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**A REVIEW OF MEASUREMENTS OF TRACE METALS IN  
COASTAL AND SHELF SEA WATER SAMPLES COLLECTED BY  
ICES AND JMP LABORATORIES DURING 1985-1987**

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# A REVIEW OF MEASUREMENTS OF TRACE METALS IN COASTAL AND SHELF SEA WATER SAMPLES COLLECTED BY ICES AND JMP LABORATORIES DURING 1985-1987

## INTRODUCTION

A proposal by the ICES Marine Chemistry Working Group (MCWG) to include measurements of trace metals in coastal and shelf sea waters as part of the 1985/1987 ICES Baseline Study of Contaminants in the North Sea and North Atlantic Ocean was accepted in principle by the Council in 1982 (C.Res. 1982/4:8). Plans for the baseline study were discussed at the 1984 meeting of MCWG (ICES Doc. C.M.1984/C:2). Laboratories submitting data to the baseline study were asked to use the ICES reporting format for contaminants in sea water and to send their data to ICES Headquarters for compilation on the ICES computer.

A sub-group of MCWG, convened by Dr G. Topping (UK), met during 13-14 February 1987 to assess the 1985 data (C.Res.1986/2:14). The sub-group established the basic criteria to be used in assessing the 1985 data, and made a number of recommendations to ICES concerning future submissions of data and the review of 1986 and 1987 data sets at the 1988 and 1989 MCWG meetings. The report of this sub-group was presented to the ICES Advisory Committee on Marine Pollution (ACMP) in 1987, following discussion and amendment at the 1987 MCWG meeting.

Since a final report on this baseline study could not be completed within the normal time period allocated to a MCWG meeting, it was decided to convene an *ad hoc* Group of MCWG to prepare a report on this baseline study (C.Res.1989/2:13:10). The Group, consisting of Dr G. Topping (UK, Chairman), Dr W. Cofino (Netherlands), Dr P. Yeats (Canada), Dr D. Schmidt (Germany), and Dr P. Balls (UK), met during 5-9 February 1990 at ICES Headquarters at Council expense.

The results of this study provide an improved perspective to that given in a much earlier ICES report (Topping *et al.*, 1980) that attempted to assess the baseline distributions of trace metals in sea water throughout the entire ICES area.

## APPROACH TO THE REVIEW

Prior to the Council's decision to convene the *ad hoc* Group, Dr S. Wilson (ICES) distributed data sets to members of the Group. Each member was assigned the task of assessing data quality for one of the five main metals (cadmium, copper, lead, mercury, zinc). Dr D. Schmidt similarly distributed sub-sets of data collected during the ZISCH (Zirkulation und Schadstoffumsatz in der Nordsee) project.

The criteria to be used in the pre-meeting assessments were those agreed by MCWG at its meeting in 1989, namely:

- a) The review would be confined to data based on measurements in samples of sea water with a salinity of  $> 20$  in all areas other than the Baltic Sea and the Kattegat.
- b) Only data for filtered samples would be considered, unless the concentration of suspended particulate material (SPM) in unfiltered samples was  $< 1$  mg/litre.
- c) Laboratories submitting data should have successfully participated in the ICES inter-comparison exercises for metals in sea water (i.e., 5/TM/SW, Berman *et al.*, 1986; and 6/TM/SW, Berman and Boyko, 1987).
- d) Comparability of data would also be assessed on the basis of results for samples collected at ICES reference stations.
- e) In the absence of fulfilment of (c) and/or (d), the data quality would be assessed by peer review, i.e., the *ad hoc* Group's knowledge of trace metal levels in the relevant sea areas based on publications in recent research reports.

Each member of the *ad hoc* Group was requested to examine the data in accordance with the above

criteria, and to provisionally identify data which could be used to:

- a) Prepare box-and-whisker plots for each metal, for each salinity range and for each area.
- b) Examine the relationship between salinity and dissolved metal concentrations for those areas where there were sufficient data points along the salinity gradient.

It was clear from the presentation of the pre-meeting work that each member had adopted a slightly different approach to this task. Therefore, in order to have a uniform approach to data selection and analysis, it was necessary for each data set to be incorporated into a single data-management/analysis system. For this purpose, the REFLEX® software used by Dr Cofino was selected and used in conjunction with other PC data analysis software. Before commencing the final data analysis, the Group re-examined the criteria to be used for the final selection of data.

## SELECTION OF DATA

Although the Group agreed that the original MCWG criteria were still relevant, it considered that their rigorous application would effectively eliminate the data for some laboratories, and almost all of the ZISCH data, since these were based on measurements made on unfiltered samples for which there were no SPM data. In the absence of SPM data, it was difficult to assess the contribution of particulate metal to the "total" metal concentration. Since the ZISCH (Kersten *et al.*, 1988) data set was one of two sets which covered the offshore areas in the main body of the North Sea, there was some reluctance on the part of the Group to eliminate it from the review. It was, therefore, proposed to adopt a pragmatic approach by reviewing ZISCH measurements on unfiltered samples against SPM data which had been reported for the North Sea in 1986 by the ZISCH geology and mineralogy team (see Project G2, "Zirkulation und Schadstoffumsatz in der Nordsee, BMFT-Projekt MFU 0545, 2. Zwischenbericht, 01 01 86-31 12 86", University of Hamburg, June 1987).

Following an examination of the relevant contour maps of SPM, it was agreed that, where the maps indicated time-averaged SPM levels at < 2 mg/litre, ZISCH data for unfiltered samples from such loca-

tions in North Sea areas could be included in the study. The relevant areas are those in Figure 1 identified by the following codes: NS1, NS2, NS3A, NS6, SKAG, NS7A and NS7B.

It was also decided to include data on unfiltered samples from other laboratories which had reported that their decision not to filter was based on the results of separate studies which had shown that the waters sampled contained low SPM concentrations.

Since it was agreed that the presence of SPM was unlikely to have significant effects on measurements of dissolved cadmium in unfiltered samples of sea water, the Group decided to include all measurements of cadmium in the data evaluation.

Finally, it was agreed to restrict the study to consider only those data for samples in the 0-10 m depth interval as insufficient data were available from depths > 10 m for any meaningful comparisons to be made.

## PRESENTATION OF DATA

The Group decided that a spatial breakdown of the data based on a number of defined areas was appropriate. Data density and coverage were insufficient for application of the ICES statistical rectangle grid. However, a spatial breakdown of data based on the hydro-biological sub-divisions defined in the ICES study of flushing times of the North Sea (ICES, 1983) was considered. Additional sub-divisions were (arbitrarily) defined for the other ICES regions. The sub-divisions used for the North Sea, English Channel, Skagerrak and Kattegat areas correspond closely to those subsequently adopted by the North Sea Task Force (NSTF) for its monitoring activities. It should be made clear that, although the data set contained information from the Baltic Sea, this was exclusively from the southern and southwestern part of the Baltic Sea (see Figure 2). One data set (laboratory BIOC) was also reported for a section across the Scotian Shelf (east coast of Canada), but is not considered further in this report.

The individual geographical sub-divisions are shown in Figure 1. Since not all sub-divisions were uniformly surveyed, Figure 2 is included to indicate the actual sampling locations. The tendency for sampling locations to be concentrated close inshore will mean that average concentrations reported for

a sub-division may not accurately represent average concentrations for the whole sub-division. This is an important consideration to be borne in mind should this report be used in the preparation of quality status assessments. For such purposes, only data corresponding to high salinity waters are suitable.

## RESULTS

The names, addresses and ICES codes of laboratories that submitted data on measurements of metals in coastal and shelf sea waters of the North Atlantic area are given in Annex 1.

The sampling areas, identified by the codes given in Figure 1, and the identification of the individual laboratories which collected samples for measurements of Cd, Cu, Pb, Hg, and Zn are given in Table 1.

### Box-and-Whisker Plots

The data were explored using "Notched Box-and-Whisker Plots"; an explanation of this plot is included at Annex 2. The relevant plots for Cd, Cu, Pb, Hg, and Zn are given respectively in Figures 3, 8, 11, 15 and 19. Each figure contains a series of box-and-whisker plots for each area for each of three salinity ranges (20-25, 25-30 and >30), with an additional figure showing the data from the Baltic Sea/Kattegat areas.

Summary statistics of these data (consisting of average concentrations of each metal for each area, standard deviations of these concentrations, and number of samples for each location) are also given in numerical form in Tables 2, 3, 4, 5 and 6, respectively.

### Metal versus Salinity Relationships

Because of the limited number of measurements along the salinity gradient in some areas, detailed investigations of the metal-salinity relationships were only attempted for a few selected areas. Relevant plots and descriptive statistics are given in Figures 4-7 (cadmium), 9-10 (copper), 12-14 (lead), 16-18 (mercury), and 20-21 (zinc).

The main value of metal-salinity relationships for this report is to help to describe the metal distributions found in a sub-division. In estuarine regions,

these relationships can also be used to estimate net inputs of metals from the estuary (GESAMP, 1987). This aspect of the ICES data set has not been fully investigated and could provide a profitable avenue for further work.

## DISCUSSION

### Cadmium (Cd)

The Cd data displayed in Figures 3a-d are based on 1,771 results from 14 different laboratories for all 21 geographical areas. Average concentrations of Cd in samples for each area according to eight different salinity classes are given in Table 2. In general, the agreement among laboratories for any sub-division is good.

The Cd concentrations for the higher salinity range of 30-35, displayed in Figure 3a, and average concentrations for the salinity ranges 30-35 and >35, in Table 2, show a decrease from 0.03-0.05  $\mu\text{g/l}$  in the coastal waters to 0.01-0.02  $\mu\text{g/l}$  in the central and northern parts of the North Sea. These values are consistent with recent literature values for these regions (see Table 7).

The waters to the south and west of Britain (0.03 - 0.07  $\mu\text{g/l}$ ; CHNL, CELT, IRSH and WESC) and off the northern coast of Spain (0.05-0.09  $\mu\text{g/l}$ ; BISC and IBER) appear to have higher concentrations than those of the North Sea. These findings do not agree well with the literature data for waters to the west of Britain, which generally show Cd concentrations < 0.020  $\mu\text{g/l}$ , and for the Irish Sea and English Channel, where a value of *ca.* 0.025  $\mu\text{g/l}$  has been reported (Table 7). The ICES Fifth Round Intercalibration sample (Berman *et al.*, 1986), collected in nearshore waters of the Bay of Biscay off St Nazaire, France (salinity 35.4), had a Cd concentration of 0.020  $\mu\text{g/l}$ . These apparent discrepancies between the baseline and literature data result partly from differences in sampling location; in general, the baseline samples were collected from nearshore locations, while those referred to in the literature (Table 7) mostly concern samples taken further offshore. One ICES baseline data set, based on samples collected from the Scotian Shelf, North-west Atlantic waters, gave an average Cd concentration of 0.015  $\mu\text{g/l}$  for waters of salinity >30.

Many of the laboratories collected samples in high salinity waters from the same area for at least two

of the three years covered by the baseline survey. If average Cd concentrations and standard deviations for these yearly surveys are compared, for the 24 examples where at least six samples with salinities  $> 33$  were collected in an area, no significant between-year differences are observed.

The Cd concentrations for salinity ranges 20-25 and 25-30 are noticeably higher, and show more variability from area to area, than those for the salinity range 30-35 (see Figures 3c and 3b and Table 2). This is perhaps an indication of the influence of inputs of cadmium from estuaries into the adjacent coastal areas. The relevant Cd concentrations in Baltic waters are relatively low, similar to those found in offshore North Sea waters, and somewhat less than those reported in the literature, e.g.,  $0.03 \mu\text{g/l}$  (Brügmann, 1988).

In many regions, the Cd concentrations in the offshore waters (salinity range 30-35) appear to exhibit a linear inverse correlation with salinity. This can be illustrated with the data for the Irish Sea (Figure 4) which show a distinct trend of decreasing Cd concentration with increasing salinity, provided that the data for a few samples are excluded. Other regions for which there are data covering a reasonable range of salinity in the offshore waters also show similar relationships between Cd concentrations and salinity. Recent studies have also shown inverse cadmium-salinity relationships for offshore coastal waters (e.g., Kremling, 1985; Balls, 1985; Yeats, 1988). The regression slopes for the Cd-salinity relationships for European coastal waters, reported by Kremling (1985) for sections from Hamburg to the north of Scotland and to the eastern Atlantic Ocean, and from Hamburg through the English Channel to the Atlantic, and by Balls (1987) for the Irish Sea and west of Scotland, are similar to those found in this baseline study for the Irish Sea (Figure 4) and for areas to the Southwest of the UK and the southern North Sea. On the western side of the North Atlantic, the slopes of the regressions are considerably smaller (Yeats, 1988).

In the course of the baseline study, cadmium concentrations were measured in the outer parts of a number of estuaries. These include the Severn, Forth, Humber, Inner German Bight (Weser/Elbe) and Scheldt. The Cd-salinity regressions for these areas are relatively strong (e.g., the Severn estuary, Figure 5, and Humber estuary, Figure 6), with slopes of the regression varying from  $0.011 \mu\text{g/l}$

per psu (practical salinity unit) for the Forth estuary and German Bight to  $0.039 \mu\text{g/l}$  per psu for the Severn. The slopes for the coastal water regressions lie between these extremes.

The results for the coastal and estuarine surveys suggest that a linear relationship between Cd and salinity exists for salinity values  $> 20$ . However, the estuarine surveys, which cover a salinity range of 0-36, indicate that this linear relationship does not extend down to zero salinity; rather, a maximum concentration is observed at mid-salinity. This type of distribution has been observed elsewhere (e.g., Mart *et al.*, 1985) and can be illustrated by the Scheldt data (Figure 7). This plot, which includes data from a number of sampling periods and which exhibits a fair amount of scatter, illustrates that the concentrations of Cd in the river and brackish sections are lower than those in the mid-salinity region. At high salinity, Cd concentrations decrease to an average of *ca.*  $0.05 \mu\text{g/l}$ , i.e., that observed for the NS4 sub-division.

### Copper (Cu)

The Cu data displayed in Figures 8a-d are based on 992 results reported by 11 laboratories for 19 of the 21 geographical areas. Average concentrations of Cu for each area according to eight different salinity classes are given in Table 3.

The average values for samples with salinity  $> 30$  range from  $0.1\text{--}0.2 \mu\text{g/l}$ , in the offshore waters of the North Sea, to  $0.5\text{--}1.0 \mu\text{g/l}$  for the coastal areas. In almost all cases, average values for the coastal sub-divisions are higher than those reported in the literature for the respective areas (Table 7). By contrast, the values for offshore waters of the central North Sea are similar to those reported in the literature. The highest average concentration ( $1.05 \mu\text{g/l}$ ) was found in the German Bight; the lowest concentration ( $0.11 \mu\text{g/l}$ ) was in the central part of the northern North Sea.

Samples with a salinity in the ranges 25-30 and 20-25 were largely confined to the coastal sub-divisions; in all cases, the average concentration of Cu decreases with increasing salinity. In the salinity range 25-30, average concentrations of copper of  $> 1.5 \mu\text{g/l}$  were found in three areas: the German Bight, west of Scotland, and the approaches to the English Channel. It is important to realise that, in some of the areas, there is a bias towards sampling near sources of contamination, e.g., WESC where



data come from the estuary and Firth of the River Clyde. In the salinity range 20-25, there were two other locations with average concentrations in excess of 1.5  $\mu\text{g/l}$ : the Forth estuary, and off the Dutch coast. The highest concentrations were found in sub-division NORC, originating from one fjord, and obviously not representing typical levels along the Norwegian coast.

The relationships between dissolved copper and salinity (for values  $>20$  to  $<35$ ) were examined for a number of areas where sufficient measurements had been made along the salinity gradient. The slopes of these relationships varied from area to area, ranging from  $-0.01 \mu\text{g/l}$  per psu for the Baltic areas to  $-0.18 \mu\text{g/l}$  per psu for the Severn Estuary. Intermediate values of  $-0.03$ ,  $-0.07$ ,  $-0.11$ ,  $-0.14$  and  $-0.17$  were obtained for the Scotian Shelf (east coast of Canada), Dutch coastal area and Elbe Estuary, western Scheldt, Forth estuary and Firth of Clyde, respectively. Examples of these plots are presented in Figure 9 (Kattegat/Skagerrak) and Figure 10 (Dutch coastal waters).

### Lead (Pb)

The Pb data displayed in Figures 11a-d are based on 918 results from seven laboratories for 19 geographical areas. Average concentrations of Pb in samples for each area according to eight salinity ranges are given in Table 4. These data were augmented by ZISCH data consisting of measurements on unfiltered sea water samples from areas where time-averaged SPM concentrations are approximately  $<2 \text{ mg/l}$ , and data on unfiltered sea water samples from two laboratories which sampled in low SPM areas.

The Pb concentrations in waters of the salinity range 30-35 (Figure 11a and Table 4) show average values varying from *ca.* 0.01 to 0.06  $\mu\text{g/l}$ . The highest concentrations of Pb for this salinity range were observed in areas IRSH, CELT, NS7A and NS7B, and the lowest in areas CHNL and WESC. It is an interesting feature of these high salinity data that the highest concentrations of Pb in the North Sea are found in areas NS7A and NS7B rather than in the adjacent coastal regions. Recent literature values for Pb in these areas also give average concentrations of 0.01 to 0.06  $\mu\text{g/l}$  (Balls, 1985; Brüggemann *et al.*, 1985; Mart and Nurnberg, 1986; Balls, 1987; Harper, 1988). The literature values also show a tendency to higher values in areas further offshore (i.e., NS1, NS2 and NS7A).

Samples from the 25-30 and 20-25 salinity ranges (Figures 11b-c) generally exhibit higher Pb concentrations than the respective samples from the  $>30$  salinity range (Figure 11a). Values for CELT and IRSH are higher than those from NORC and NS3B. The increase in concentration from BALT to KATT would appear to be somewhat artificial, as one laboratory reported rather high values for unfiltered samples from the KATT area (Figure 11d). Literature values for the Baltic Sea are also rather inconsistent, varying between 0.016  $\mu\text{g/l}$  (Danielsson and Westerlund, 1984) and 0.05  $\mu\text{g/l}$  (Brüggemann, 1988).

In the higher salinity ranges, 30-35 and  $>35$ , the lead concentrations increase with increasing salinity, i.e., from nearshore areas of NS4, NS5 and NS3B to the open North Sea areas of NS7A, NS7B, NS2 and NS1. Within any area, however, the lead concentrations decrease with increasing salinity. These trends are particularly noticeable for inshore and coastal waters (e.g., Irish Sea, Figure 12), but they also exist for central North Sea areas (e.g., Figure 13). Although the lead data for estuarine regions were not very extensive, there were some indications of negative correlations with salinity extending at least into the outer part of several estuaries (e.g., Severn estuary, Figure 14). However, it should be noted that all of these regressions are rather scattered, but, despite the analytical problems usually encountered for lead, the relationships shown in Figures 12-14 are worth recording.

### Mercury (Hg)

The Hg data displayed in Figures 15a-d are based on 471 results from six laboratories for 16 of the 21 geographical sub-divisions. Average concentrations of Hg for some of these areas according to eight salinity classes are given in Table 5.

The data set for samples of salinity  $>30$  indicate that the median values for all sub-divisions are remarkably similar (Figure 15a), most of them falling into a range of values with a spread of a few ng/l. The average values for this salinity class, given in Table 5, indicate that the lowest concentrations of Hg are to be found in coastal waters rather than in the offshore waters, i.e., the highest average value of 8-9 ng/l in samples with a salinity in the range 30-35 were located in the central North Sea, whereas the lowest values (1-3 ng/l) were located in coastal waters off Scotland, England, the Netherlands, and Norway.

The data set for samples of salinity < 30 was much smaller and confined to measurements in eight sub-divisions. With the exception of the Irish Sea, the values for this salinity range were similar to the respective values for the higher salinity range. The concentrations of Hg in Irish Sea samples (mean value 124 ng/l) were at least an order of magnitude higher than any value recorded for the other sub-divisions. The Irish Sea results may be biased towards a higher concentration due to sampling in the locality of the contaminated Mersey estuary. The Hg concentrations observed in the Kattegat also appear anomalously high; assuming the data are analytically sound, there are no obvious explanations for these high concentrations.

The data for the salinity range 20-25 were limited to a small number of measurements in a few sub-divisions. The spread of mean values was very small, with concentrations ranging from 1-3 ng/l.

Although relevant data sets were available for the examination of the relationship between salinity and Hg concentrations, no strong correlations were observed; indeed, in general, the data exhibited a high degree of scatter. Examples of the relationships for North Sea coastal and offshore data are displayed in Figures 16 and 17 (North Sea) and Figure 18 (Forth Estuary).

The only recent literature data available for comparative purposes are the values of 6-12 ng/l by Baeyens *et al.* (1987) for sub-division NS4. This range is higher than the mean values of 1.7 ng/l, based on 17 measurements by one laboratory (BLUK), reported in this study for this area.

### Zinc (Zn)

Examination of Zn data from the ICES data-bank was limited to filtered samples. The rationale for this is that SPM typically contains > 200 mg/kg Zn which is relatively labile. Acidification of unfiltered samples is likely, therefore, to release sufficient metal to bias the dissolved phase concentrations. Although ten of the unfiltered samples contained < 1 mg/l SPM, these were not considered in the assessment.

The zinc data presented in Table 6, and in Figures 19a-d, consisted of 440 values from eight laboratories for eight sub-divisions. It is clear that, by comparison with the Cd, Pb and Cu data, the Zn

data are limited, being largely confined to coastal sub-divisions.

It is apparent from the box-and-whisker plots for different areas that, in the higher salinity ranges, concentrations of Zn are very similar; for the lower salinity ranges, some differences are apparent. However, caution must be exercised in drawing conclusions regarding the relative degree of contamination of different areas since the literature values for these areas (Table 7) are in general less (by a factor of 2-3) than those reported by participants in this study.

Other than a general decrease in metal concentration with increasing salinity, there were few data sets which could be considered to display strong metal-salinity relationships. This is likely to be related to the relative imprecision of the data, probably caused by contamination during sampling and analysis. Within some areas, however, there was a clearer relationship, notably in the high salinity region of the Forth estuary (Figure 21), and that area of the Dutch coast associated with the outflow of the River Rhine (Figure 20). For these data, it should be noted that the concentrations at the highest salinity values are in the range of values recently reported in the literature (Table 7). Although conservative mixing can explain the behaviour of zinc in some areas, such behaviour is unlikely to be maintained throughout the estuary; published data tend to confirm this, e.g., Campbell *et al.* (1988). The estimation of inputs by extrapolation to zero salinity must, therefore, be undertaken with considerable caution.

The relatively good agreement between zinc concentration and salinity for these areas is encouraging and suggests an improvement in the quality of the more recent zinc data.

## CONCLUSIONS

### All Metals

- a) It is now possible to establish baseline levels of the metals studied for most of the areas covered in this study.
- b) Concentrations of Cu, Zn, Hg, Cd, and Pb for the salinity range > 30 are remarkably similar throughout the North Sea and other adjacent coastal waters.

- c) A number of ICES/JMP laboratories, considered by MCWG in 1984 as not being sufficiently experienced in trace metal measurements in sea water, have now achieved the capability of producing good data. Others will have to improve.

#### **Cadmium**

- a) Concentrations of dissolved Cd are higher in inshore waters; levels reported by participants for offshore areas are similar to those reported in the literature, 0.01-0.02 µg/l.
- b) The highest Cd concentrations in inshore areas were reported in the eastern Irish Sea. These originate from sampling in the proximity of contaminated estuaries (Mersey) and known discharges.
- c) Inverse relationships exist between dissolved Cd and salinity for a number of areas; the slope of the regression line varies from area to area.
- d) Non-conservative behaviour of Cd, with maximum values observed in the salinity range 20-25, is seen in some estuaries.

#### **Copper**

- a) The highest values of Cu for samples of salinity > 30 are found in inshore areas.
- b) In general, the baseline levels for areas with a salinity > 30 are similar to those reported in the recent literature for these areas, and ranged from 0.1-0.2 µg/l in the offshore waters.
- c) Inverse dissolved Cu *versus* salinity relationships were observed for most of the areas covered; the slopes of the regressions varied from area to area.

#### **Lead**

- a) In the salinity range > 30, the highest Pb concentrations were found in the central North Sea.
- b) Central North Sea and open shelf water lead concentrations are similar to those for surface waters of the oceanic Northeast Atlantic.

#### **Mercury**

- a) Median values for the salinity range > 30 vary from 0.6-2.5 ng/l.
- b) No strong relationships between dissolved mercury and salinity were identified.

#### **Zinc**

- a) There are strong inverse relationships between dissolved Zn concentrations and salinity in a few areas.
- b) As behaviour is not conservative throughout the entire salinity range of 0-35, extrapolation of metal concentrations to zero salinity should be done with caution.

### **OBSERVATIONS RELEVANT TO THE DESIGN AND CONDUCT OF SIMILAR BASELINE STUDIES**

In 1984, it was generally agreed that there was a sufficient number of European laboratories, with the capability to carry out accurate and precise measurements of trace metals in sea water, to participate in a baseline study of metals in coastal and shelf sea waters of ICES member states. In view of this, and the request from ACMP to do this task as soon as it was practicable, the Marine Chemistry Working Group (MCWG) drew up proposals for a baseline study (see 1984 MCWG report (ICES Doc. C.M.1984/C:2) and the paper by Topping and Bowers (1984)). These proposals included a quality control mechanism (sampling at reference stations) and identified the need to measure other parameters (salinity, temperature, SPM (mg/l), dissolved oxygen, nitrate, phosphate, silicate) in samples collected for trace metal analysis to assist the assessment of baseline data.

