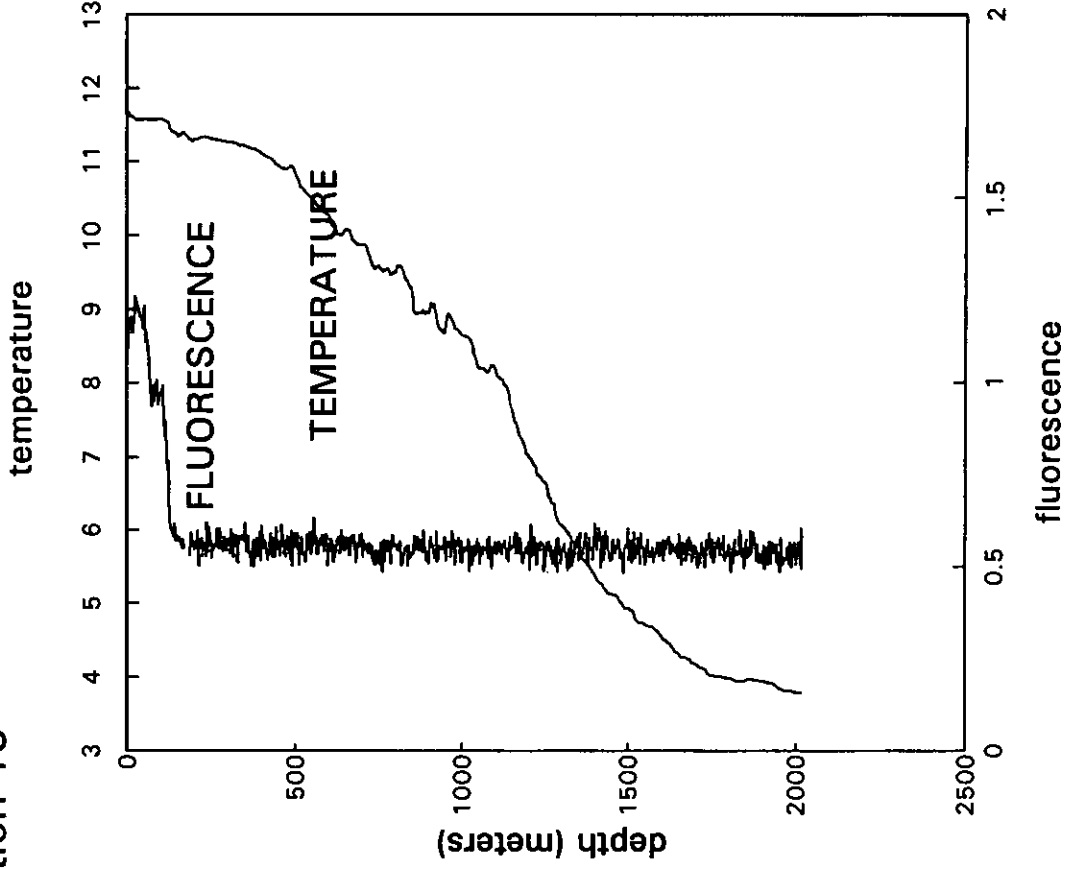
salinity



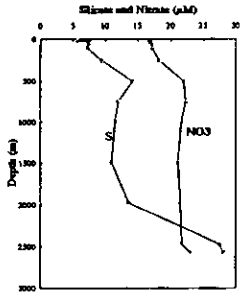
temperature



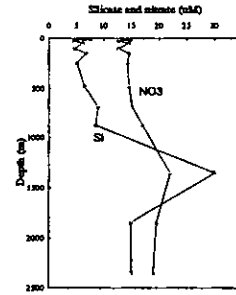
Station 13



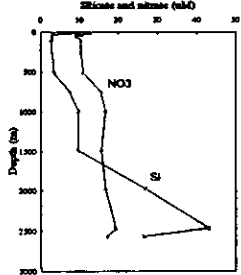
Station 2 Silicate and Nitrate (μM)



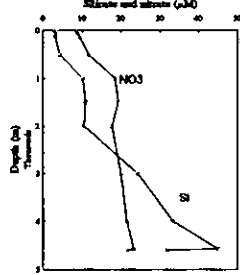
Station 1



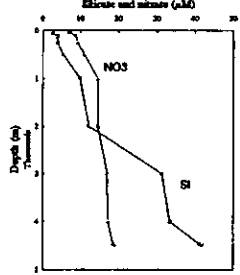
Station 3



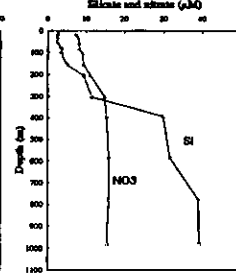
Station 11



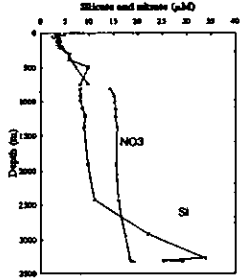
Station 12



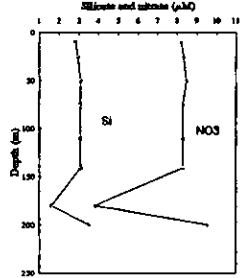
Station 13



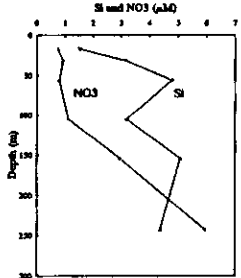
Station 4



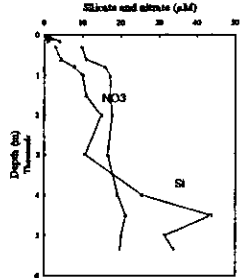
Station 10



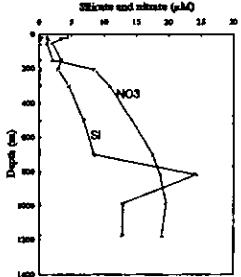
Station 5



Station 9



Station 6



Station 8