It was assumed that the adoption of these guidelines by participants would lead to a reasonably comparable data set and that the task of assessing such a data set, in relation to the main aims of the work, would be straightforward.

Unfortunately, for a number of reasons which will be outlined and discussed below, the task of assessing the baseline data was both difficult and time consuming:

- a) The majority of participants in the baseline study were inexperienced in the collection of sea water samples and their analysis for trace metals. Of the six core institutes and eight reasonably experienced institutes, listed by MCWG (ICES Doc. C.M.1984/C:2) as potential participants, only two of the first group and two of the second group took part in the baseline study.
- b) Only a few participants (four) conducted measurements on samples collected at one or more of the ICES reference stations; thus, in the absence of other quality control data (e.g., successful participation in ICES intercomparison exercises), the assessment of data from the majority of the participants had to be based on the knowledge and experience of the assessment group. A summary of data reported from the reference stations is included as Table 8.
- c) Many of the data were collected without adherence to the guidelines. Some of the data submitted were from surveys undertaken by particular laboratories concerning specific discharges. Such data were inappropriate to the baseline survey and were, as far as possible, excluded from the review.
- d) Many of the data submitted were from locations close inshore; thus, comparison with the literature data (offshore or oceanic waters) is rather difficult.
- e) Participants were asked to conduct measurements on filtered samples and, where relevant, to collect such samples along a salinity gradient. A number of the participating laboratories did not carry out these requests, with the result that a large proportion of results submitted were for unfiltered samples with no accompanying data on SPM and, in some cases, the salinity values were not reported. Despite the absence of SPM measurements, the assessment group felt that it should review some of these data which appeared from the preliminary screening to be acceptable. In order to judge whether data on unfiltered samples could be included in the assessments, the group spent considerable time examining the data sets for each individual area, and had to introduce pragmatic criteria, such as using SPM information derived from published reports on other studies (e.g., the ZISCH sub-project on suspended sediments).
- f) The results of the survey indicate that we are not really in a position to use data collected from a large number of laboratories. These data were compiled to monitor geographical distributions of metals in sea water but we do not fully understand the hydrographic and seasonal controls on concentrations. It is possible that, at present, sampling and analytical measurement uncertainties may be larger than any trend that could be anticipated. Within estuaries, concentrations will be influenced by tide, season, fresh water discharge, etc.
- g) Because the majority of data presented in this report originate from inshore areas, particularly from estuaries and other nearshore regions likely to be affected by local sources, and, as the information presented here depends to a large extent on the selected geographical subdivisions, caution should be exercised in using these data for assessment purposes involving different geographical sub-divisions (as, for example, those designated by the NSTF). Data from offshore areas may well be suitable for characterizing wholly offshore sub-areas, but care should be exercised when data are provided from only a limited number of stations.
- h) The assessment of the data was begun in 1987 with rather limited expectations of the extent to which metal distributions could be described. Despite the difficulties in assessing the data described above, a fairly extensive description of the distributions of the metals for 1985-1987 has been achieved. It would now appear promising for an experiment to be run by a single competent laboratory. Data collected for a well-designed and extensive sampling grid during a single season could be expected to more clearly detect spatial patterns in metal distributions. In addition, a more detailed investigation of metal-salinity relationships in estuarine waters, focusing on seasonal studies of the estuarine contaminant distributions, could yield a valuable assessment of metal inputs to nearshore waters.



## REFERENCES

- Baeyens, W., Gillain, G., Decadt, G. and Elskens, I. 1987. Trace metals in the eastern part of the North Sea. I: Analyses and short-term distributions. *Oceanologica Acta*, **10**: 169-179.
- Balls, P.W. 1985. Trace metal fronts in Scottish coastal waters. *Estuarine, Coastal and Shelf Science*, **20**: 717-728.
- Balls, P.W. 1985. Trace metals in the Northern North Sea. *Marine Pollution Bulletin*, **16**: 203-207.
- Balls, P.W. 1987. Dispersion of dissolved trace metals from the Irish Sea into Scottish coastal waters. *Continental Shelf Research*, **7**: 685-698.
- Berman, S.S. and Boyko, V.J. 1987. ICES Sixth Round Intercalibration for Trace Metals in Estuarine Water. *ICES Coop. Res. Rep. No.* 152.
- Berman, S.S., Mykytiuk, A.P., Yeats, P.A. and Bowers, J.M. 1986. ICES Fifth Round Intercalibration for Trace Metals in Sea Water. *ICES Coop. Res. Rep. No.* 136, pp. 27-66.
- Brügmann, L. 1988. Some peculiarities of the trace metal distribution in Baltic waters and sediments. *Marine Chemistry*, **23**: 425-440.
- Brügmann, L., Danielsson, L.-G., Magnusson, B. and Westerlund, S. 1985. Lead in the North Sea and the north-east Atlantic Ocean. *Marine Chemistry*, **16**: 47-60.
- Campbell, J.A., Whitelaw, K., Riley, J.P., Head, P.C. and Jones, P.D. 1988. Contrasting behaviour of dissolved and particulate nickel and zinc in a polluted estuary. *The Science of the Total Environment*, **71**: 141-155.
- Danielsson, L.-G., Magnusson, B. and Westerlund, S. 1985. Cadmium, copper, iron, nickel and zinc in the north-east Atlantic Ocean. *Marine Chemistry*, **17**: 23-41.
- Danielsson, L.-G. and Westerlund, S. 1984. Short-term variations in trace metal concentrations in the Baltic. *Marine Chemistry*, **15**: 273-277.
- GESAMP - IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution, 1987. Land-sea boundary flux of contaminants: Contributions from rivers. GESAMP Reports and Studies No. 32. UNESCO, Paris. 172 pp.
- Harper, D. 1988. Dissolved cadmium and lead in the Thames estuary. *Marine Pollution Bulletin*, **19**: 535-538.
- ICES, 1983. Flushing times of the North Sea. *ICES Coop. Res. Rep. No.* 123.
- Kersten, M., Dicke, M., Kriews, M., Naumann, K., Schmidt, D., Schultz, M., Schwikowski, M. and Steiger, M. 1988. Distribution and fate of heavy metals in the North Sea. In: *Pollution of the North Sea: An Assessment*, Ed. by W. Salomons, B.L. Bayne, E.K. Duursma and U. Förstner. pp. 300-347. Springer-Verlag.
- Kremling, K. 1985. The distribution of cadmium, copper, nickel, manganese, and aluminium in surface waters of the open Atlantic and European shelf area. *Deep-Sea Research*, **32**: 531-555.
- Kremling, K. and Hydes, D. 1988. Summer distribution of dissolved Al, Cd, Co, Cu, Mn and Ni in surface waters around the British Isles. *Continental Shelf Research*, **8**: 89-105.
- Kremling, K. and Petersen, H. 1984. Synoptic survey on dissolved trace metal levels in Baltic surface waters. *Marine Pollution Bulletin*, **15**: 329-334.
- Mart, L. and Nurnburg, H.W. 1986. Cd, Pb, Cu, Ni and Co distribution in the German Bight. *Marine Chemistry*, **18**: 197-213.
- Mart, L., Nurnberg, H.W. and Rutzel, H. 1985. Levels of heavy metals in the tidal Elbe and its estuary and the heavy metal input into the sea. *The Science of the Total Environment*, **44**: 35-49.
- Topping, G., Bowers, J.M., and Jones, P.G.W. 1980. A review of the past and present measurements of selected trace metals in sea water in the Oslo Commission and ICNAF (-NAFO) areas. *ICES Coop. Res. Rep. No.* 97.

Topping, G., Bowers, J.M., and Jones, P.G.W.  
1984. A proposal for the inclusion of surveys  
of metals in seawater in the 1985 ICES Baseline  
Study of Contaminants in the Oslo Commission  
and NAFO Areas. ICES Doc. C.M.1984/E:39.

Yeats, P.A. 1988. The distribution of trace metals  
in ocean waters. *The Science of the Total Envi-  
ronment*, **72**: 131-149.

TABLE 1 : MEASUREMENTS OF METALS BY AREA AND LABORATORY

COUNTRY	LAB.	AREA																CHNL	CELT	IRSH	WESC	BISC	IBER
		NS1.	NS2.	NS3A	NS3B	NS4.	NS5.	NS6.	NS7A	NS7B	NOSC	NORC	SKAG	KATT	S&BL	BALT							
BELGIUM	IHEB					Cd, Cu																	
DENMARK	HFLD						Cd, Cu						Cd, Cu	Cd									
	ICDK						Hg						Hg	Hg									
GERMAN, DEM. REP.	IGDR													Cd, Cu Pb, Zn	Cd, Cu Pb, Zn	Cd, Cu Pb, Zn							
GERMANY, FED. REP.	DHIG	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg Zn	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg		Cd, Cu Pb, Hg						Cd, Cu Pb, Hg				
	LWOK						Cd, Cu Pb, Zn																
	FITG						Cd, Cu																
	ISHG						Cd, Cu Pb																
	BFGG					Cu	Cd, Cu Pb, Zn																
NETHERLANDS	DWGN					Cd, Cu Hg, Pb Zn	Cd, Cu Pb, Hg Zn																
	RIZA					Cd, Cu Pb, Zn Zn																	
	IBWL					Zn																	
NORWAY	NIVA											Cd, Cu Pb	Cd, Cu Pb										
	SERI											Hg	Hg										
PORTUGAL	IHLP																					Hg	
SPAIN	IEOM																				Cd, Pb Zn	Cd, Pb Zn	
SWEDEN	LCRS												Cd, Cu Hg, Pb	Cd, Hg Pb									
UK	ALUK																		Cd, Cu Pb	Cd, Cu Pb			
	BLUK		Cd, Pb	Cd, Pb Hg	Cd, Cu Hg, Pb	Cd, Pb Hg	Cd, Pb Hg	Cd, Pb	Cd, Pb Hg	Cd, Pb Hg			Cd, Pb Hg				Cd, Cu Pb, Hg	Cd, Cu Pb, Hg	Cd, Cu Pb, Hg				
	CRUK																			Cd, Cu Pb, Hg Zn			
	FRUK			Cd, Cu Hg, Pb Zn																			
	HGUK				Cd, Cu Hg, Zn																		
	NRUK			Cd, Cu Zn																			
	NWUK																		Cd, Cu Hg				
	SWUK																Cd, Cu Zn						
	TWUK				Cd, Cu Hg, Zn																		
	WWUK																		Cd, Cu Hg, Zn				
Number of labora- tories reporting data for each area		1	2	4	4	7	8	2	2	2	1	1	5	3	1	1	2	2	3	3	1	1	
Number of countri- es reporting data for each area		1	2	2	2	4	4	2	2	2	1	1	5	3	1	1	1	1	1	2	1	1	

**TABLE 2 : SUMMARY TABLE - CADMIUM DATA BY AREA AND SALINITY RANGE**

line 1 - Average concentration (µg/l) : line 2 - Standard deviation : line 3 - Number of values

Area code	Salinity range							
	00 - 05	05 - 10	10 - 15	15 - 20	20 - 25	25 - 30	30 - 35	35 - 40
BALT BALT BALT		0.0220 0.0127 15						
BISC BISC BISC							0.0602 0.0228 5	0.0490 0.0159 6
CELT CELT CELT					0.4600 0.0472 8	0.3752 0.0632 12	0.0692 0.0576 51	0.0148 0.0069 17
CHNL CHNL CHNL							0.0489 0.0641 30	0.0163 0.0045 26
IBER IBER IBER								0.0890 0.0843 12
IRSH IRSH IRSH						0.0918 0.0272 11	0.0606 0.0470 218	0.0060 - 1
KATT KATT KATT				0.0208 0.0072 23	0.0307 0.0053 6	0.0540 - 1		
NORC NORC NORC	0.0480 - 1	0.0480 - 1	0.0755 0.0205 2	0.0575 0.0065 2	0.0424 0.0174 5	0.0299 0.0102 9	0.0255 0.0005 2	
NOSC NOSC NOSC							0.0192 0.0055 4	0.0103 0.0026 3
NS1. NS1. NS1.							0.0087 0.0009 3	0.0217 0.0223 6
NS2. NS2. NS2.							0.0170 0.0069 10	0.0241 0.0154 8
NS3A NS3A NS3A	0.0320 0.0130 2	0.0510 - 1	0.0190 - 1	0.0350 - 1	0.1600 0.1910 3	0.0346 0.0086 13	0.0545 0.0884 96	
NS3B NS3B NS3B				0.3900 0.1485 3	0.2741 0.0946 10	0.1937 0.1087 23	0.0382 0.0321 104	0.0440 - 1
NS4. NS4. NS4.	0.1006 0.0945 33	0.1263 0.0612 19	0.2078 0.0954 9	0.2171 0.1498 7	0.1971 0.1394 21	0.0836 0.0849 99	0.0528 0.0497 285	0.0234 0.0074 16
NS5. NS5. NS5.	0.0932 0.0895 37	0.0632 0.0467 19	0.0608 0.0371 25	0.0784 0.0569 37	0.0669 0.0342 42	0.0580 0.0498 73	0.0320 0.0260 93	
NS6. NS6. NS6.						0.0080 - 1	0.0142 0.0071 13	0.0060 0.0033 4
NS7A NS7A NS7A							0.0169 0.0101 61	0.0180 - 1
NS7B NS7B NS7B							0.0287 0.0306 52	
S&BL S&BL S&BL			0.0189 0.0070 8					
SKAG SKAG SKAG					0.0400 0.0216 3	0.0218 0.0060 16	0.0197 0.0077 19	
WESC WESC WESC							0.0315 0.0083 22	

TABLE 3 : SUMMARY TABLE - COPPER DATA BY AREA AND SALINITY RANGE

line 1 - Average concentration (µg/l) : line 2 - Standard deviation : line 3 - Number of values

Area code	Salinity range							
	00 - 05	05 - 10	10 - 15	15 - 20	20 - 25	25 - 30	30 - 35	35 - 40
BALT BALT BALT		0.603 0.087 15						
CELT CELT CELT					2.287 0.448 8	1.689 0.555 9	0.787 0.729 36	0.262 0.084 6
CHNL CHNL CHNL							0.452 0.261 5	0.196 0.094 7
IRSH IRSH IRSH							0.520 0.306 3	0.590 - 1
KATT KATT KATT			0.627 - 1	0.709 0.409 19	0.627 0.056 6			
NORC NORC NORC	2.220 - 1	17.90 - 1	11.03 2.775 2	10.07 3.725 2	4.936 2.285 5	1.477 0.612 9	0.640 0.120 2	
NOSC NOSC NOSC							0.419 0.133 4	0.111 0.175 4
NS1. NS1. NS1.							0.111 0.138 4	0.162 0.135 6
NS2. NS2. NS2.							0.263 0.195 9	0.149 0.130 7
NS3A NS3A NS3A	2.253 1.343 3	1.613 0.622 3	2.390 - 1	1.850 - 1	1.760 0.662 3	1.386 0.302 13	0.750 0.550 77	
NS3B NS3B NS3B							0.955 0.045 2	
NS4. NS4. NS4.	2.300 0.100 2	1.983 0.687 6	2.080 0.966 5	2.100 1.042 6	1.594 0.768 16	0.941 0.377 97	0.533 0.242 149	0.300 0.078 13
NS5. NS5. NS5.	2.856 1.373 27	2.287 0.947 16	1.925 0.655 24	2.067 1.094 36	1.694 0.633 42	1.465 0.778 75	1.048 0.538 55	
NS6. NS6. NS6.						0.122 - 1	0.181 0.092 10	0.058 0.031 4
NS7A NS7A NS7A							0.188 0.157 33	
NS7B NS7B NS7B							0.333 0.420 19	
S&BL S&BL S&BL			0.517 0.053 8					
SKAG SKAG SKAG					0.397 0.113 3	0.460 0.256 16	0.285 0.161 14	
WESC WESC WESC	4.075 1.524 11	4.775 0.045 2				1.805 0.045 2	0.587 0.258 25	

**TABLE 4 : SUMMARY TABLE - LEAD DATA BY AREA AND SALINITY RANGE**

line 1 - Average concentration (µg/l) : line 2 - Standard deviation : line 3 - Number of values

Area code	Salinity range							
	00 - 05	05 - 10	10 - 15	15 - 20	20 - 25	25 - 30	30 - 35	35 - 40
BALT BALT BALT		0.0353 0.0182 15						
CELT CELT CELT					0.2933 0.1151 6	0.1417 0.0608 9	0.1426 0.2209 50	0.0311 0.0066 15
CHNL CHNL CHNL							0.0326 0.0284 29	0.0230 0.0088 26
IRSH IRSH IRSH						0.1356 0.0570 9	0.0626 0.0533 285	0.0130 - 1
KATT KATT KATT			0.0800 - 1	0.0914 0.0814 11				
NORC NORC NORC	0.0070 - 1	0.1100 - 1	0.0365 0.0015 2	0.0520 0.0040 2	0.0758 0.0546 4	0.0810 0.0816 9	0.0510 0.0170 2	
NOSC NOSC NOSC							0.0386 0.0159 4	0.0510 0.0149 4
NS1. NS1. NS1.							0.0369 0.0109 4	0.0323 0.0145 6
NS2. NS2. NS2.							0.0356 0.0220 10	0.0442 0.0180 7
NS3A NS3A NS3A			0.1500 - 1		0.1000 - 1		0.0605 0.0579 23	
NS3B NS3B NS3B				0.5777 0.6460 3	0.1009 0.0933 9	0.0969 0.1511 24	0.0411 0.0391 92	0.0470 - 1
NS4. NS4. NS4.							0.0484 0.0382 23	0.0310 0.0140 2
NS5. NS5. NS5.						0.0186 0.0075 9	0.0269 0.0090 25	
NS6. NS6. NS6.						0.0416 - 1	0.0326 0.0129 13	0.0191 0.0037 4
NS7A NS7A NS7A							0.0564 0.0455 60	0.0220 - 1
NS7B NS7B NS7B							0.0616 0.0400 52	
S&BL S&BL S&BL			0.0658 0.0428 8					
SKAG SKAG SKAG					0.0550 0.0193 3	0.0510 0.0225 15	0.0375 0.0194 13	
WESC WESC WESC							0.0145 0.0086 22	

**TABLE 5 : SUMMARY TABLE - MERCURY DATA BY AREA AND SALINITY RANGE**

line 1 - Average concentration ( $\mu\text{g/l}$ ) : line 2 - Standard deviation : line 3 - Number of values

Area code	Salinity range							
	00 - 05	05 - 10	10 - 15	15 - 20	20 - 25	25 - 30	30 - 35	35 - 40
CELT CELT CELT					0.0012 0.0002 7	0.0012 0.0003 8	0.0011 0.0008 39	0.0006 0.0003 6
CHNL CHNL CHNL							0.0006 0.0001 11	0.0005 0.0000 8
IRSH IRSH IRSH						0.1239 0.0963 7	0.0058 0.0161 52	
KATT KATT KATT			0.0040 - 1	0.0035 0.0015 4	0.0190 0.0100 2	0.0030 - 1		
NORC NORC NORC	0.0009 - 1	0.0005 - 1	0.0015 - 1	0.0006 - 1	0.0003 - 1	0.0015 0.0008 6	0.0009 - 1	
NOSC NOSC NOSC							0.0029 0.0007 4	0.0075 0.0067 3
NS1. NS1. NS1.							0.0019 0.0003 2	0.0016 0.0007 6
NS2. NS2. NS2.							0.0083 0.0145 8	0.0054 0.0043 5
NS3A NS3A NS3A					0.0030 0.0006 2	0.0037 0.0029 13	0.0029 0.0031 41	
NS3B NS3B NS3B					0.0038 0.0015 7	0.0042 0.0034 17	0.0020 0.0022 39	
NS4. NS4. NS4.							0.0017 0.0008 17	
NS5. NS5. NS5.						0.0050 0.0061 4	0.0041 0.0045 24	
NS6. NS6. NS6.						0.0007 - 1	0.0028 0.0020 10	0.0019 0.0006 4
NS7A NS7A NS7A							0.0053 0.0114 45	
NS7B NS7B NS7B							0.0079 0.0265 34	
SKAG SKAG SKAG					0.0020 - 1	0.0046 0.0045 16	0.0090 0.0208 10	

**TABLE 6 : SUMMARY TABLE - ZINC DATA BY AREA AND SALINITY RANGE**

line 1 - Average concentration (µg/l) : line 2 - Standard deviation : line 3 - Number of values

Area code	Salinity range							
	00 - 05	05 - 10	10 - 15	15 - 20	20 - 25	25 - 30	30 - 35	35 - 40
BALT BALT BALT		0.78 0.39 14						
CHNL CHNL CHNL						4.30 0.70 2	2.08 1.07 10	
KATT KATT KATT				0.66 0.15 6				
NS3A NS3A NS3A	4.81 3.11 3	4.93 1.30 3	7.62 - 1	3.75 - 1	4.71 2.19 3	2.57 0.92 13	1.64 2.67 68	
NS4. NS4. NS4.	7.00 2.00 2	7.83 2.67 6	7.80 4.83 5	6.75 2.28 4	4.14 2.15 13	2.54 1.01 47	2.25 2.08 30	0.87 0.82 3
NS5. NS5. NS5.	7.23 3.09 27	4.86 2.48 13	4.01 2.03 20	4.28 2.66 29	3.41 1.43 25	3.01 1.85 54	1.73 0.90 14	
S&BL S&BL S&BL			0.64 0.18 8					
WESC WESC WESC	12.29 3.25 10	17.05 0.15 2				11.15 0.35 2	3.36 0.14 2	



Table 7: Summary of recent published data for trace metal concentrations in different areas.

Area	Cd( $\text{ngl}^{-1}$ )	Cu( $\mu\text{gl}^{-1}$ )	Zn( $\mu\text{gl}^{-1}$ )	Pb( $\text{ngl}^{-1}$ )	Hg( $\text{ngl}^{-1}$ )
NS1.	26 a 15 e	0.29 a 0.12 e	0.53 a	60 b 33 e	
NS2.	25 a 13 c 12 d 9 e	0.13 a 0.22 c 0.20 d 0.08 e	0.25 a	57 b   35 e	
NS3A	19 c 15 d 17 e	0.24 c 0.16 d 0.12 e		32 e	
NS3B	32 g			39 g	
NS4.	20 a 53 d 14-170 f	0.34 a 0.47 d 0.28-2.5 f	0.66 a  0.25-8.8 f	33 b  45-660 f	6-12 f
NS5.	45 c 49 d	3.5 c 0.80 d			
NS6.	18 e	0.19 e		30 e	
NS7A	16 c 18 d	0.17 c 0.21 d			
NS7B	28 a 21 c 25 d	0.29 a 0.40 c 0.35 d	0.52 a	16 b	
SKAG	30 a	0.40 a	0.82 a	50 b	
BALT	27 h	0.66 h	0.92 h		
S&BL	29 h	0.58 h	1.1 h		
WESC	13 c 14 d	0.23 c 0.15 d			
IRSH	25 c	0.44 c			
CELT	12 a 15 c 19 d	0.08 a 0.26 c 0.21 d	0.12 a	35 b	
CHNL	25 a 15 c 24 d	0.20 a 0.26 c 0.32 d	0.42 a	13 b	

a Danielsson et al. (1985).

b Brugmann et al. (1985).

c Kremling and Hydes (1988).

d Kremling (1985).

e Balls (1985).

f Baeyens et al. (1987).

g Harper (1988).

h Kremling and Peterson (1984).

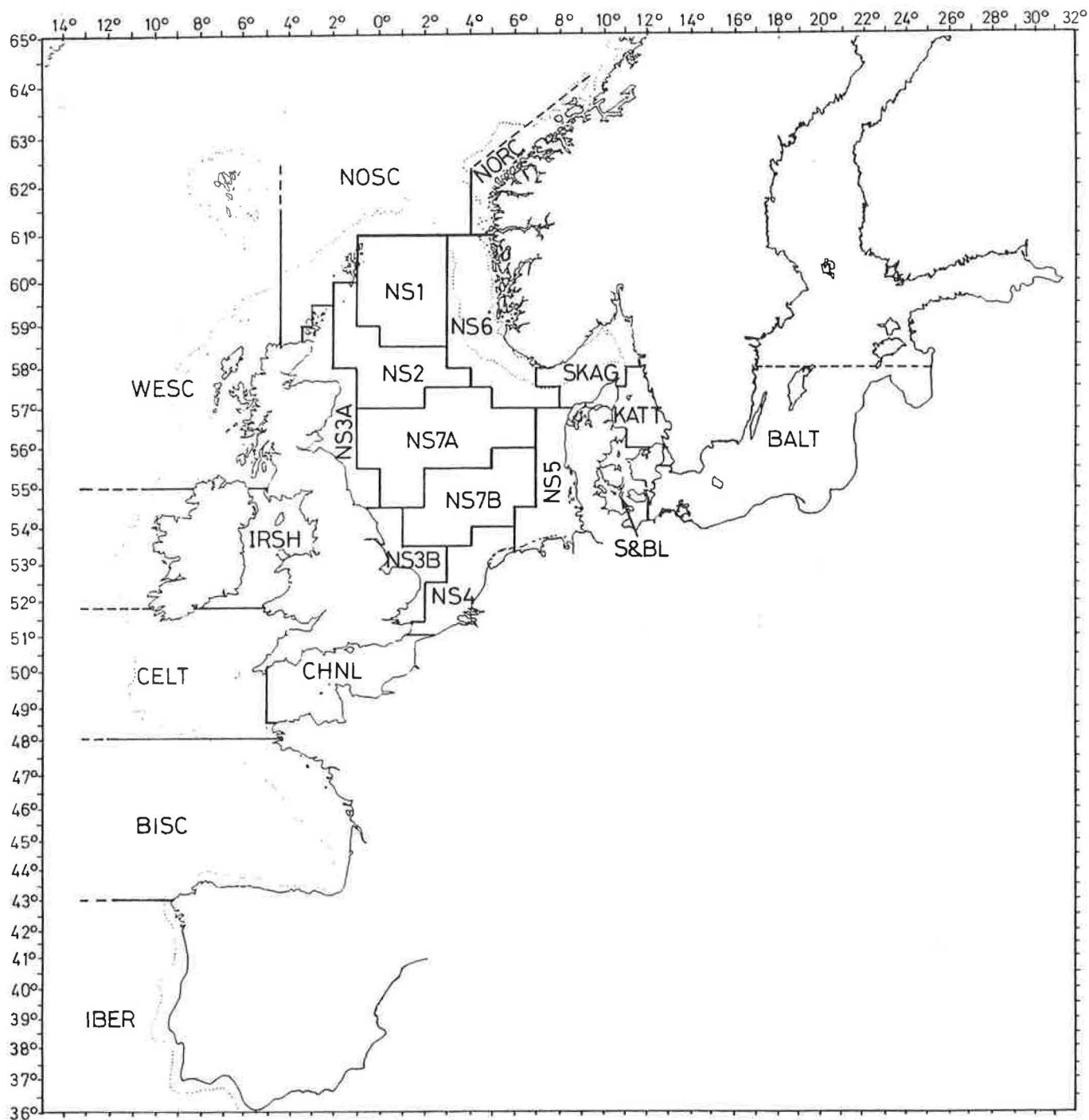
**Table 8: Measurements of metals in sea water at ICES reference stations**

**NW Scotland - 60°30'N 5°00'W**

Laboratory	Date	Position	Depth (m)	Cu (µg/l)	Pb (µg/l)	Cd (µg/l)	Hg (ng/l) (total)
ALUK	5/85	60°30'N 5°00'W	1,000	0.180	0.009	0.021	-
BLUK	5/88	60°30'N 5°00'W	950	0.170	0.013	0.021	0.47
DHIG	5/86	60°30'N 5°00'W	800	-	-	0.013	0.50
Danielsson <i>et al.</i> , 1985; Brügmann <i>et al.</i> , 1985	5/81	62°30'N 00°30'W	800	0.092	0.005	0.021	-
Danielsson <i>et al.</i> , 1985; Brügmann <i>et al.</i> , 1985	5/81	64°10'N 5°40'E	1,000	0.095	0.010	0.025	-

**Skagerrak - 58°10'N 9°30'E**

Laboratory	Date	Position	Depth (m)	Cu (µg/l)	Pb (µg/l)	Cd (µg/l)	Hg (ng/l) (total)
DHIG	6/86	58°10'N 9°30'E	300	-	0.010	0.010	2.2
Danielsson <i>et al.</i> , 1985; Brügmann <i>et al.</i> , 1985	6/81	58°00'N 9°00'E	200	0.12	0.023	0.018	-



**Figure 1** Designation of Areas used in Baseline Study of Trace Metals in Coastal and Shelf Sea waters.

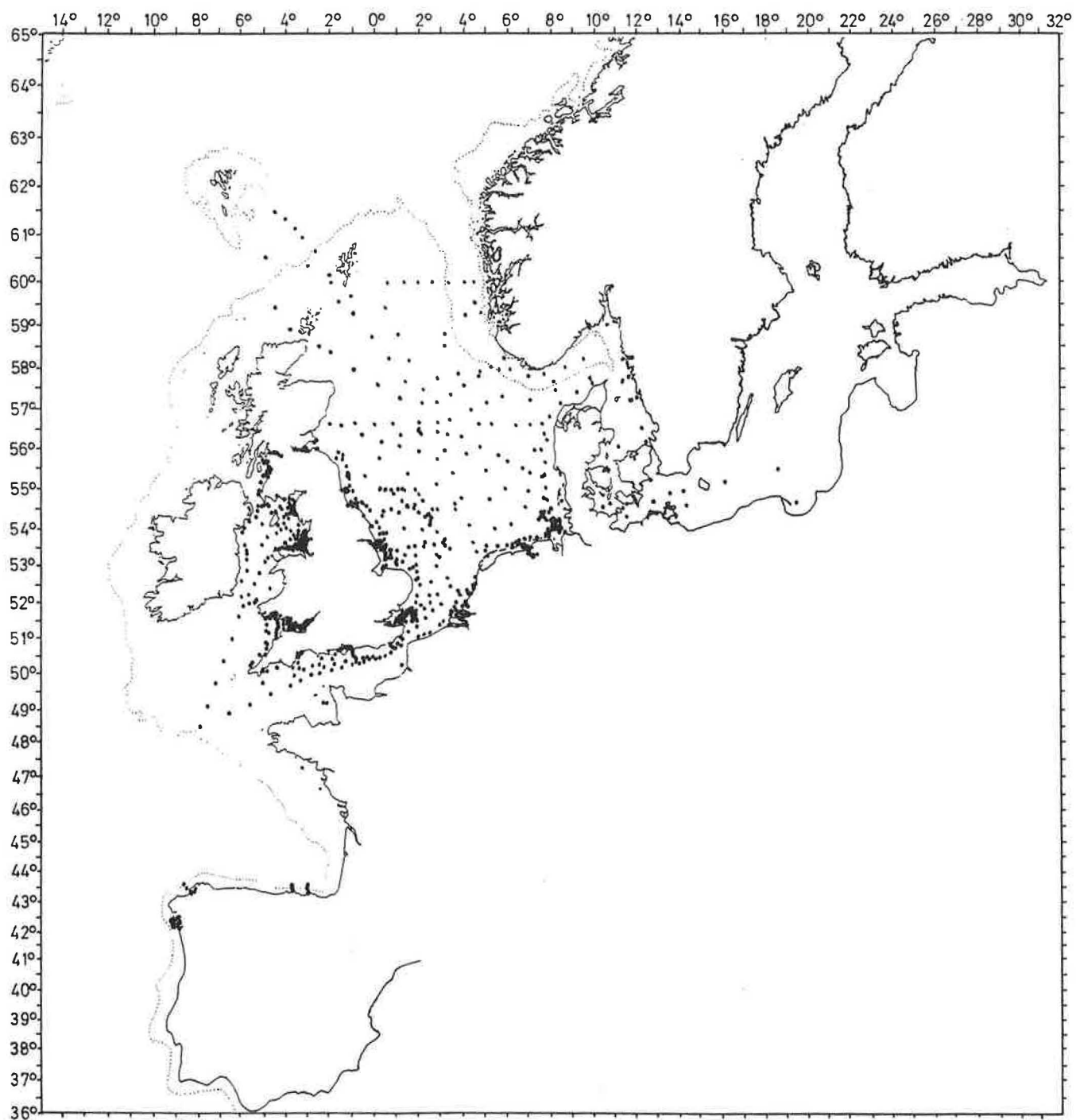


Figure 2 Locations sampled for one or more metals.

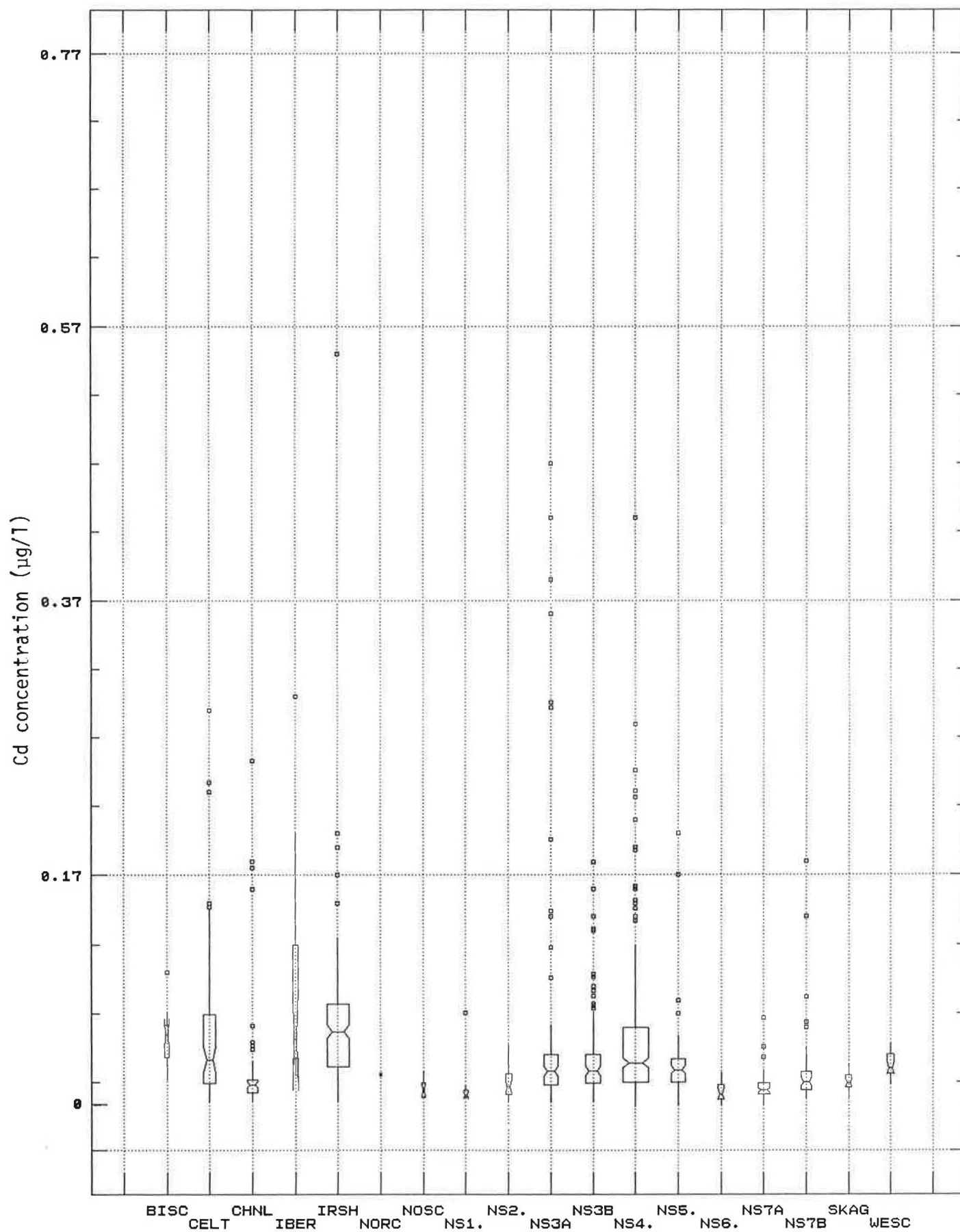


Figure 3(a) Cadmium data for salinities > 30

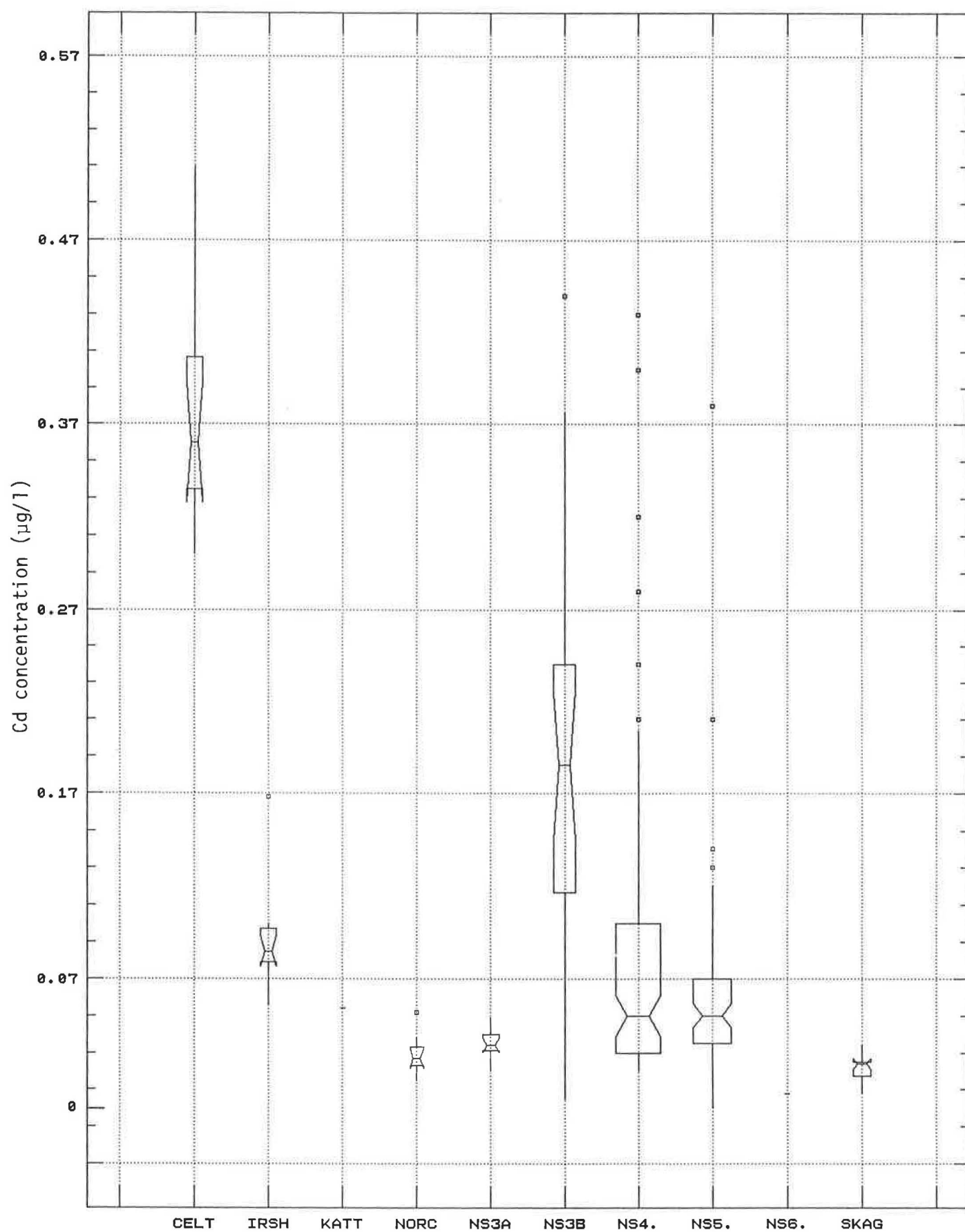


Figure 3(b) Cadmium data for salinities 25-30

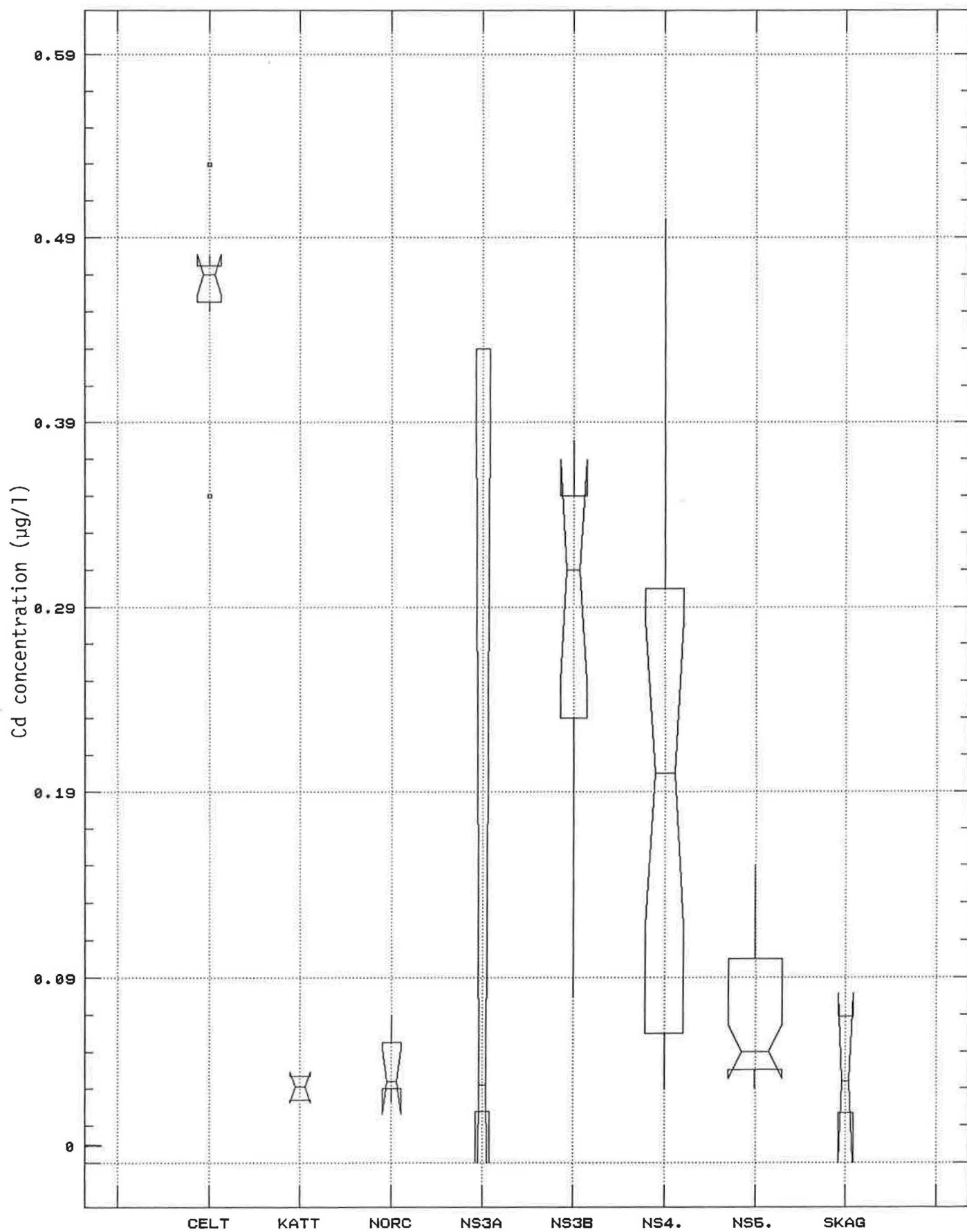


Figure 3(c) Cadmium data for salinities 20-25

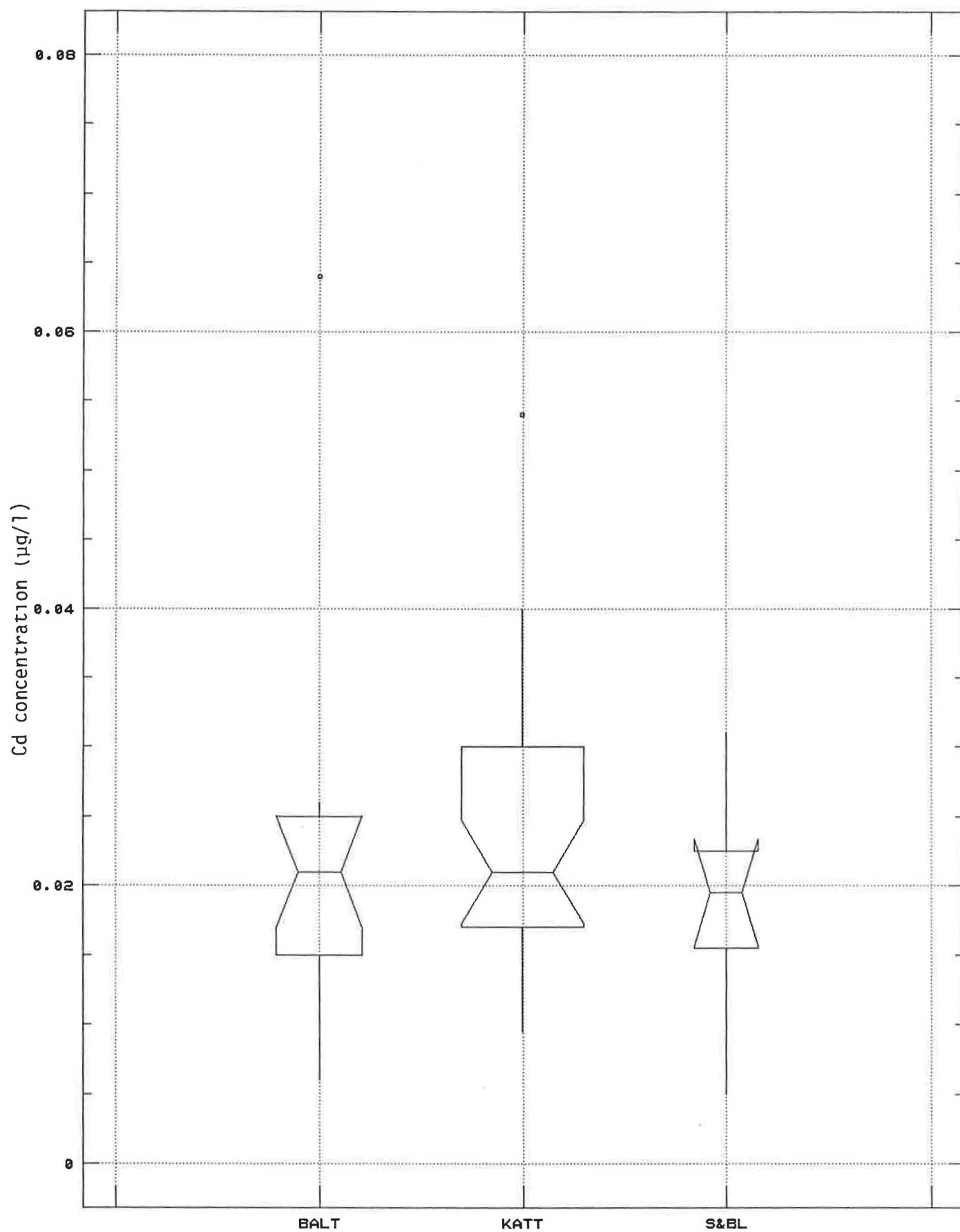


Figure 3(d) Cadmium data for areas KATT, S&BL and BALT.



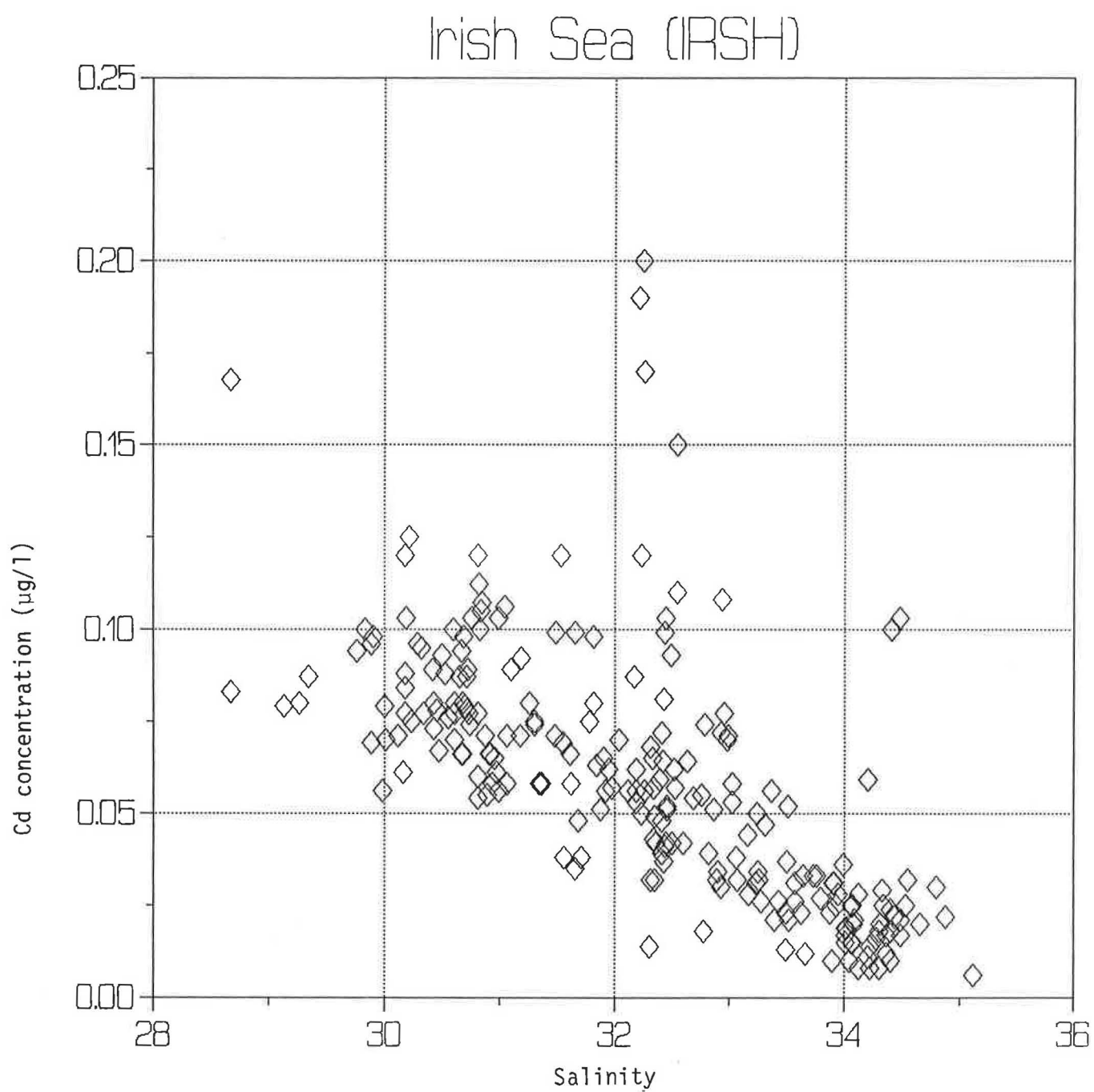
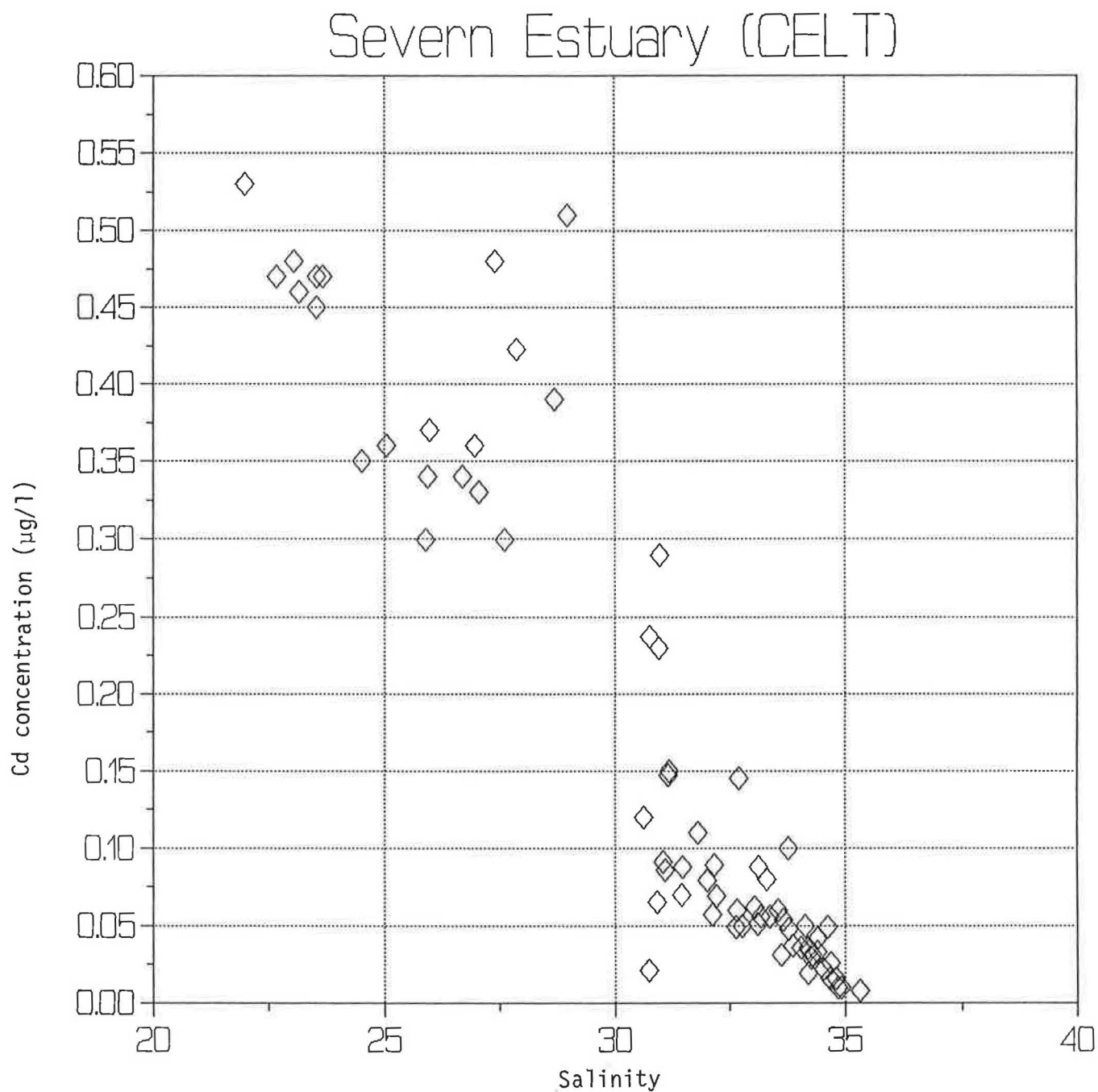


Figure 4 Cadmium vs. salinity from area IRSH.



**Figure 5** Cadmium vs. salinity for the Severn Estuary and Bristol Channel parts of the area CELT.

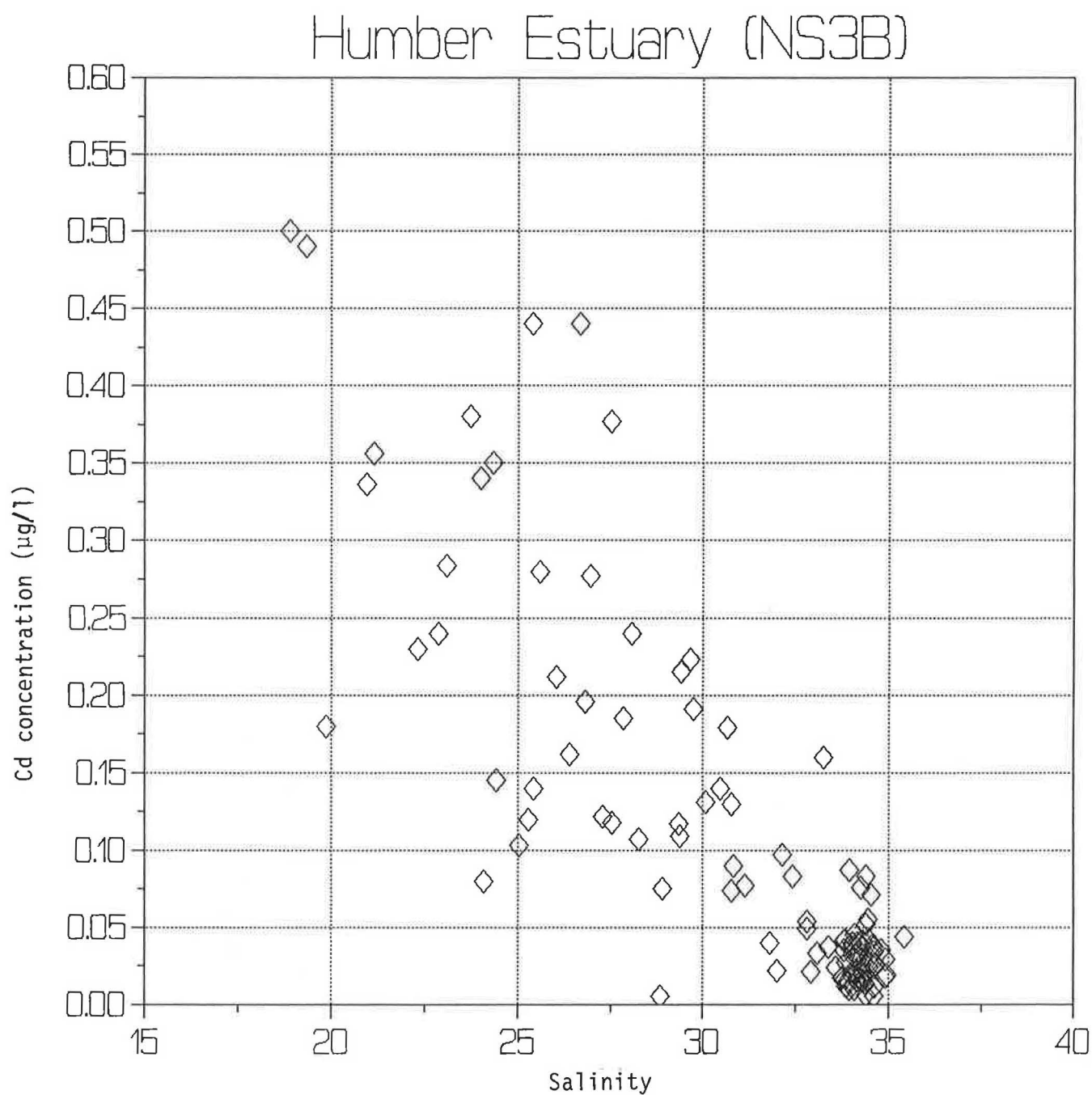


Figure 6 Cadmium vs. salinity for the part of area NS3B around the Humber Estuary.

# W. Scheldt

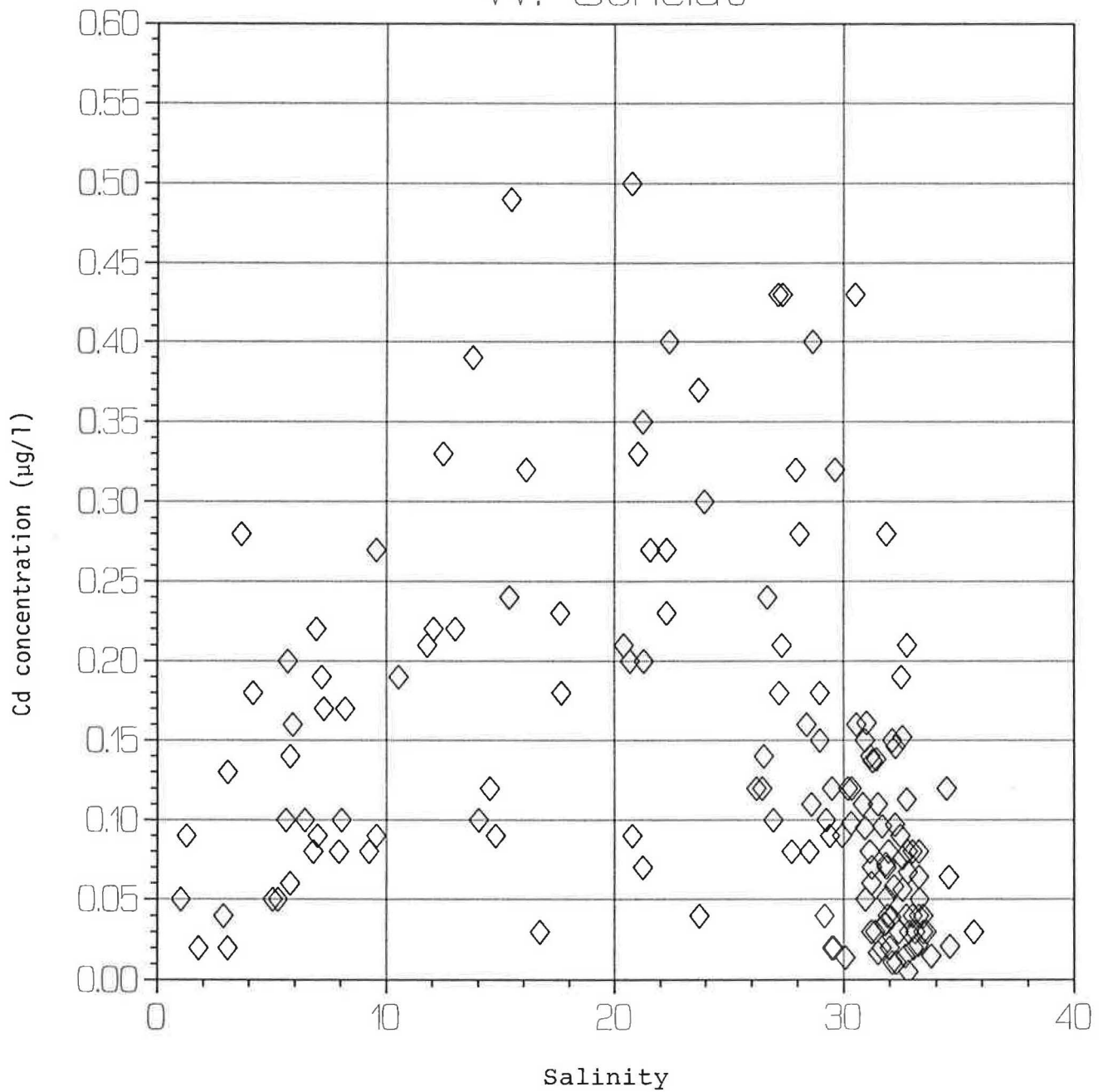


Figure 7 Cadmium vs. salinity for the Western Scheldt and coastal areas of NS4.

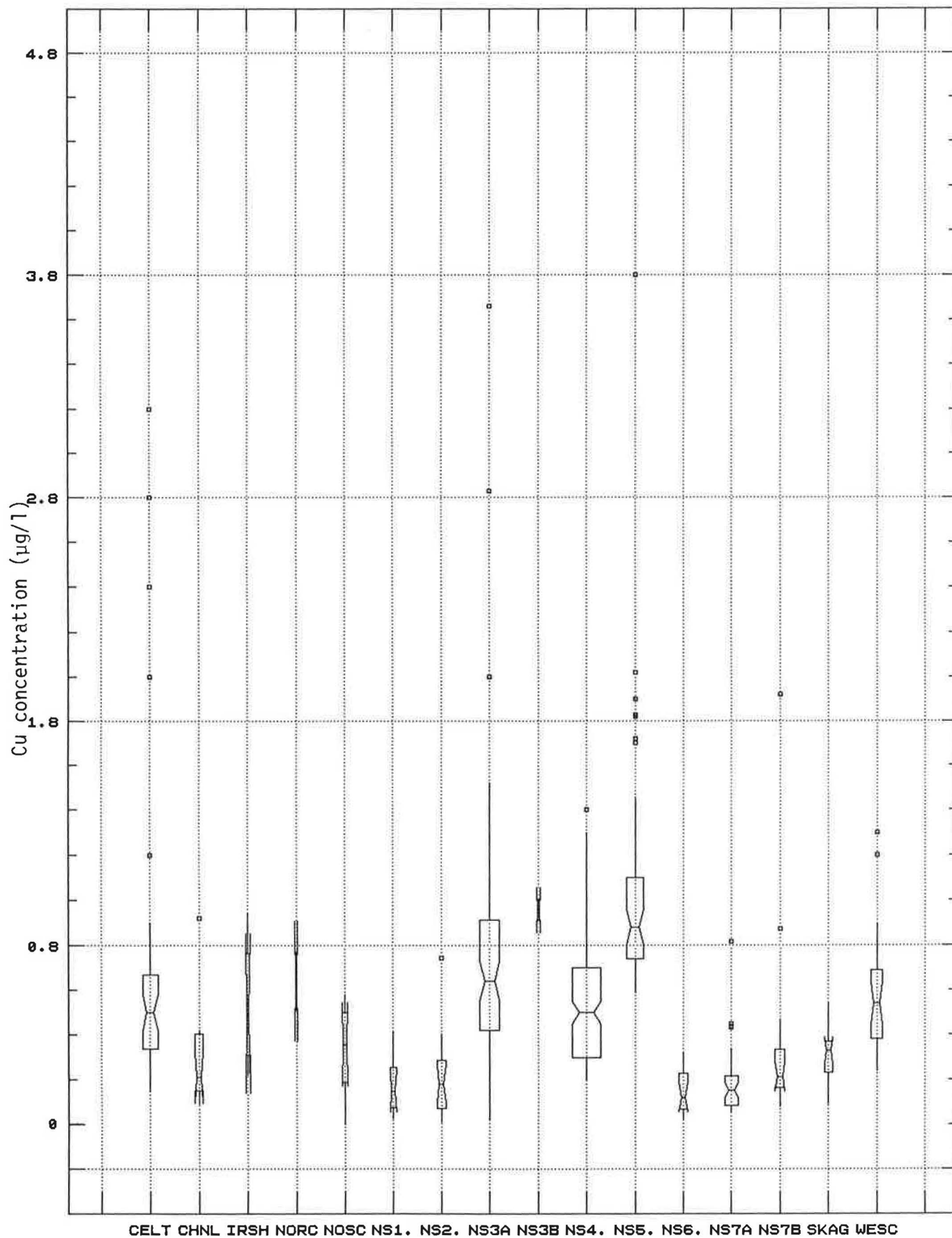


Figure 8(a) Copper data for salinities > 30

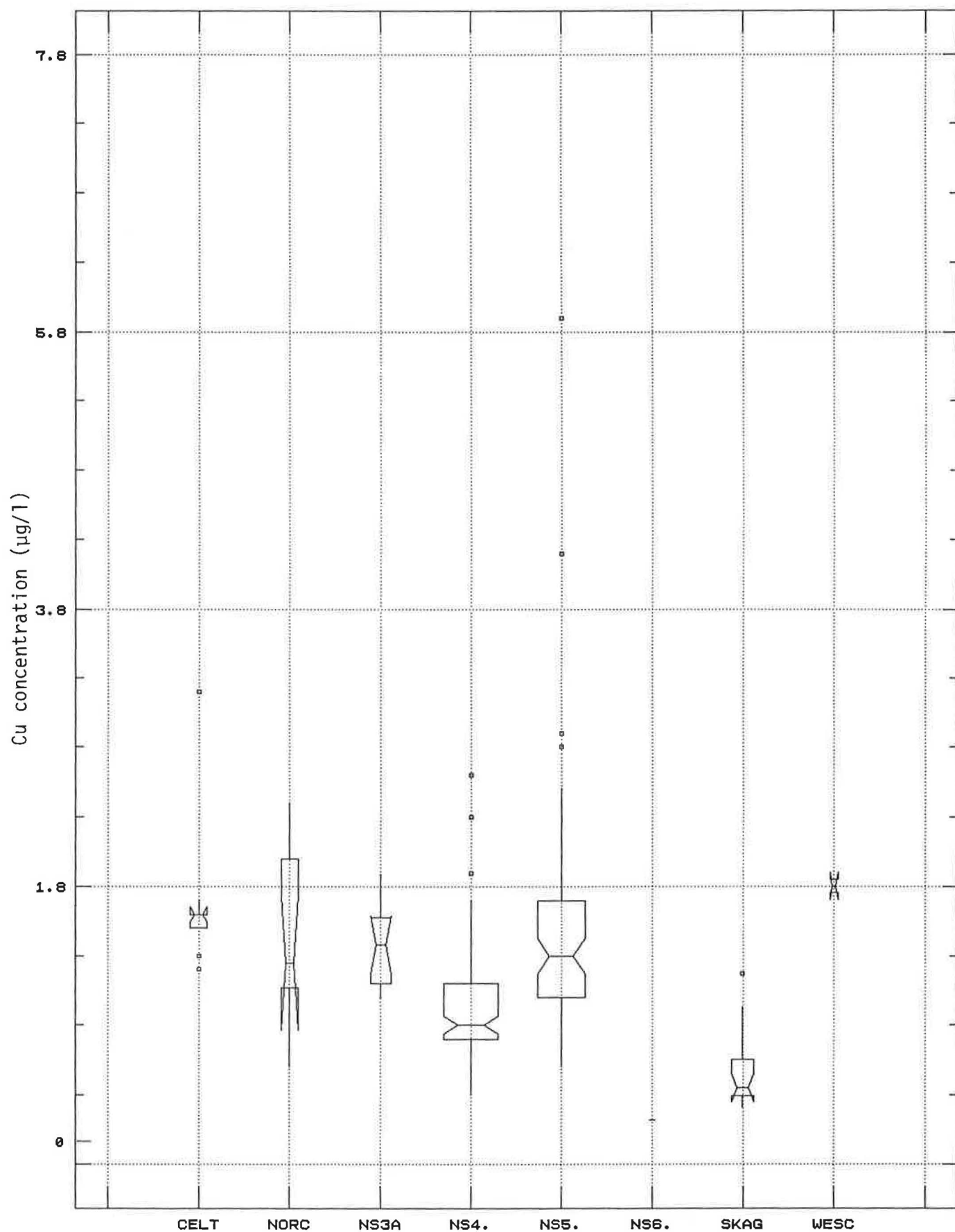


Figure 8(b) Copper data for salinities 25-30

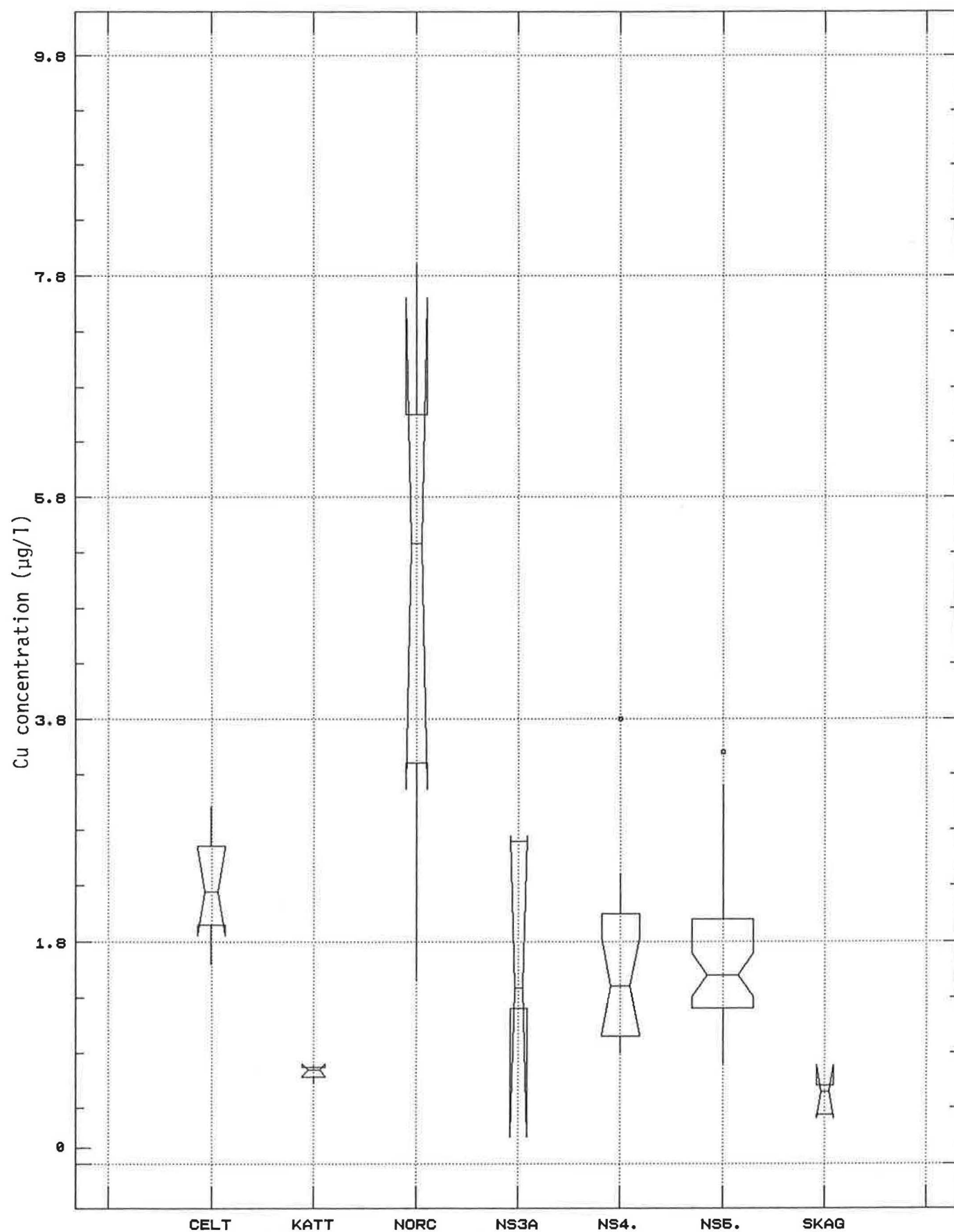


Figure 8(c) Copper data for salinities 20-25

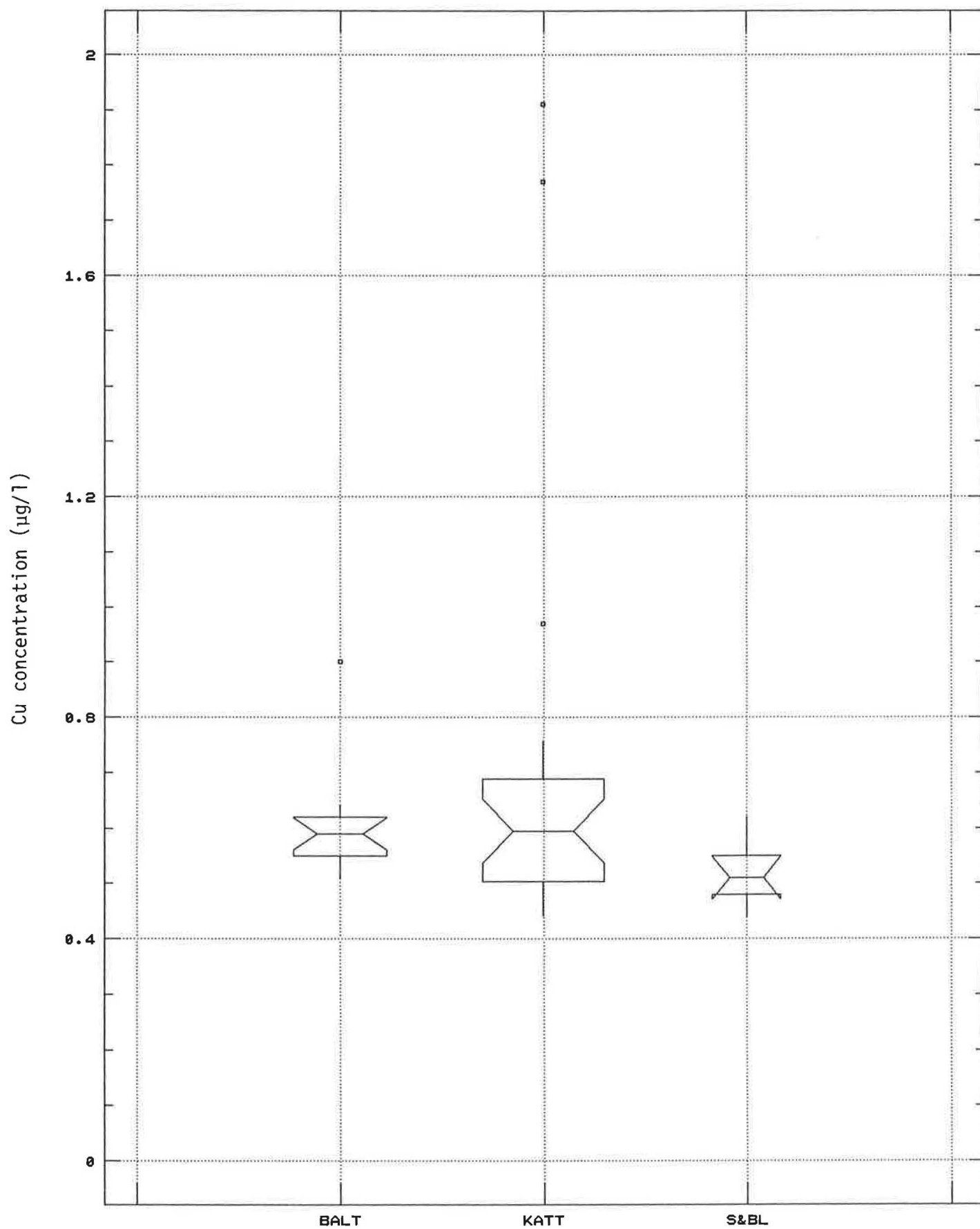


Figure 8(d) Copper data for areas KATT, S&BL and BALT.



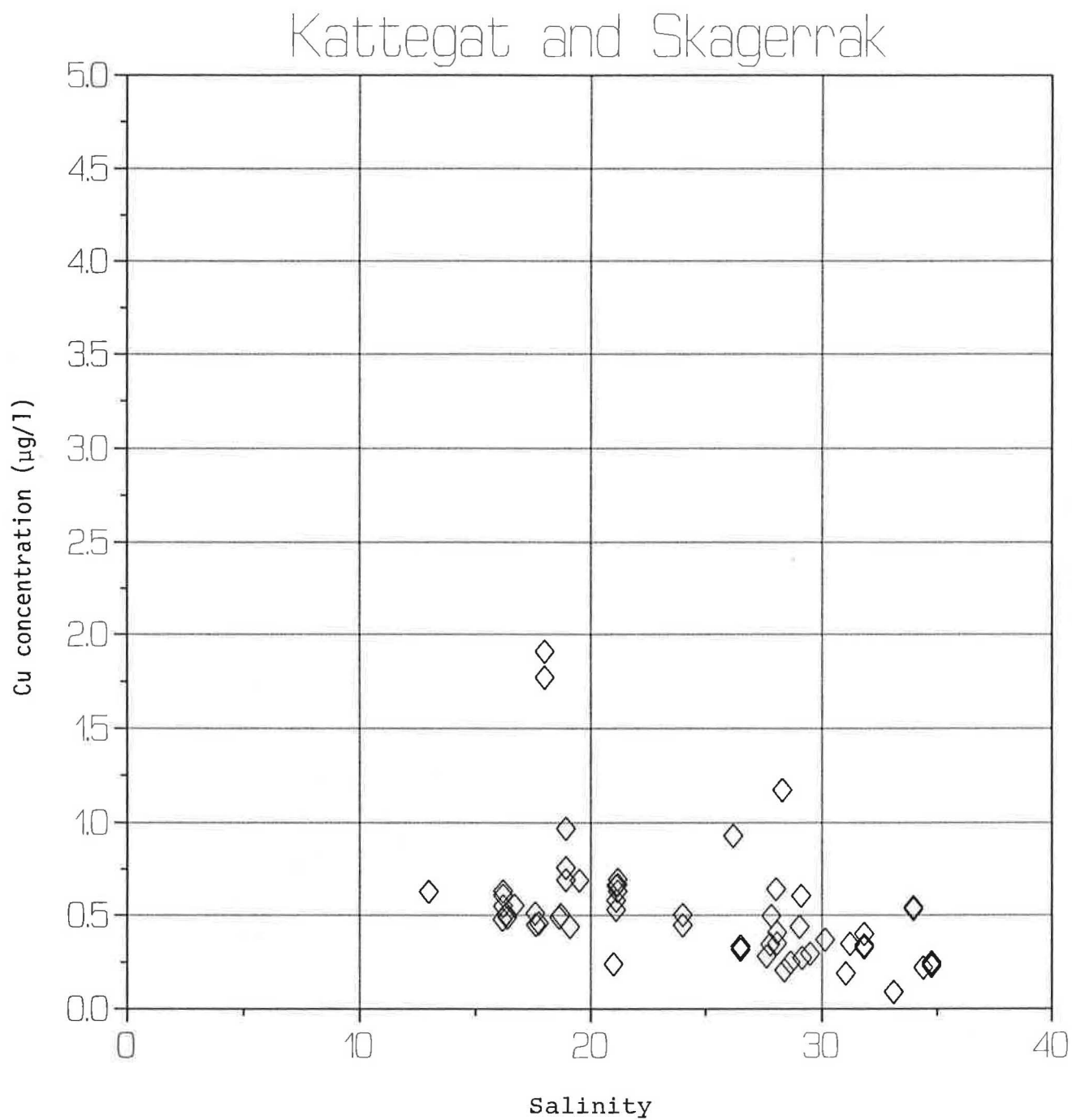


Figure 9 Copper vs. salinity from areas KATT and SKAG.

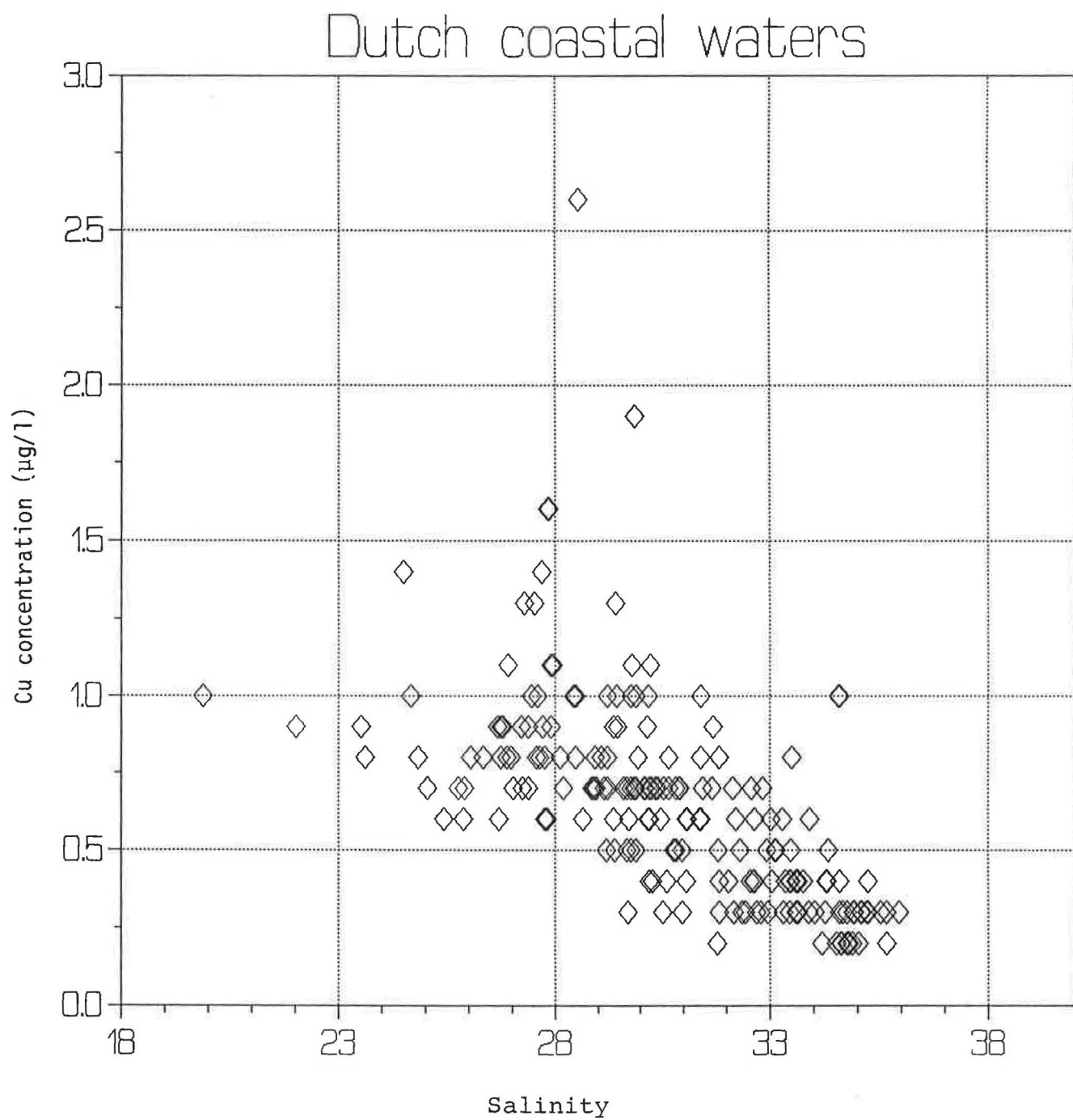


Figure 10 Copper vs. salinity from Dutch coastal part of NS4.

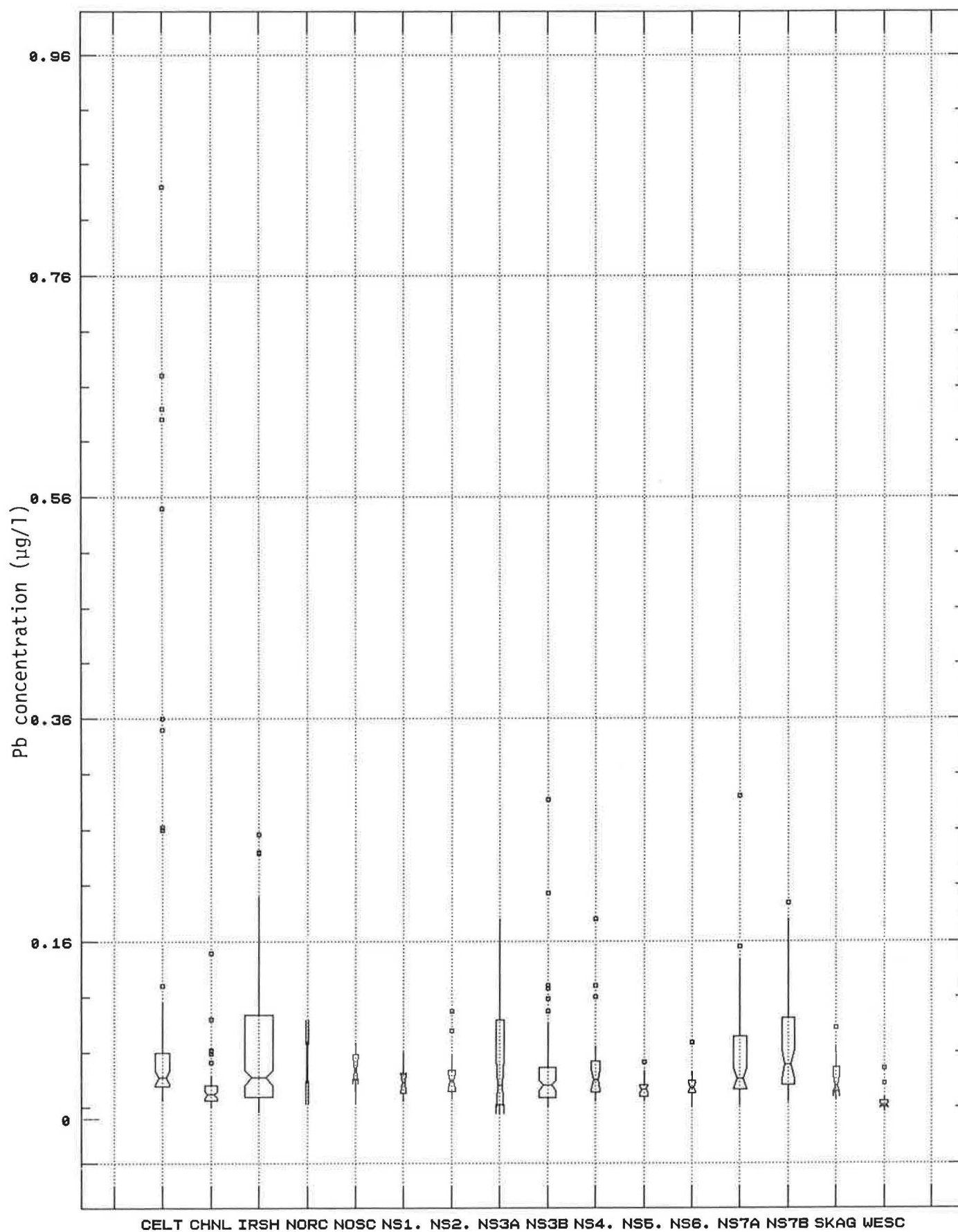


Figure 11(a) Lead data for salinities > 30

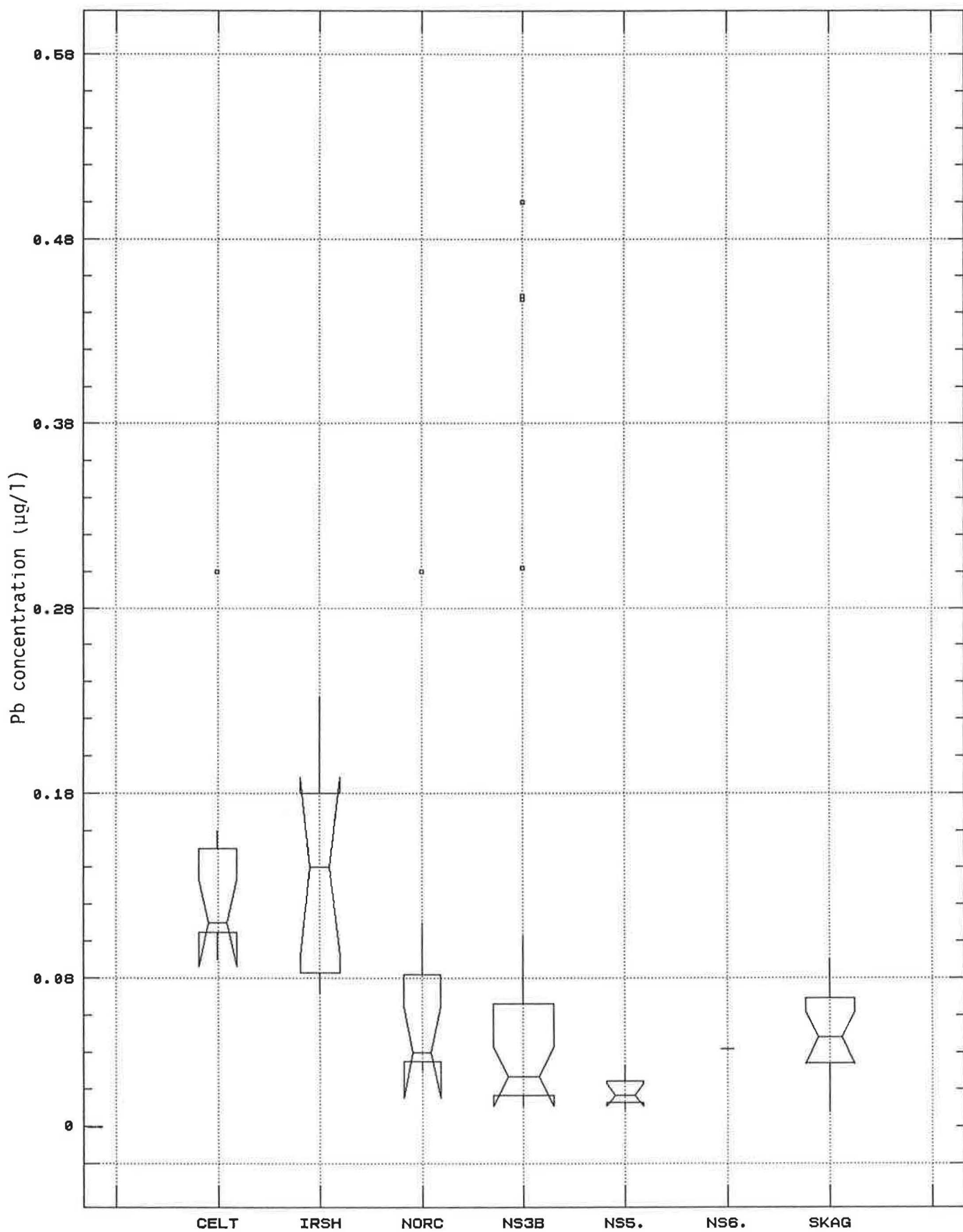


Figure 11(b) Lead data for salinities 25-30

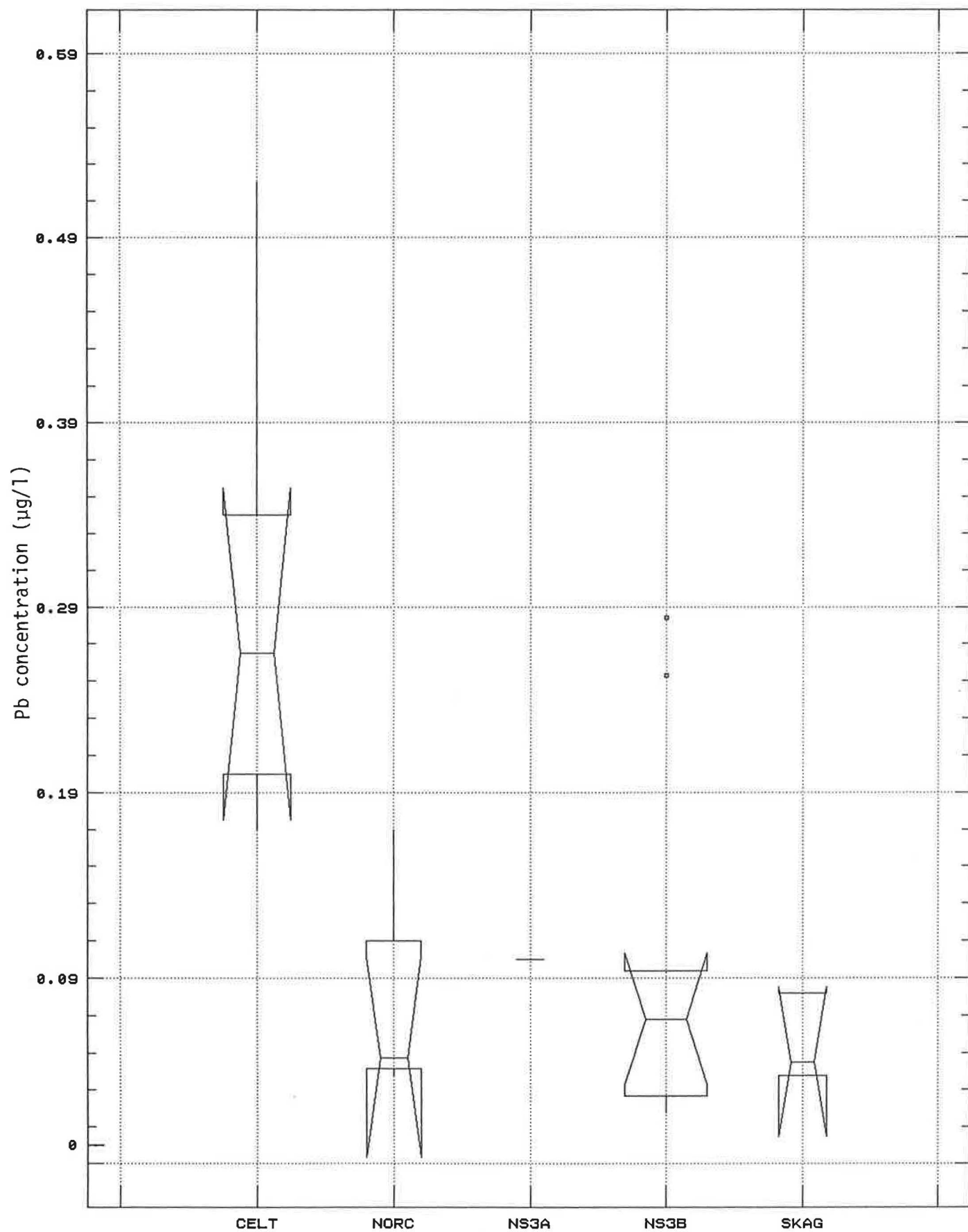


Figure 11(c) Lead data for salinities 20-25

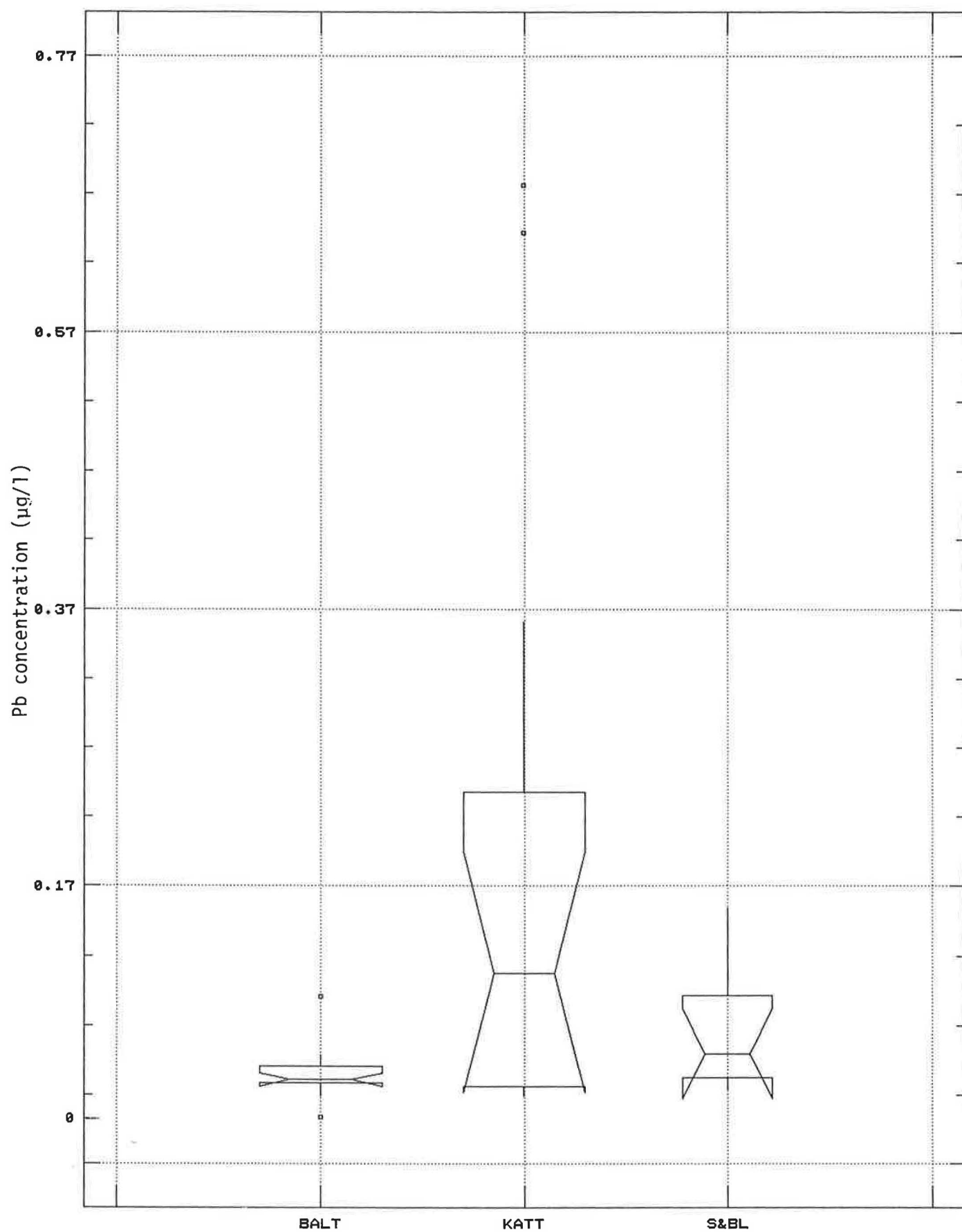


Figure 11(d) Lead data for areas KATT, S&BL and BALT.

# Irish Sea (IRSH)

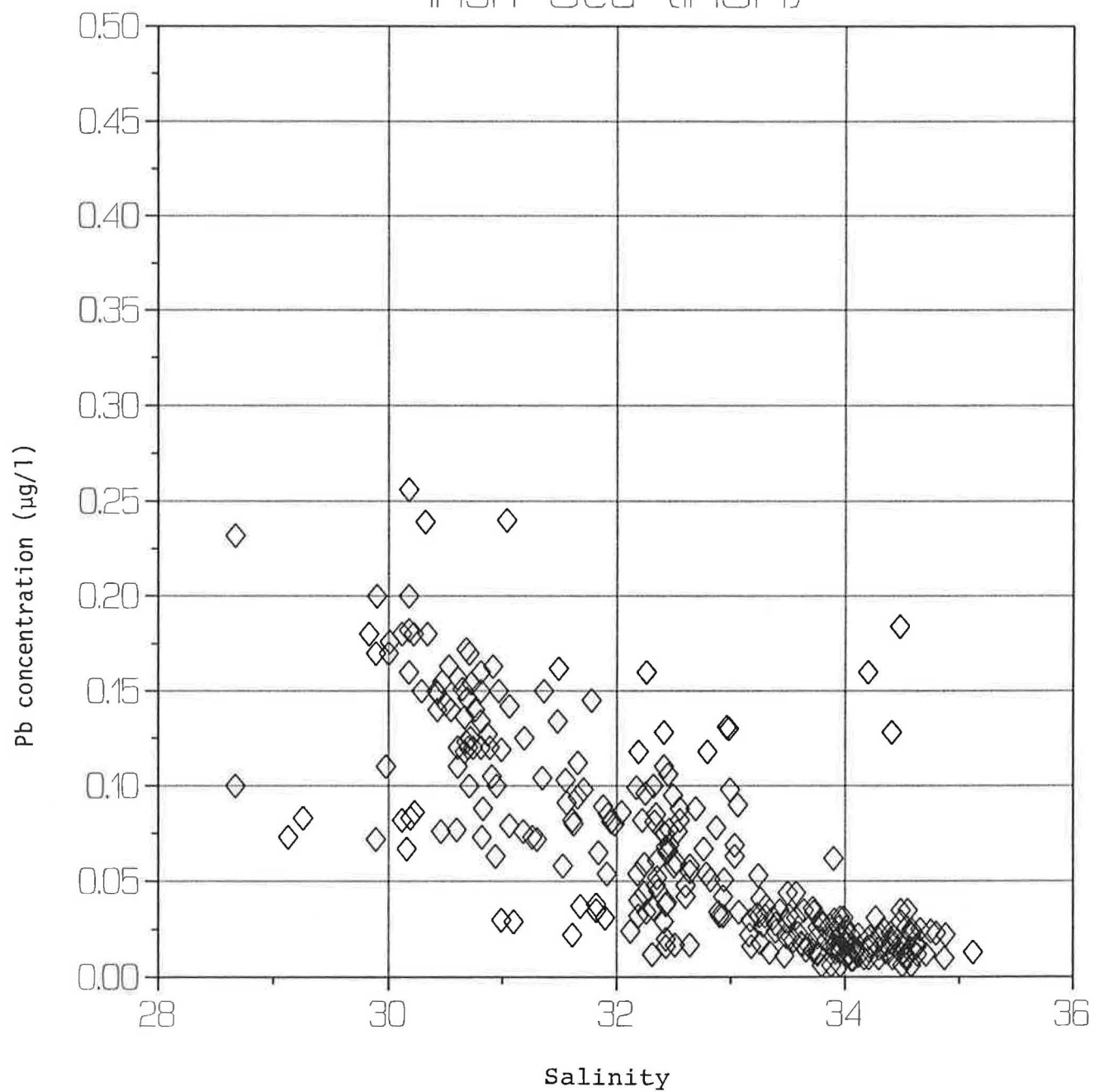


Figure 12 Lead vs. salinity from area IRSH.

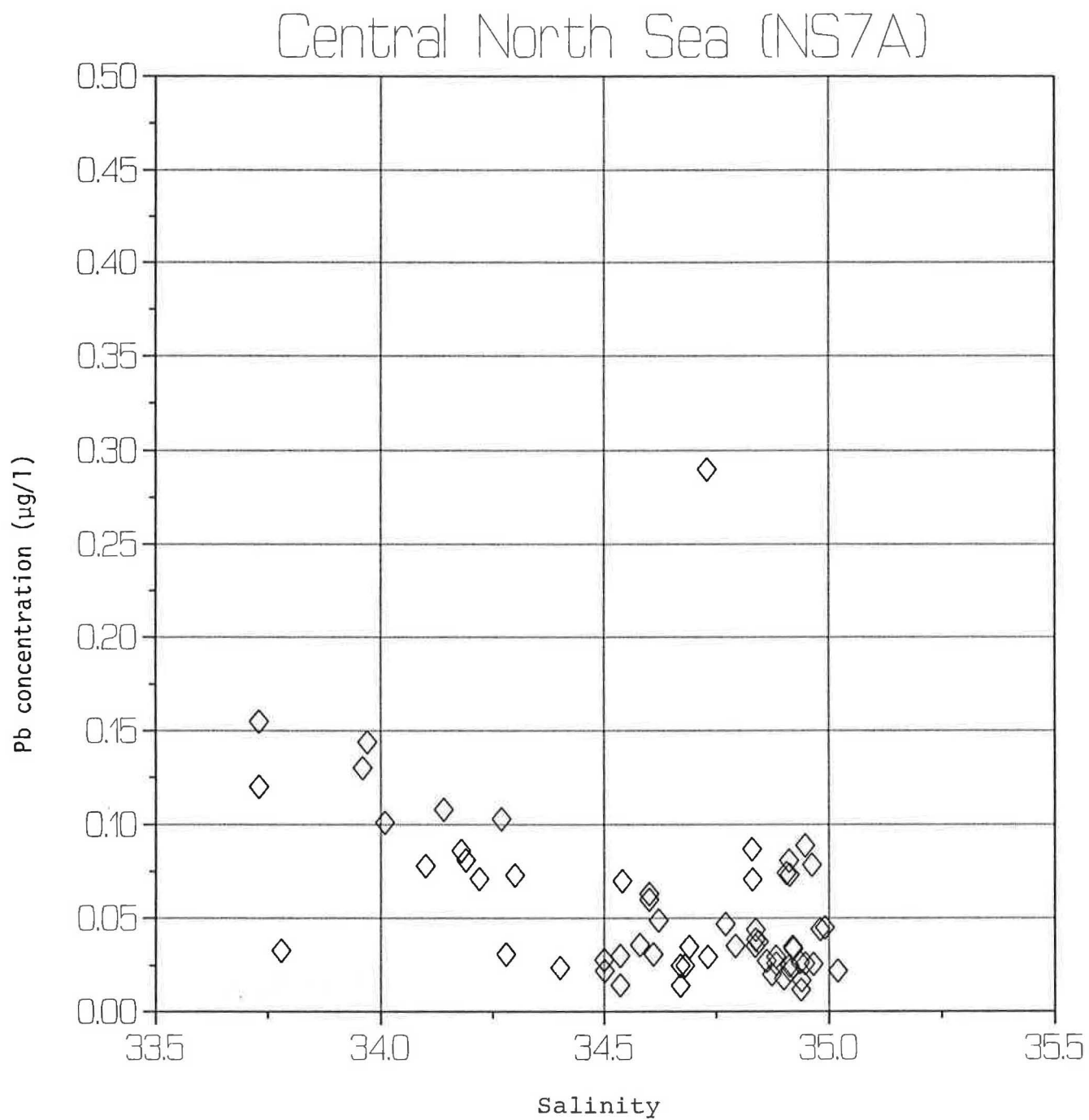


Figure 13 Lead vs. salinity from NS7A.



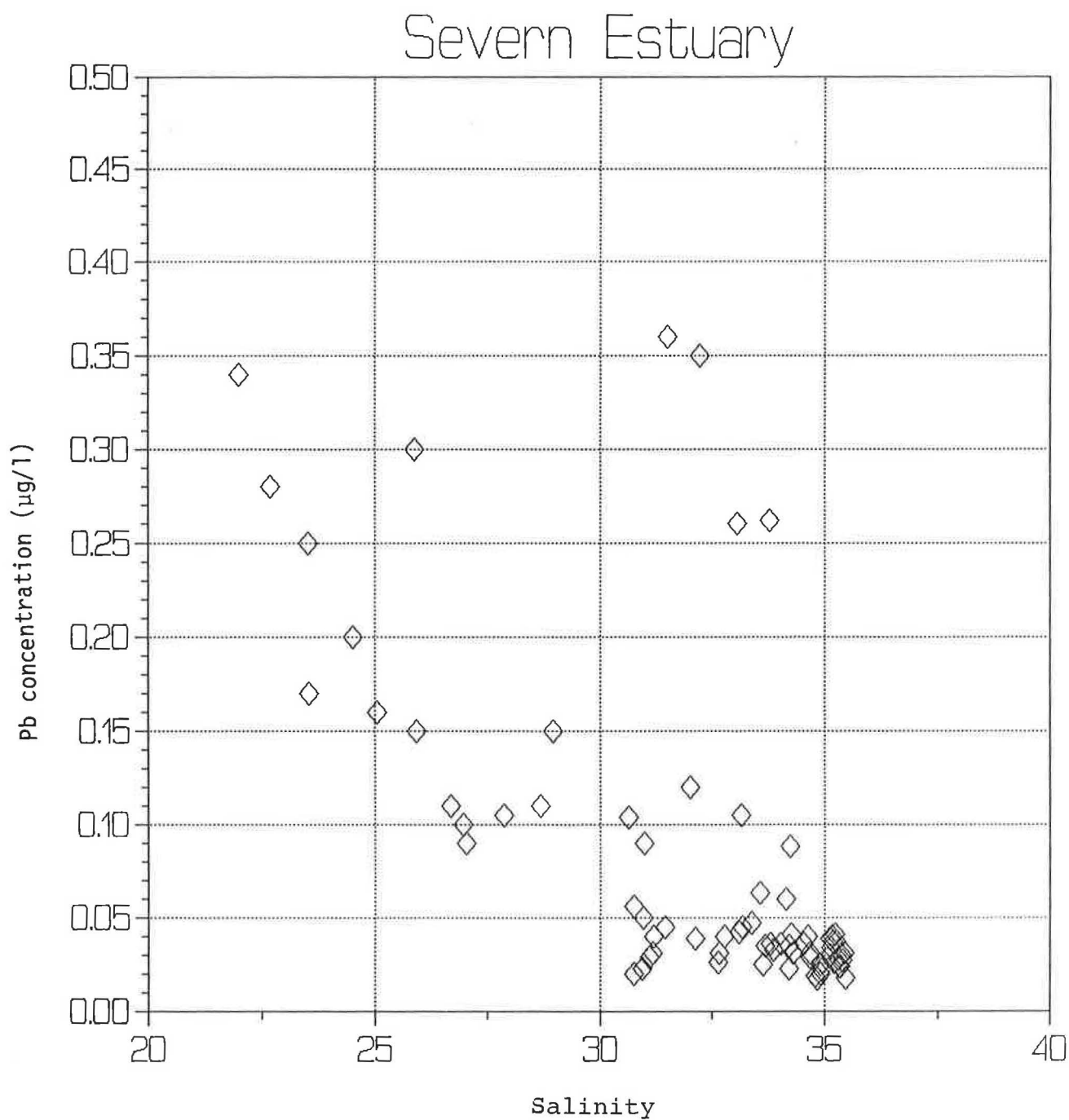


Figure 14 Lead vs. salinity from the Severn Estuary.

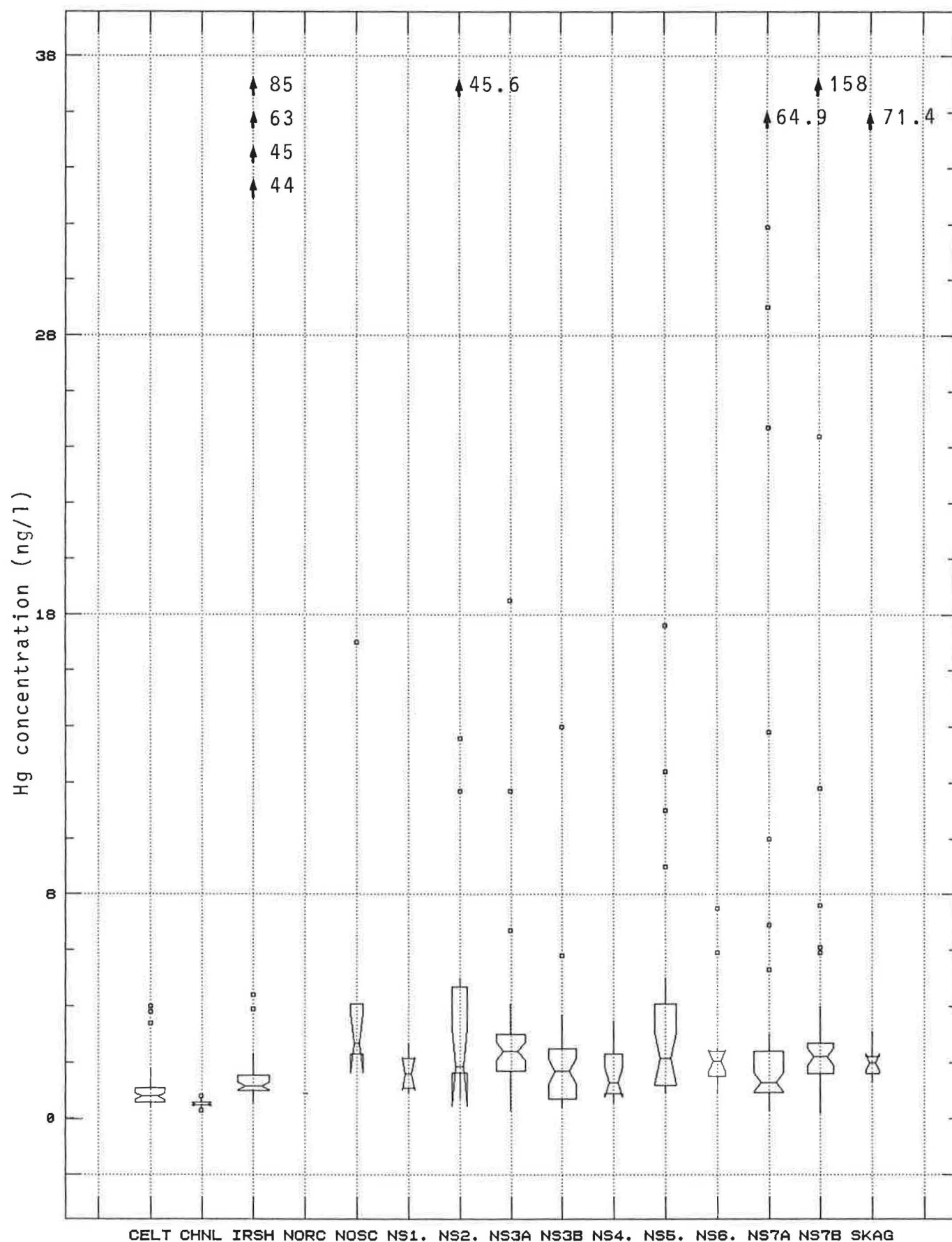


Figure 15(a) Mercury data for salinities > 30

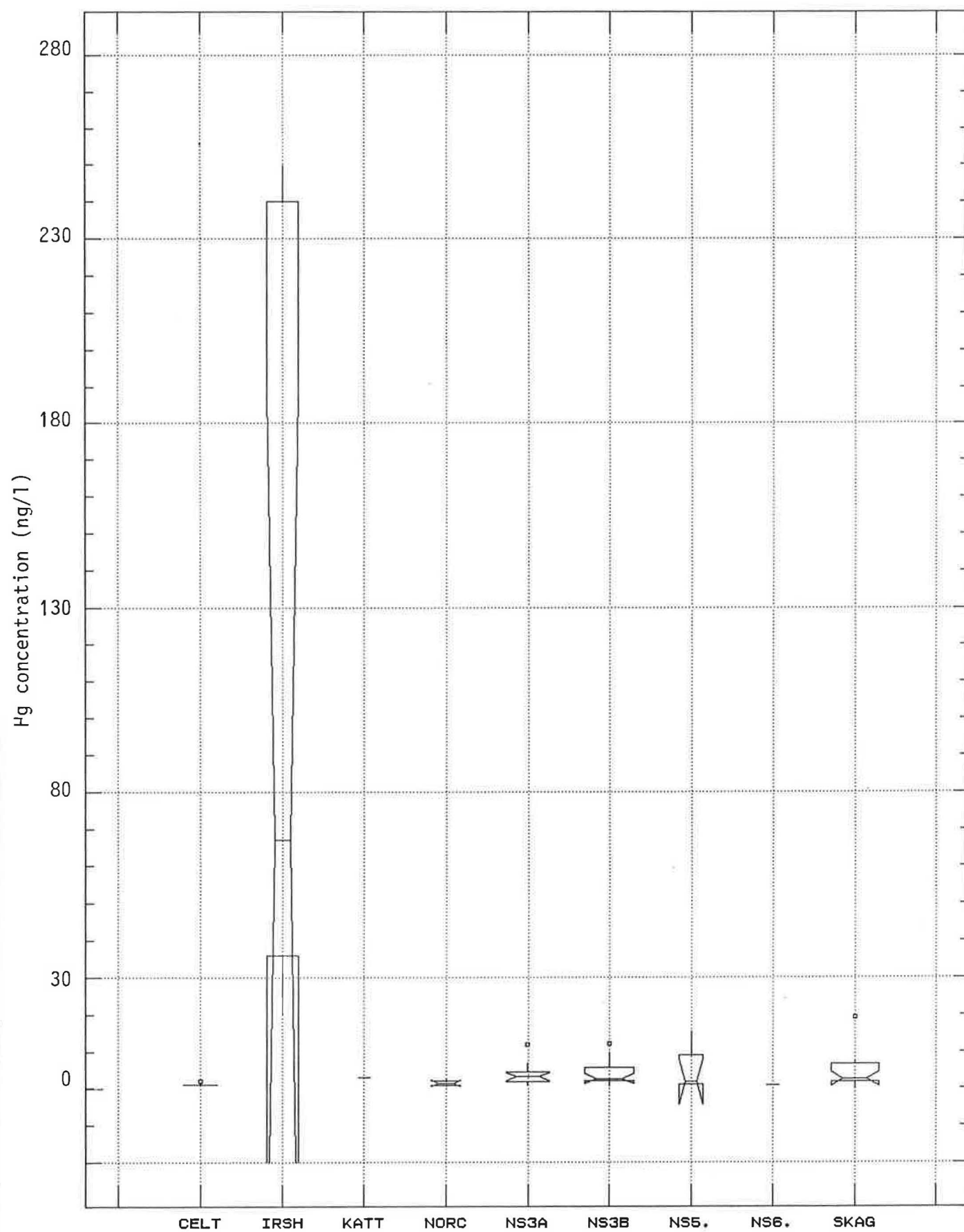


Figure 15(b) Mercury data for salinities 25-30

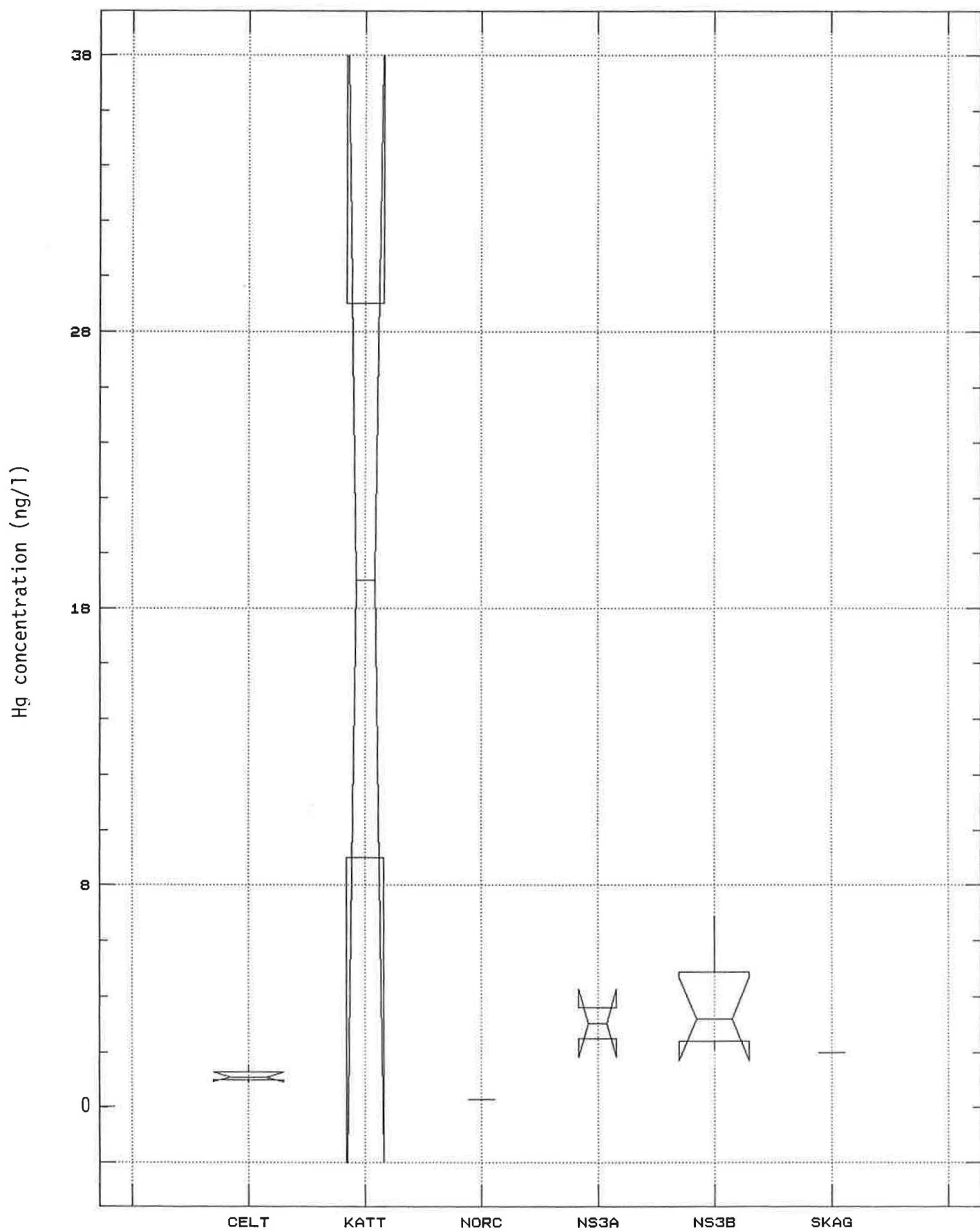


Figure 15c Mercury data for salinities 20-25

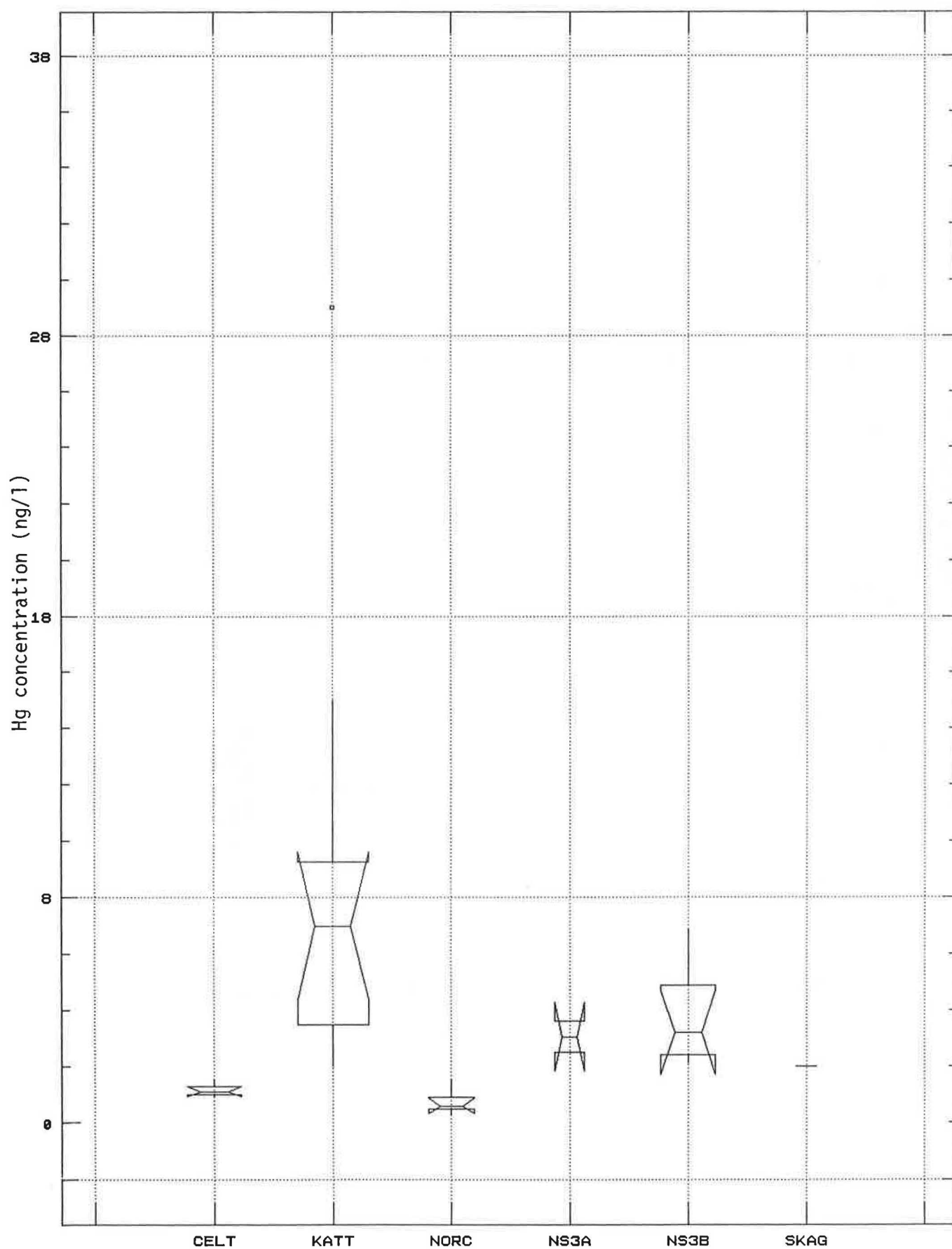


Figure 15d Mercury data for salinities 20-25 and > 20 in area KATT

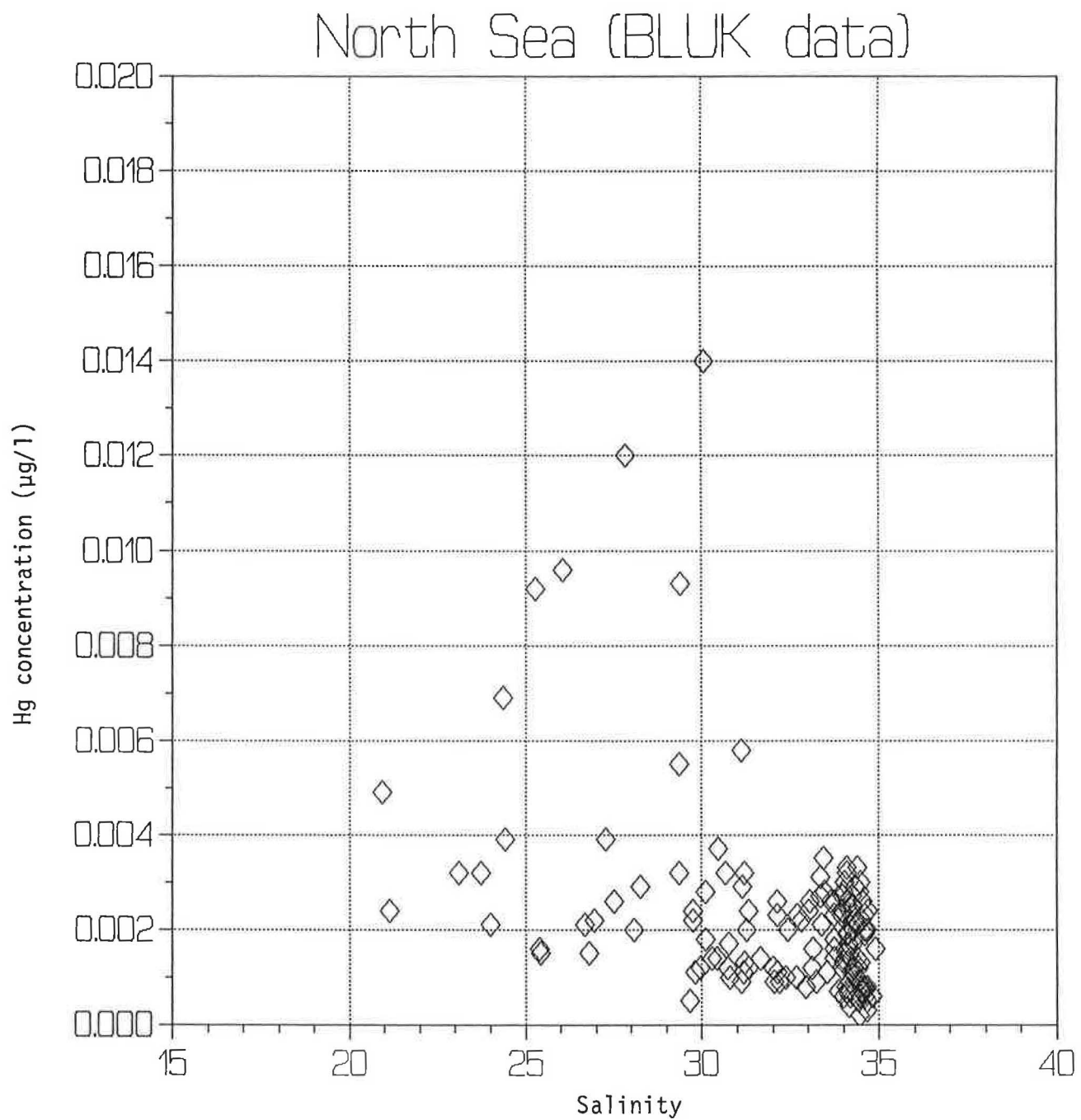


Figure 16 Mercury vs. salinity from BLUK North Sea data.

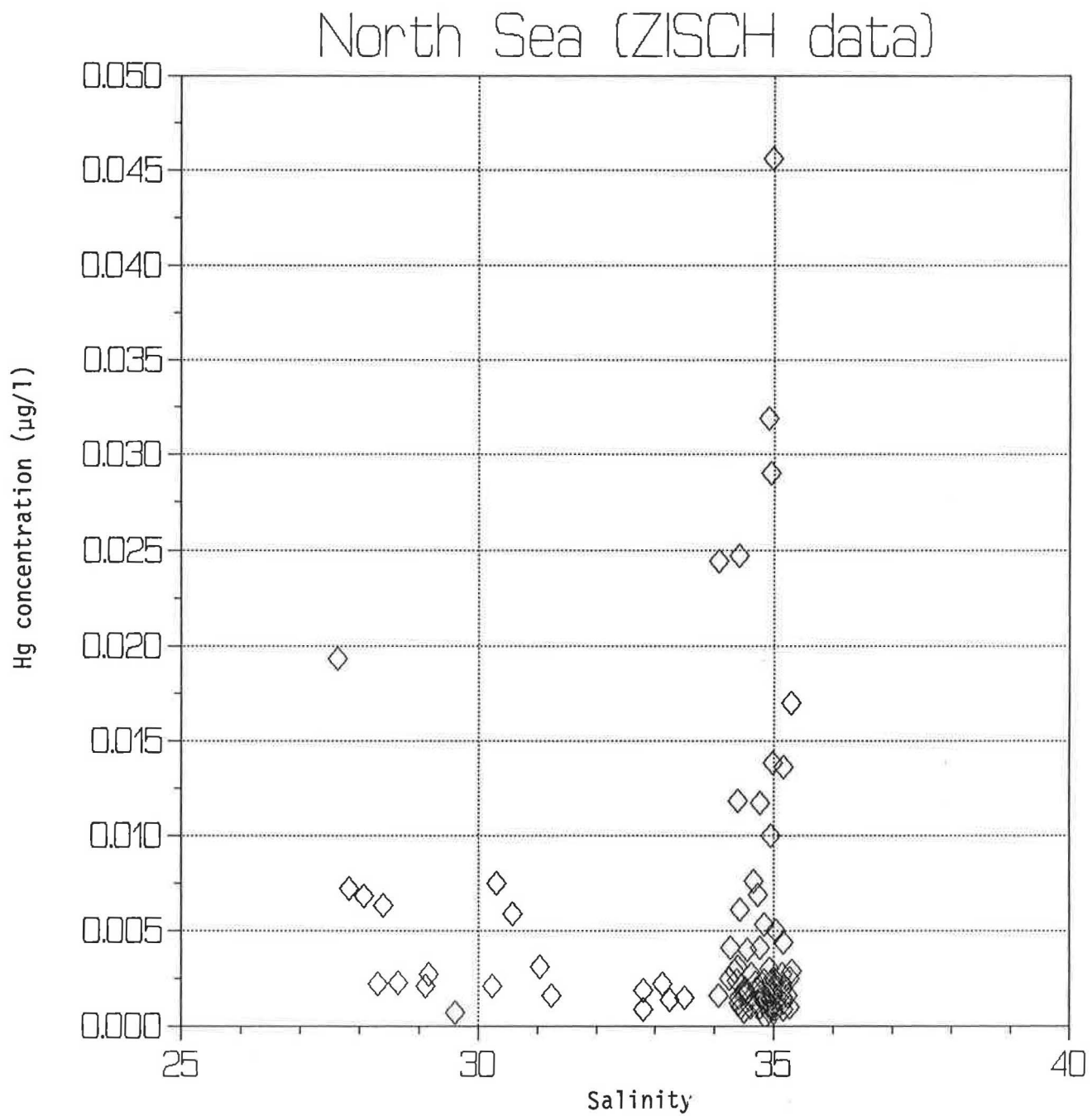


Figure 17 Mercury vs. salinity from ZISCH project North Sea data.

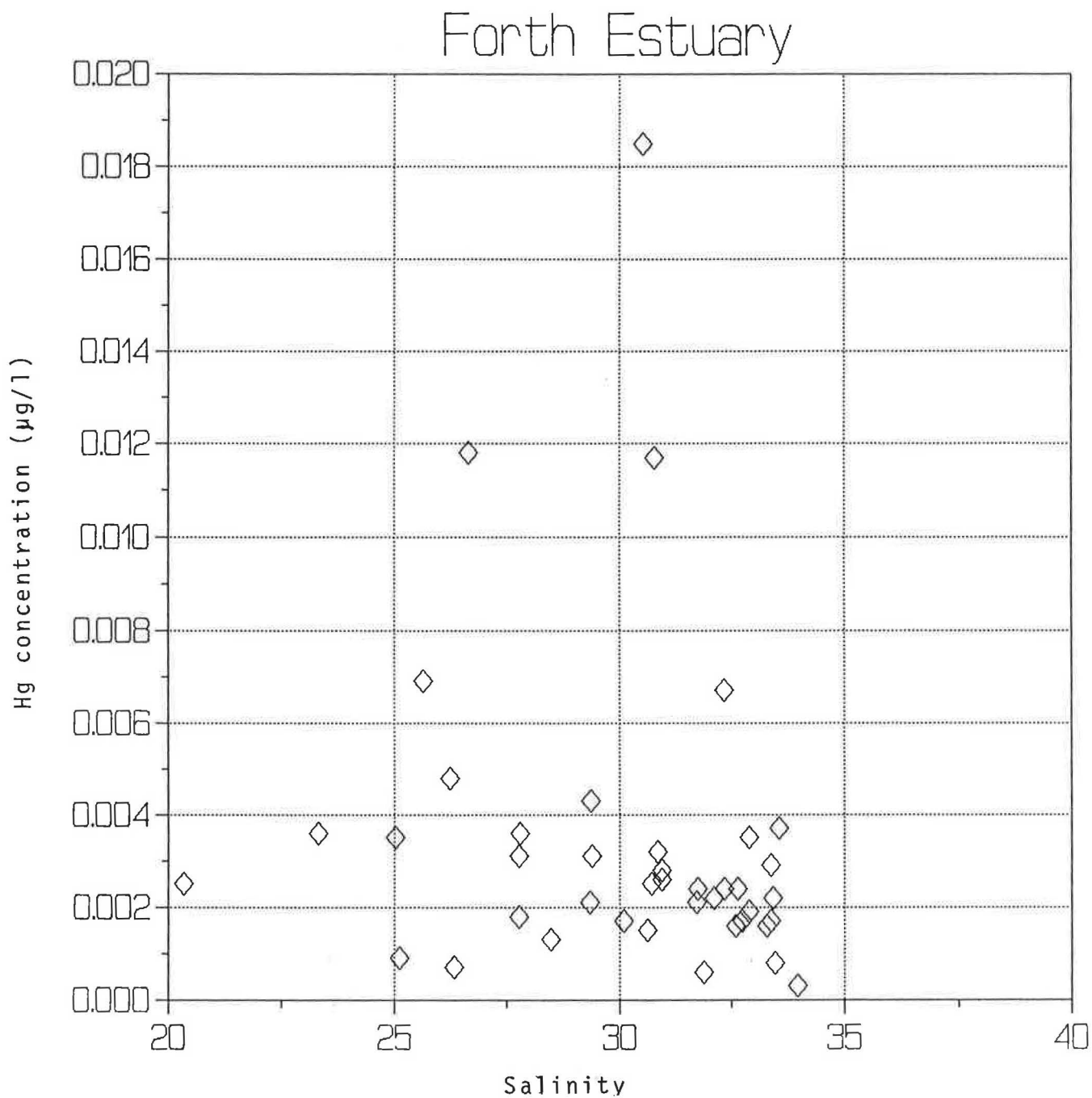


Figure 18 Mercury vs. salinity for the Forth Estuary.



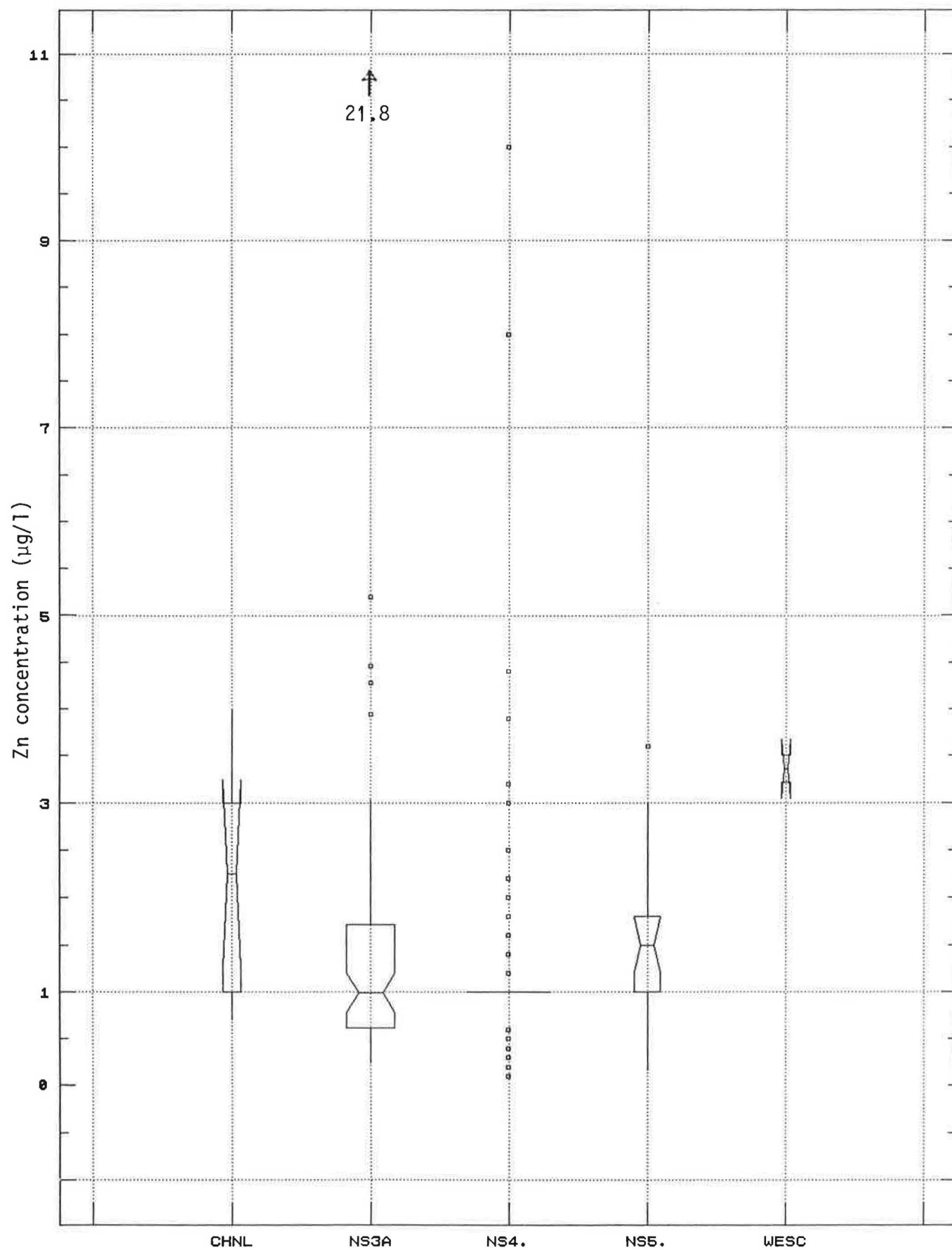


Figure 19(a) Zinc data for salinities > 30

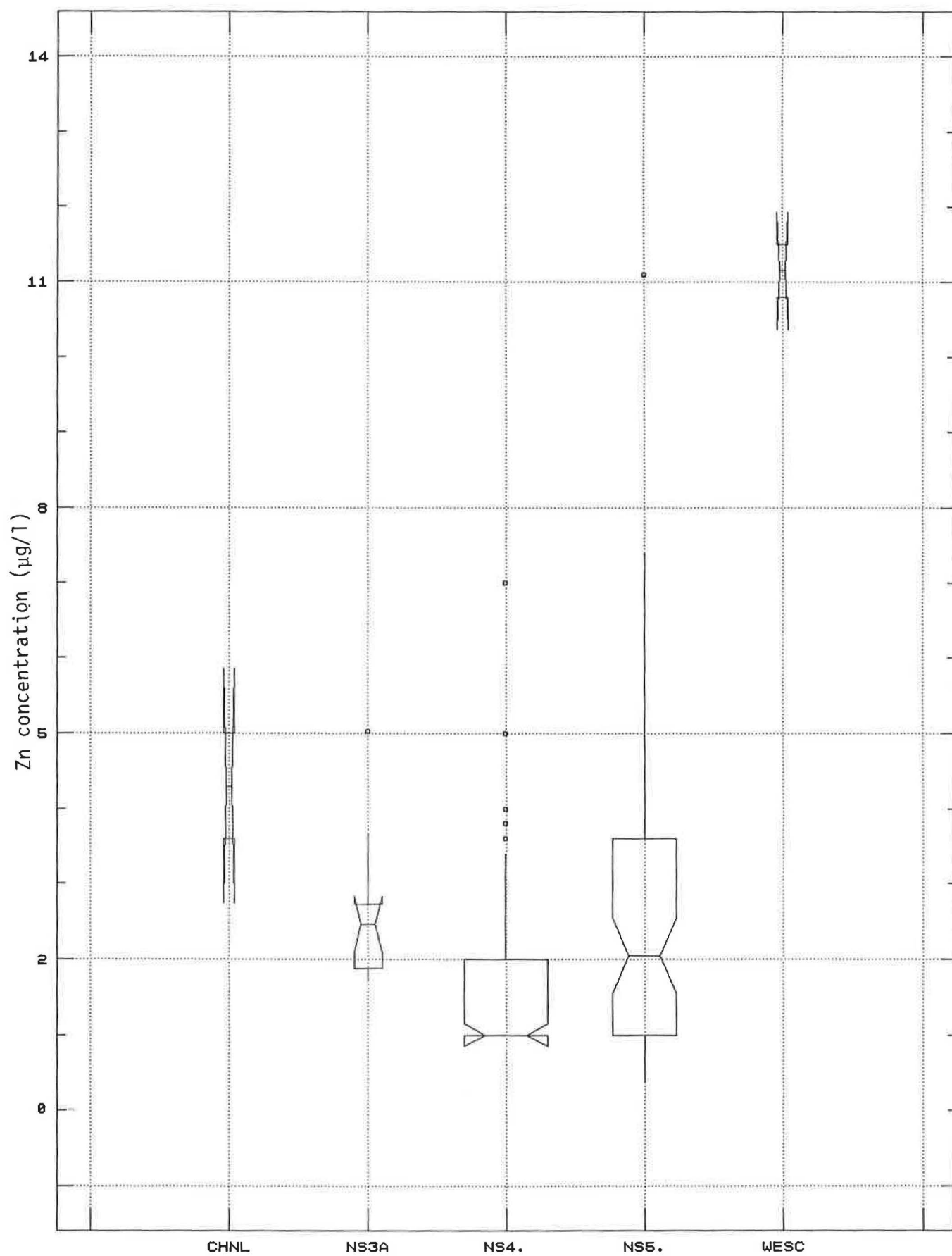


Figure 19(b) Zinc data for salinities 25-30

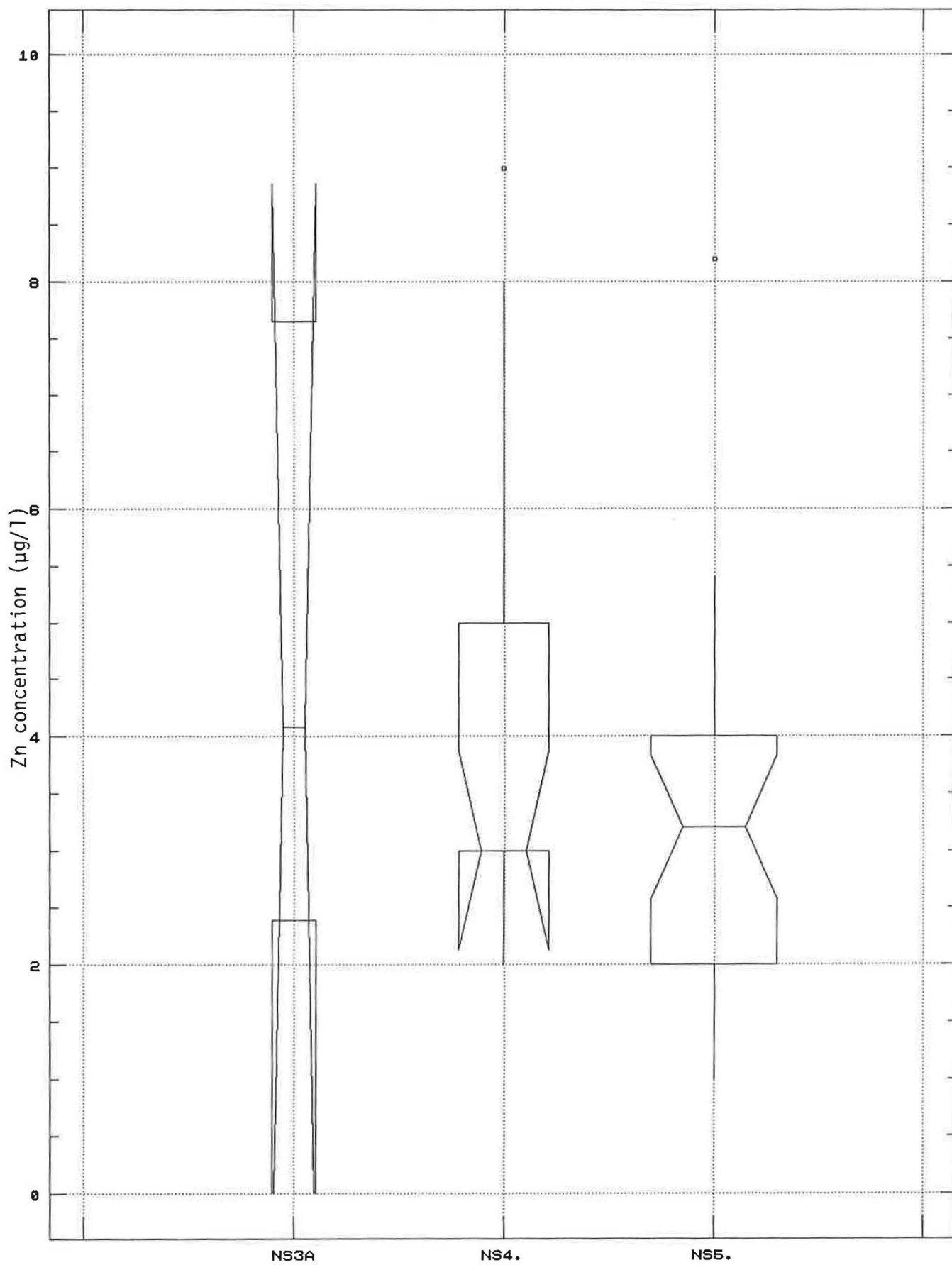


Figure 19(c) Zn data for salinities 20-25

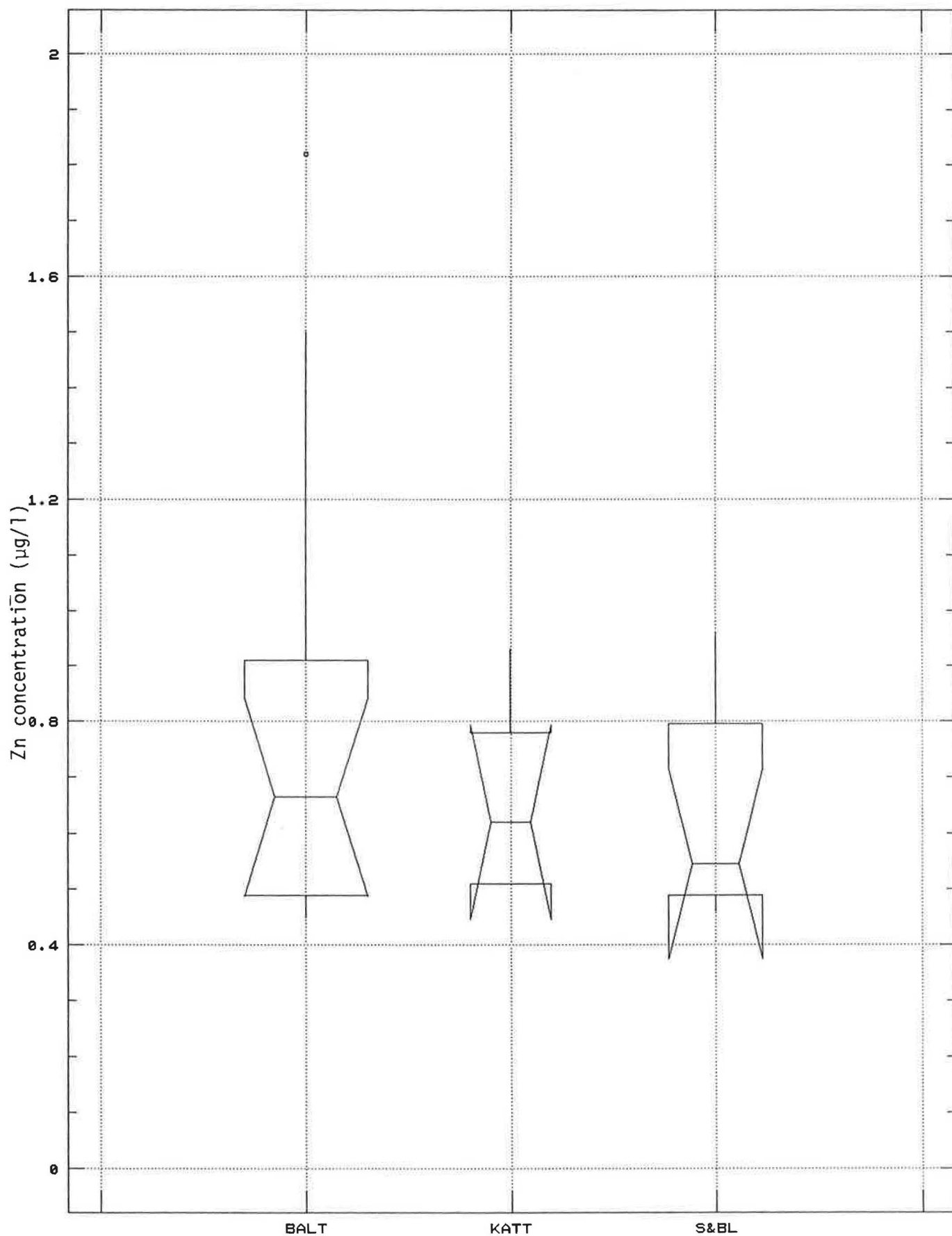


Figure 19(d) Zinc data for areas KATT, S&BL and BALT.

# Dutch coast (NS4.)

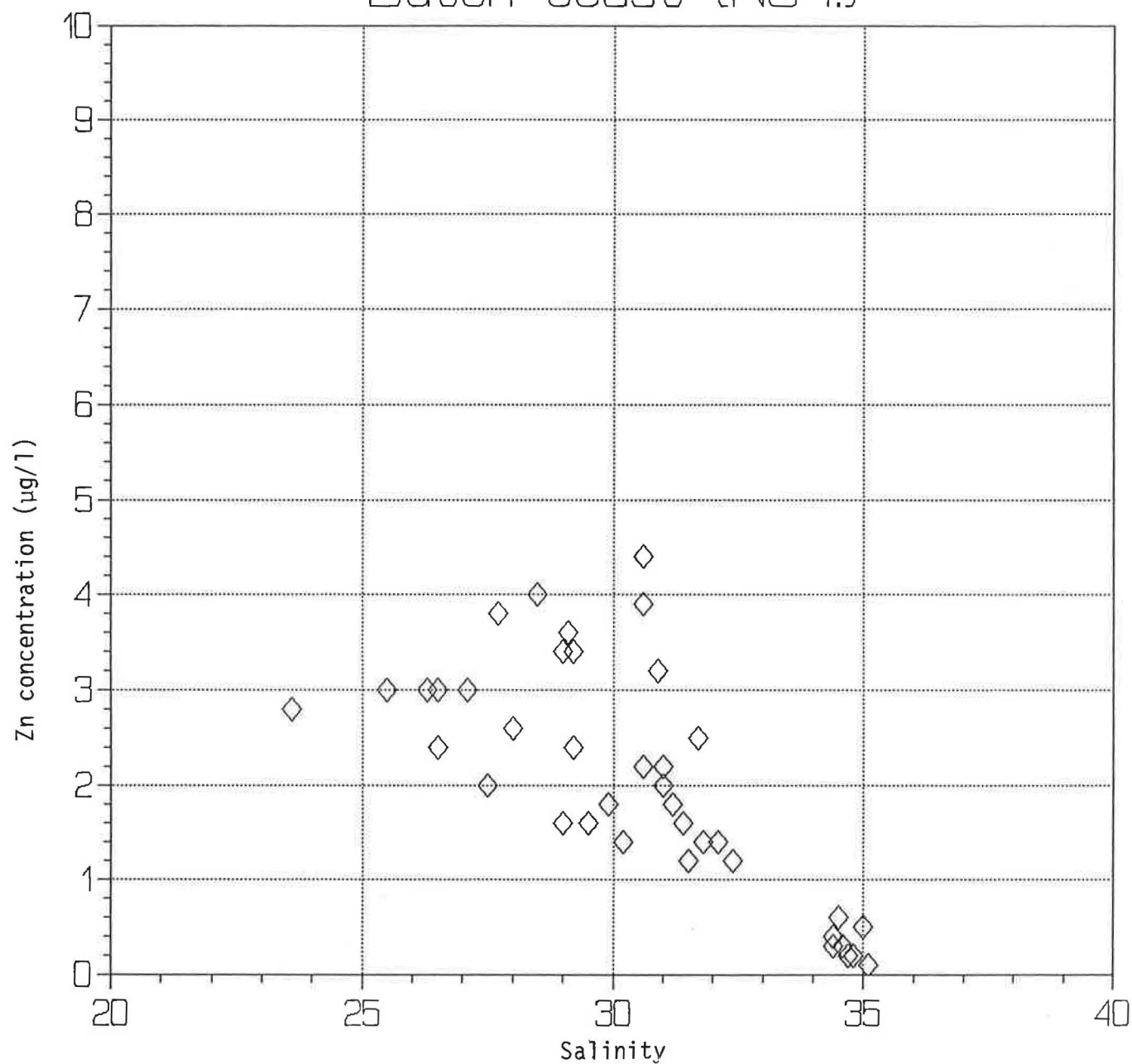


Figure 20 Zinc vs. salinity for the Dutch coastal area of NS4; data from laboratory IBWL.

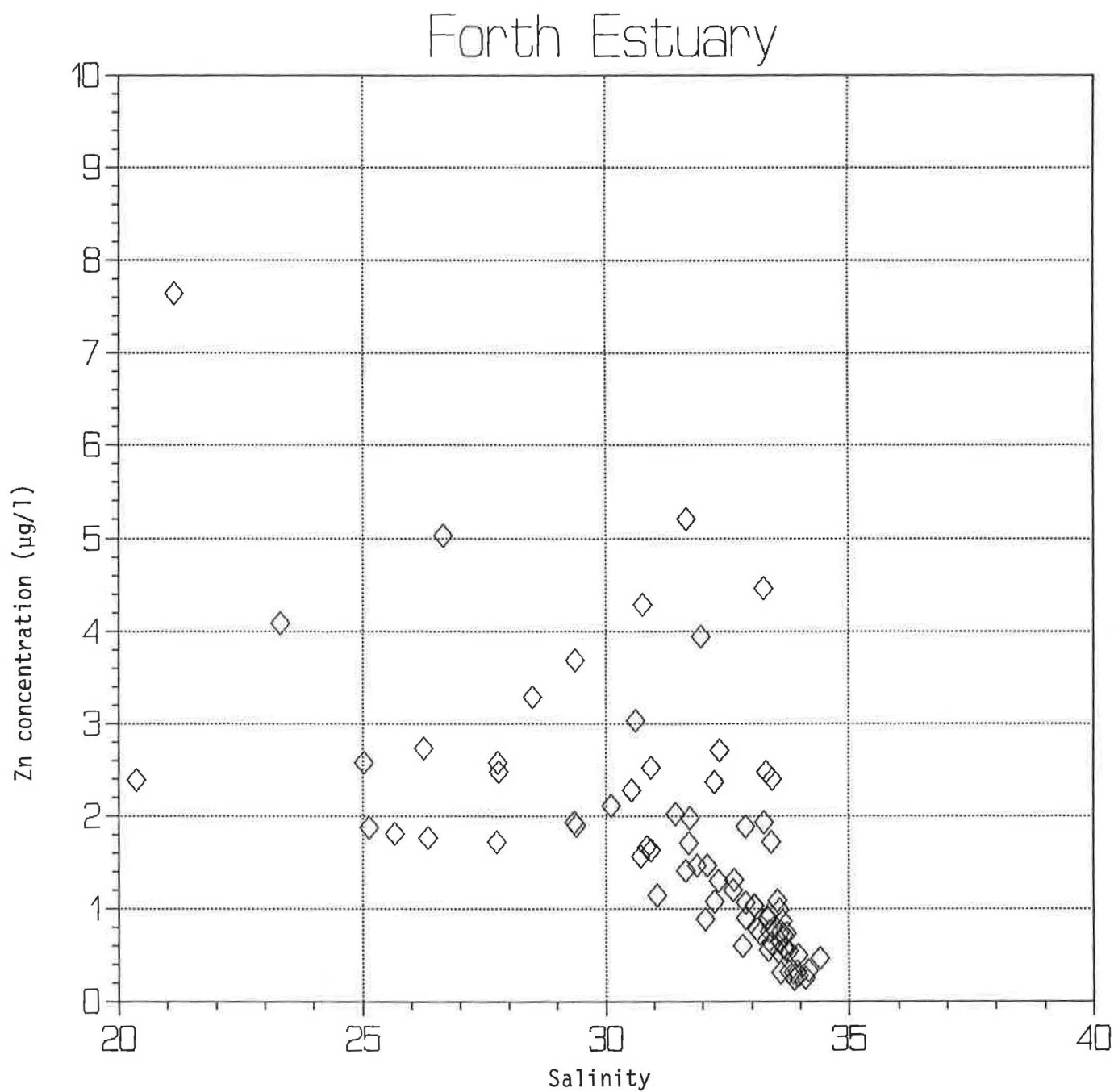


Figure 21 Zinc vs. salinity for the Forth Estuary.

## ANNEX 1

### CODES AND ADDRESSES OF ANALYTICAL LABORATORIES

BELGIUM	IHEB	Instituut voor Hygiëne en Epidemiologie Management Unit of the North Sea and Scheldt Estuary Mathematical Models Gulledelle 100, B-1200 Brussels
DENMARK	HFLD	Miljøstyrelsens Havforureningslaboratorium Jægersborg Allé 1B DK-2920 Charlottenlund
	ICDK	Danish Isotope Center Skelbækgade 2 DK-1717 Copenhagen V
GERMANY	IGDR	Institut für Meereskunde Akademie der Wissenschaften der DDR Seestraße 15 D-O 2530 Rostock-Warnemünde
	BFGG	Bundesanstalt für Gewässerkunde Kaiserin-Augusta-Anlagen 15-17 D-W 5400 Koblenz
	DHIG	Deutsches Hydrographisches Institut Bernhard-Nocht-Straße 78 D-W 2000 Hamburg 50
	FITG	Fresenius Institut Chemische und Biologische Laboratorien GmbH D-W 6204 Taunusstein-Neuhof
	ISHG	Institut Schumacher Laboratorium für Wasser-, Abwasser- und Flanalytik Sophie-Dethleffs-Straße 4 D-W 2240 Heide
	LWKG	Landesamt für Wasserhaushalt und Küsten Saarbrückenstraße 38 D-W 2300 Kiel 1
NETHERLANDS	DGWN	Rijkswaterstaat Dienst Getijdewateen Hooftskade 1 NL-2526 KA The Hague
	RIZA	Rijksinstituut voor Zuivering van Afvalwater P.O. Box 17 NL-8200 AA Lelystad

## ANNEX 1 (contd)

NETHERLANDS (contd)	IBWL	Instituut voor Bodemvruchtbaarheid Oosterweg 92 NL-9750 Ra Haren
NORWAY	NIVA	Norwegian Institute for Water Research P.O. Box 69, Korsvoll N-0808 Oslo 8
PORTUGAL	IHLP	Instituto Hydrografico Rua das Trinas 49 1296 Lisbon Codex
SPAIN	IEOM	Centro Oceanográfico del Mar Menor, Magallanes 2, Lopagan San Pedro del Pinatar Murcia
SWEDEN	LCRS	Swedish Environmental Protection Agency Laboratory for Coastal Research S-170 11 Drottningholm
	SERI	Swedish Environmental Research Institute Box 5207, Sten Sturegatan 42 S-402 24 Gothenburg
UNITED KINGDOM	ALUK	Department of Agriculture and Fisheries Marine Laboratory P.O. Box 101, Victoria Road Aberdeen AB9 8DB
	BLUK	Ministry of Agriculture, Fisheries and Food Fisheries Laboratory Remembrance Avenue Burnham-on-Crouch, Essex CMO 8HA
	CRUK	Clyde River Purification Board Rivers House Murray Road East Kilbride Glasgow G75 0LA
	FRUK	Forth River Purification Board Colinton Dell House West Mill Road Colinton Edinburgh EH13 0PH
	NWUK	Northwest Water Authority Dawson House, Great Sankey Warrington WA5 3LW



## **ANNEX 1 (contd)**

### **UNITED KINGDOM (contd)**

- SWUK** Southern Water Authority  
Hampshire Divisional Laboratory  
Sparrowgrove  
Otterbourne  
Winchester  
Hampshire SO21 2SW
- TWUK** Thames Water Authority  
Rivers House  
Crossness Works  
Abbey Wood, London SE2 9AQ
- WWUK** Wessex Water Authority  
Bristol Avon Divisional Laboratory  
Mead Lane  
Saltford, Bristol BS18 3ER
- NRUK** Northumbrian Water  
Howdon Laboratory  
Howdon Sewage Works  
Northumberland Dock Road  
Wallsend  
Tyne and Wear
- HGUK** Humber Estuary Management Group

## ANNEX 2

### NOTCHED BOX-AND-WHISKER PLOTS

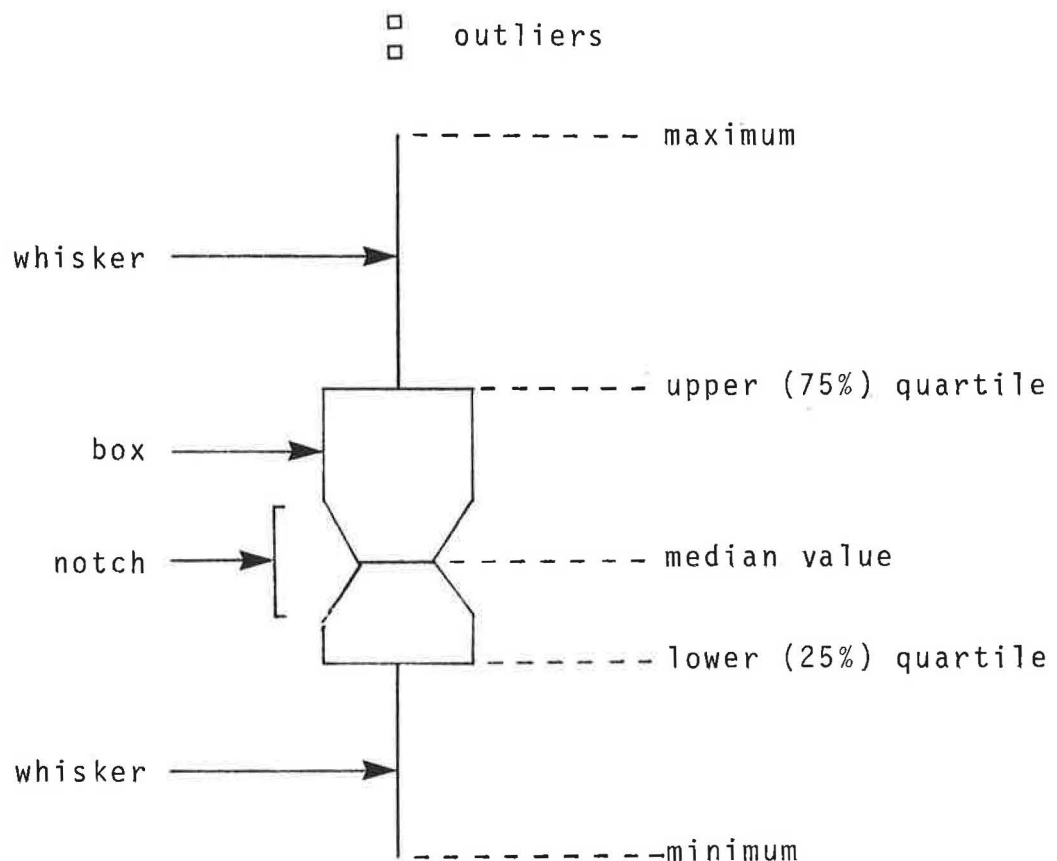
The notched box-and-whisker plot provides a statistical summary of a numerical data set, sub-divided by groups if required. It provides a useful means of detecting outliers and asymmetric behaviour, and comparing data distributions between groups.

The central box covers the middle 50% of the data values, between the upper (75%) quartile and the lower (25%) quartile. The whiskers extend to the maximum and minimum values

and the central line represents the median (50%) value. Outside values may be plotted as points beyond the whiskers.

The notches correspond to the width of a confidence interval for the median. Pairwise comparisons can be performed at the 95% level by examining whether two notches overlap.

The width of each box is proportional to the square root of the number of observations.



## **ANNEX 3**

### **DATA TABLES BY AREA AND LABORATORY**

The data reported for the five metals have been broken down by laboratory and area sub-division in the five tables that comprise this annex. This formulation was found to be useful in the assessment of the data. Comparison of the results submitted by various laboratories for an area must be approached very cautiously since

the data were often collected in different parts of the respective area during different seasons, and often have very different salinities. The results in these tables should not, therefore, be used to make comparisons of the analytical capabilities of the various laboratories.

**TABLE 9: SUMMARY TABLE - CADMIUM DATA BY AREA AND LABORATORY**

line 1 - Average concentration (µg/l) : line 2 - Standard deviation : line 3 - Number of values

Area code	Analytical Laboratory													
	ALUK	BFGG	BLUK	DGWN	DHIG	FRUK	HFLD	IEOM	IGDR	IHEB	LCRS	LWKG	NIVA	RIZA
BALT BALT BALT									0.0220 0.0127 15					
BISC BISC BISC								0.0541 0.0201 11						
CELT CELT CELT			0.1359 0.1595 88											
CHNL CHNL CHNL			0.0338 0.0498 56											
IBER IBER IBER								0.0890 0.0843 12						
IRSH IRSH IRSH	0.0290 0.0000 1		0.0620 0.0468 229											
KATT KATT KATT							0.0237 0.0061 18		0.0156 0.0039 6		0.0325 0.0140 6			
NORC NORC NORC													0.0406 0.0191 22	
NOSC NOSC NOSC					0.0154 0.0063 7									
NS1. NS1. NS1.					0.0173 0.0192 9									
NS2. NS2. NS2.			0.0185 0.0045 2		0.0204 0.0126 16									
NS3A NS3A NS3A			0.0216 0.0122 19		0.0232 0.0186 5	0.0625 0.0965 93								
NS3B NS3B NS3B			0.0923 0.1120 130		0.0347 0.0229 11									
NS4. NS4. NS4.			0.0406 0.0181 24	0.0672 0.0774 280	0.0210 0.0179 15					0.0649 0.0552 102				0.1503 0.1099 68
NS5. NS5. NS5.		0.0704 0.0564 138	0.0269 0.0113 24	0.0631 0.0532 71	0.0224 0.0131 28		0.0299 0.0075 33					0.0822 0.0653 32		
NS6. NS6. NS6.			0.0210 0.0033 3		0.0103 0.0064 15									
NS7A NS7A NS7A			0.0215 0.0119 29		0.0128 0.0054 33									
NS7B NS7B NS7B			0.0341 0.0363 34		0.0186 0.0070 18									
S&BL S&BL S&BL									0.0189 0.0070 8					
SKAG SKAG SKAG			0.0154 0.0040 6		0.0177 0.0075 12		0.0256 0.0064 8				0.0313 0.0179 6		0.0243 0.0005 6	
WESC WESC WESC	0.0315 0.0083 22													

TABLE 10: SUMMARY TABLE - COPPER DATA BY AREA AND LABORATORY

line 1 - Average concentration ( $\mu\text{g/l}$ ) : line 2 - Standard deviation :  
 line 3 - Number of values

Area code	Analytical Laboratory										
	ALUK	BFGG	BLUK	CRUK	DGWN	DHIG	FRUK	HFLD	IGDR	LCRS	NIVA
BALT BALT BALT									0.603 0.087 15		
CELT CELT CELT			1.075 0.880 59								
CHNL CHNL CHNL			0.302 0.223 12								
IRSH IRSH IRSH	0.495 0.095 2		0.580 0.360 2								
KATT KATT KATT								0.832 0.425 14	0.480 0.020 6	0.554 0.082 6	
NORC NORC NORC											4.617 4.850 22
NOSC NOSC NOSC						0.265 0.219 8					
NS1. NS1. NS1.						0.142 0.138 10					
NS2. NS2. NS2.						0.213 0.179 16					
NS3A NS3A NS3A						0.203 0.078 5	0.998 0.693 96				
NS3B NS3B NS3B			0.955 0.045 2								
NS4. NS4. NS4.					0.815 0.592 294						
NS5. NS5. NS5.		2.147 1.139 138			1.491 0.593 80	0.934 0.225 31		1.092 0.409 26			
NS6. NS6. NS6.						0.144 0.094 15					
NS7A NS7A NS7A						0.188 0.157 33					
NS7B NS7B NS7B						0.333 0.420 19					
S&BL S&BL S&BL									0.517 0.053 8		
SKAG SKAG SKAG						0.338 0.293 13		0.359 0.118 8		0.357 0.091 6	0.523 0.206 6
WESC WESC WESC	0.529 0.175 23			3.558 1.685 17							

**TABLE 11: SUMMARY TABLE - LEAD DATA BY AREA AND LABORATORY**

line 1 - Average concentration (µg/l) :  
line 2 - Standard deviation :  
line 3 - Number of values

Area code	Analytical Laboratory						
	ALUK	BLUK	DHIG	FRUK	IGDR	LCRS	NIVA
BALT BALT BALT					0.0353 0.0182 15		
CELT CELT CELT		0.1329 0.1894 80					
CHNL CHNL CHNL		0.0281 0.0220 55					
IRSH IRSH IRSH	0.0173 0.0074 69	0.0791 0.0550 226					
KATT KATT KATT					0.0242 0.0042 6	0.1567 0.0582 6	
NORC NORC NORC							0.0680 0.0628 21
NOSC NOSC NOSC			0.0448 0.0166 8				
NS1. NS1. NS1.			0.0341 0.0134 10				
NS2. NS2. NS2.		0.0410 0.0030 2	0.0389 0.0222 15				
NS3A NS3A NS3A		0.0617 0.0645 18	0.0560 0.0214 5	0.1250 0.0250 2			
NS3B NS3B NS3B		0.0682 0.1498 129					
NS4. NS4. NS4.		0.0470 0.0372 25					
NS5. NS5. NS5.		0.0267 0.0095 24	0.0201 0.0071 10				
NS6. NS6. NS6.		0.0260 0.0029 3	0.0310 0.0137 15				
NS7A NS7A NS7A		0.0670 0.0397 28	0.0464 0.0477 33				
NS7B NS7B NS7B		0.0724 0.0454 34	0.0412 0.0095 18				
S&BL S&BL S&BL					0.0658 0.0428 8		
SKAG SKAG SKAG		0.0250 0.0039 7	0.0446 0.0142 13			0.0624 0.0177 5	0.0583 0.0303 6
WESC WESC WESC	0.0145 0.0086 22						

TABLE 12: SUMMARY TABLE -  
MERCURY DATA BY AREA AND LABORATORY

line 1 - Average concentration ( $\mu\text{g/l}$ )

line 2 - Standard deviation

line 3 - Number of values

Area code	Analytical			Laboratory		
	BLUK	DHIG	FRUK	ICDK	LCRS	SERI
CELT	0.0011					
CELT	0.0007					
CELT	60					
CHNL	0.0005					
CHNL	0.0001					
CHNL	19					
IRSH	0.0198					
IRSH	0.0528					
IRSH	59					
KATT				0.0190	0.0035	
KATT				0.0100	0.0013	
KATT				2	6	
NORC						0.0011
NORC						0.0007
NORC						12
NOSC		0.0048				
NOSC		0.0050				
NOSC		7				
NS1.		0.0017				
NS1.		0.0006				
NS1.		8				
NS2.		0.0071				
NS2.		0.0118				
NS2.		13				
NS3A	0.0022	0.0024	0.0034			
NS3A	0.0010	0.0011	0.0034			
NS3A	10	5	41			
NS3B	0.0028					
NS3B	0.0027					
NS3B	63					
NS4.	0.0017					
NS4.	0.0008					
NS4.	17					
NS5.	0.0018	0.0166		0.0097		
NS5.	0.0008	0.0010		0.0026		
NS5.	21	2		5		
NS6.		0.0024				
NS6.		0.0018				
NS6.		15				
NS7A	0.0013	0.0084				
NS7A	0.0007	0.0146				
NS7A	20	25				
NS7B	0.0021	0.0161				
NS7B	0.0011	0.0398				
NS7B	20	14				
SKAG	0.0022	0.0046		0.0714	0.0053	0.0011
SKAG	0.0002	0.0047		-	0.0019	0.0006
SKAG	3	13		1	4	6

TABLE 13: SUMMARY TABLE - ZINC DATA BY AREA AND LABORATORY

line 1 - Average concentration ( $\mu\text{g/l}$ ) : line 2 - Standard deviation :  
line 3 - Number of values

Area code	Analytical				Laboratory		IGDR	SWUK
	BFGG	CRUK	DGWN	DHIG	FRUK	IBWL		
BALT BALT BALT							0.78 0.39 14	
CHNL CHNL CHNL								2.45 1.31 12
KATT KATT KATT							0.66 0.15 6	
NS3A NS3A NS3A					2.17 2.68 92			
NS4. NS4. NS4.			4.08 3.04 71			2.06 1.19 39		
NS5. NS5. NS5.	4.66 2.74 136		2.61 1.09 36	0.76 0.36 10				
S&BL S&BL S&BL							0.64 0.18 8	
WESC WESC WESC		11.63 4.37 16						





